Graphitic Carbon-Based Functional Nanomaterials for Environmental Remediation and Energy Conversion Applications

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ABSTRACT

Carbon-based nanomaterials have attracted significant attention due to their unique optical, electrical, thermal and mechanical properties. In recent years, a large number of carbon-based nanomaterials have been investigated including carbon nanotubes, graphitic carbon nitride (g-C$_3$N$_4$), graphene, carbon nanofibers, carbon nanodots (CNDs), heteroatom-doped carbon, and carbon-based materials obtained from biomass etc. The unique and superior properties of such carbon-based materials make them useful for a wide range of applications in the fields such as environmental remediation and energy conversions.

Although significant progress has been made over the past decade or so, few drawbacks of carbon-based materials still remain unresolved. For example, as a photocatalyst, the weak van der Waals interactions between adjacent conjugated planes of g-C$_3$N$_4$ and poor electronic properties affect negatively on the photocatalytic activity. Despite a variety of synthetic methods have been investigated, to fabricate undoped and doped carbon-based materials, the efficiency and level of control on the resultant products are far from satisfactory. Majority of these approaches either involve tedious and complex experimental procedures or require using harsh reaction conditions, or possessing low yield production. Furthermore, to achieve heteroatom-doped carbon-based materials, the reported approaches almost exclusively require the use of synthetic chemicals as carbon and heteroatom sources, respectively. The large-scale application of fuel cells and dye-sensitized solar cells (DSSCs) using Pt-based catalysts is hindered by the inherent disadvantages of Pt such as high cost, scarcity and low resistance to crossover effect of methanol molecule. It is therefore highly desirable to realize heteroatom doping by simple, low-cost, high yield and environmentally benign synthesis methods for fabrication of commercially viable carbon-based materials for applications in solar cells and fuel cells.

To tackle these problems, in this study, an extensive effort has been made to develop high efficiency and low-cost photo- and electro-catalysts. In order to facilitate the electron transfer and charge separation processes of g-C$_3$N$_4$ photocatalyst, reduced graphene oxide (rGO) is introduced (the composite was named as CN/rGO). By simply controlling the weight ratio of rGO, the band structure of the cross-linked CN/rGO nanocomposites can be readily tuned to adjust the oxidation power of the composites. As a photocatalyst, the fabricated CN/rGO
nanocomposite has demonstrated superior visible light photocatalytic activity for removal of organic pollutants such as rhodamine B (RhB) and 4-nitrophenol.

Biomass, especially those containing nitrogen atoms, is a class of ideal starting materials for green synthesis of N-doped carbon-based materials because they are earth-abundant, readily available and cheap to obtain. In this work, N-doped carbon nanodots (N-CNDs) and N-doped carbon nanodot/nanosheet (N-CNs) are fabricated using grass as the sole material source without the need for any synthetic chemicals via a facile hydrothermal method. However, when used as sensitizer in aqueous solar cells, the fast charge recombination pathway limited utilization efficiency of photo-excited electrons for electricity conversion. To solve this problem, we developed a new quenching principle to enable the use of such materials as effective sensitizer for solar cells. The synthesized N-CNs aggregate (N-CNAs) from grass is also successfully used as high performance electrocatalyst for oxygen reduction reaction (ORR).

In this work, for biomass utilization, we also extracted cellulose and chitin from grass and prawn shell, respectively. They are successfully utilized as materials sources to synthesize N-doped 3D-aerogel carbon materials with superior ORR electrocatalytic activity.

It has been widely recognized that co-doping of heteroatoms into carbon material can further improve the catalytic activity. However, the controllable co-doping of heteroatoms into graphitic carbon materials is difficult. In this work, we developed a self-sponsored co-doping approach to facile control the doping of S and N into graphitic carbon network structures. The required carbon and dopant (S, N) sources are self-sponsored by a sole precursor (1-allyl-2-thiourea) without the need for catalysts. With this new approach, the controllable doping and graphitic carbon growth can be concurrently achieved by simply controlling the thermolysis temperature. The resultant S, N co-doped graphitic carbon materials exhibit excellent electrocatalytic activity toward ORR.

These S and N co-doped graphitic carbon materials also exhibits excellent catalytic activity towards I$_3^-$ reduction. When used as counter electrode (CE) material in DSSCs, an enhanced light conversion efficiency of 7.86 % can be achieved which is higher than the cells assembled with Pt CE. For DSSCs applications, we also developed a facile method to directly grow (0001) faceted single crystal NiS nanosheet film onto FTO via a one-step hydrothermal process. Without the need for
further treatment, the single crystal NiS nanosheet films are successfully employed as CE materials for DSSCs, achieving an overall light conversion efficiency of 8.62% that is 17.1% higher than the cells assembled using Pt-based CE (7.36%).

This study demonstrate that high performance graphitic carbon materials can be fabricated using cheap and earth-abundant materials sources via simple, low-cost, high yield and environmentally benign synthesis methods. The findings of this study provide valuable scientific knowledge for design and fabrication of high performance graphitic carbon-based catalyst materials for energy and environmental applications.
STATEMENT OF ORIGINALITY

This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

Signature of candidate

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<td>CNDs</td>
<td>Carbon nanodots</td>
</tr>
<tr>
<td>CQDs</td>
<td>Carbon quantum dots</td>
</tr>
<tr>
<td>DSSCs</td>
<td>Dye-sensitized solar cells</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>IRR</td>
<td>Triiodide reduction reaction</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>MWNT</td>
<td>Multi-walled carbon nanotubes</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-walled carbon nanotubes</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>LIB</td>
<td>Lithium ion batteries</td>
</tr>
<tr>
<td>EDLCs</td>
<td>Electrical double layer capacitors</td>
</tr>
<tr>
<td>CNPs</td>
<td>Carbon nanoparticles</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquid</td>
</tr>
<tr>
<td>PPEI-EI</td>
<td>Poly (propionyl-ethylenimine-co-ethylenimine)</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transforms infrared spectroscopy</td>
</tr>
<tr>
<td>GQDs</td>
<td>Graphene quantum dots</td>
</tr>
<tr>
<td>CF</td>
<td>Carbon fibers</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>FL</td>
<td>Fluorescence</td>
</tr>
<tr>
<td>J_{sc}</td>
<td>Short-circuit current density</td>
</tr>
<tr>
<td>V_{oc}</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>η</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>N-CQDs</td>
<td>Nitrogen-doped carbon quantum dots</td>
</tr>
<tr>
<td>E. coli</td>
<td>Escherichia coli</td>
</tr>
<tr>
<td>Eg</td>
<td>Band gap energy</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>3D</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>N-GFs</td>
<td>N-doped graphene foams</td>
</tr>
<tr>
<td>SSA</td>
<td>Surface specific area</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-emmett-teller</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible spectroscopy</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetry</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>CCG</td>
<td>Chemically converted graphene</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>NiS</td>
<td>Nickel sulphide</td>
</tr>
<tr>
<td>CN/rGO</td>
<td>g-C₃N₄/ reduced graphene oxide</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>Graphitic carbon nitride</td>
</tr>
<tr>
<td>RhB</td>
<td>Rhodamine B</td>
</tr>
<tr>
<td>G</td>
<td>Gram</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>min</td>
<td>Minute(s)</td>
</tr>
<tr>
<td>h⁺</td>
<td>Photohole</td>
</tr>
<tr>
<td>mL</td>
<td>Milliliter</td>
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<td>L</td>
<td>Liter</td>
</tr>
<tr>
<td>$E_{fb}$</td>
<td>Flat band potentials</td>
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<tr>
<td>TEOA</td>
<td>Triethanolamine</td>
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<tr>
<td>N-CNAs</td>
<td>N-doped carbon nanodot/nanosheet aggregates</td>
</tr>
<tr>
<td>OSBE</td>
<td>Organic solvent-based electrolyte</td>
</tr>
<tr>
<td>AE</td>
<td>Aqueous electrolyte</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>QY</td>
<td>Quantum yield</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating disk electrode</td>
</tr>
<tr>
<td>RRDE</td>
<td>Rotating ring-disk electrodes</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident photon-to-current conversion efficiency</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetric</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetric</td>
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<td>F</td>
<td>Faraday constant</td>
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<td>GC</td>
<td>Glassy carbon</td>
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<tr>
<td>mV</td>
<td>Millivolt</td>
</tr>
<tr>
<td>n</td>
<td>Transferred electron number</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethylorthosilicate</td>
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<tr>
<td>rpm</td>
<td>Revolutions per minute</td>
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<tr>
<td>$J_K$</td>
<td>Kinetic limiting current densities</td>
</tr>
<tr>
<td>$J_L$</td>
<td>Diffusion limiting current densities</td>
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<tr>
<td>$\omega$</td>
<td>Angular velocity</td>
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<tr>
<td>nm</td>
<td>Nanometer</td>
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<tr>
<td>LCE</td>
<td>Light conversion efficiency</td>
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<td>$E_{pc}$</td>
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<td>$I_{pc}$</td>
<td>Cathodic peak current</td>
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<tr>
<td>$E_{pp}$</td>
<td>Peak-to-peak voltage separation</td>
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<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>Charge-transfer resistance</td>
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<tr>
<td>$R_s$</td>
<td>Series resistance</td>
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<tr>
<td>CPE</td>
<td>Constant phase element</td>
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<td>S</td>
<td>Sulfur</td>
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<td>N</td>
<td>Nitrogen</td>
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<tr>
<td>$\mu$</td>
<td>Micro (prefix)</td>
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<tr>
<td>$Z_w$</td>
<td>Nernst diffusion impedance within the electrolyte</td>
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LIST OF PUBLICATIONS


12. H.M. Zhang, Y. Wang, D.J. Yang, **Y.B. Li**, H.W. Liu, P.R. Liu, B.J. Wood, H.J. Zhao. Directly hydrothermal growth of single crystal Nb₃O₇(OH) nanorod film


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CHAPTER 1 GENERAL INTRODUCTION
1.1 Introduction

In recent years, carbon nanotubes, graphitic carbons, carbon nanodots/quantum dots (CNDs/CQDs) and their derivatives have emerged as a new class of functional materials.\textsuperscript{1-7} Owning to their superior electronic, mechanical, optical, and chemical characteristics, these carbon-based materials have been extensively investigated for a wide range of applications, especially for energy and environmental remediation.\textsuperscript{8-12,13-20} Although a noticeable progress has been made, there are many unresolved issues requiring further research.

It is highly desirable for a photocatalyst to possess a tunable bandgap structure for enhancement of light utilization efficiency and photocatalytic activity. Graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) is known as a potential visible light photocatalyst. However, pure g-C\textsubscript{3}N\textsubscript{4} possesses limited visible light photocatalytic activity due to the marginal visible light absorption and grain boundary effects.\textsuperscript{21} In this work, we propose and experimentally demonstrate a new synthetic approach to produce cross-linked g-C\textsubscript{3}N\textsubscript{4}/rGO nanocomposites with tunable bandgaps to markedly improve the visible light utilization efficiency and photocatalytic activity.\textsuperscript{22}

The vast majority of reported graphitic carbon materials are fabricated using synthetic chemical precursors made from rapidly diminished petroleum. It would be of great beneficial to environment and sustainability if the plentiful renewable biomass materials can be used to replace petroleum-based synthetic chemical precursors for fabrication of graphitic carbon materials. In this work, we develop a number of facile synthetic methods to successfully convert biomass such as grass, cellulose and chitin into N-doped graphitic carbon materials as high performance electrocatalysts for oxygen reduction reaction (ORR) and sensitizers for solar cells.\textsuperscript{23}

It has been confirmed that the electrocatalytic properties can be significantly enhanced by doping and co-doping heteroatoms into graphitic carbon structures.\textsuperscript{24,25} However, controllable doping and co-doping of heteroatoms remain a great challenge.\textsuperscript{24,26,27} This work take the challenge by developing a self-sponsored co-doping method to realize controllable co-doping of S and N into graphitic carbon network structures to produce high performance electrocatalysts for ORR and dye-sensitized solar cell counter electrodes.

In this chapter, literatures reviews relevant to the synthesis of new class carbon-based materials as well as their applications particularly in environmental
remediation and energy conversion are summarized. The scope of the thesis is also outlined.

1.2 Carbon Nanotubes (CNTs)

In 1976, Oberlin et al. showed hollow carbon fibers with nanometer-scale diameters using a vapor-growth technique, and it was not until the year of 1991 when Sumio Iijima who firstly discovered hollow, nanometer sized tubes composed of graphitic carbon by studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes that triggered researcher’s interest. In their study, they found that the central core of the cathodic deposit contained a variety of closed graphitic structures including nanoparticles and nanotubes, which had never previously been observed. The CNTs consisted of up to several tens of graphitic shells (namely, multi-walled carbon nanotubes (MWNT)) with adjacent shell separation of ~0.34 nm, diameters of ~1 nm and high length/diameter ratio. Two years later, single-walled carbon nanotubes (SWNT) were firstly synthesized by co-evaporation of a cobalt catalyst and graphite in an electric arc by Iijima, Ichihashi et al. respectively. CNTs (single- or multi-walled) can be fabricated using different methods, which mainly involve gas phase processes. Apart from the arc discharge techniques reported by Iijima and co-workers, laser ablation was later demonstrated as an alternative method for growing CNTs, and chemical vapor deposition (CVD) using transition metal nanoparticle catalysts was then developed to produce high quality single-walled and multi-walled CNTs in vertically aligned arrays. In the following paragraphs, details of the CNTs synthesized using these three methods and some of its applications will be demonstrated.

1.2.1 Synthetic Methods

CNTs are generally synthesized by three main techniques: (1) Arc Discharge, (2) Laser Ablation and (3) CVD. In arc discharge method, a carbon vapor is created by an arc discharge between two carbon electrodes with or without catalyst. In the laser ablation technique, a high-power laser beam impinges on a volume of carbon containing precursor gas (methane or C2H2). Comparing these two different methods, laser ablation produces a small amount of clean CNTs, whereas arc discharge method generally produces large quantities of impure CNTs. However, CVD results in MWNTs or poor quality SWNTs. The SWNTs produced by CVD
have a large diameter range, which can be poorly controlled. But on the other hand, the CVD method is very easy to scale up, and favors for commercial production.

**Arc Discharge**

![Diagram of Arc Discharge method](image)

**Figure 1.1** Single/multi-walled CNTs synthesized by Arc Discharge method.\(^{29}\)

The optimal conditions for nanotube generation using this technique involve the passage of a direct current (80-100 A) through two high-purity graphite electrodes separated by 1-2 mm, in a He atmosphere (500 torr) as seen in Figure 1.1. During arcing, a deposit forms at a rate of 1 mm min\(^{-1}\) on the cathode (negative electrode), while the anode (positive electrode) is consumed. Using this technology, randomly arranged MWNTs and graphitic particles were obtained.\(^{41, 47, 48}\) However, SWNTs can also be produced using the arc-discharge method if a metal catalyst is added in the process (Figure 1.1). For example, Iijima & Ichihashi have produced SWNT material by arcing Fe-graphite electrodes in a methane-argon atmosphere. Almost simultaneously, Bethune and co-workers carried out similar arc experiments involving Fe-Co-Ni-graphite mixtures in a He atmosphere.\(^2\) Nowadays, SWNTs can be produced using the carbon arc discharge method in conjunction with different metals such as Ni-Y,\(^{49}\) Co-Ru,\(^{50}\) Rh-Pt,\(^{51}\) and Co-Ni-Fe-Ce etc.\(^{52}\)

**Laser Ablation Method**

This method is using the high-power laser vaporization on pure graphite targets which located inside a furnace at higher temperatures in an inert gas protected atmosphere to generate CNTs.\(^{30, 31}\) The nanotube growth using this technique has been explained in terms of the attachment of incoming carbon species at the edges of adjacent growing graphene tubules, which is responsible for prolonging the lifetime of the open structure and normally resulted the formation of MWNTs (Figure 1.2).\(^{31}\)
However, in order to generate SWNTs using this laser technique, it is necessary to add metal particles as catalysts to the graphite targets as well.\textsuperscript{54} Because the optimum background gas and catalyst mixture are the same as in the electric arc discharge method, this method is almost similar to arc discharge. But it is mainly used for SWNTs since using this method to synthesize CNTs is very expensive.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{laser_ablation_equipment.png}
\caption{(a) Scheme of the laser ablation equipment. (b) TEM image of a bundle of SWNTs catalyzed by Ni/Y mixture, produced with a continuous laser.\textsuperscript{53}}
\end{figure}

**Chemical Vapor Deposition**

CVD is a generic name for a group of processes that involve the deposition of solid material by chemical reactions between a gaseous precursor and a substrate. This process is commonly used in the semiconductor industry for the deposition of thin films of various materials (Figure 1.3). For the synthesis of CNTs, in this typical method, different hydrocarbon sources (e.g., methane,\textsuperscript{55,56} benzene,\textsuperscript{28,57} acetylene,\textsuperscript{36,37} naphthalene,\textsuperscript{58} ethylene\textsuperscript{59} etc.) combined with metal catalysts (e.g., Co,\textsuperscript{60} Ni,\textsuperscript{61} Fe,\textsuperscript{62} Mo,\textsuperscript{63} Pt,\textsuperscript{64} and Pd\textsuperscript{65}) were used. For example, Dai et al\textsuperscript{63} reported the generation of SWNTs via thermolysis processes involving Mo particles in conjunction with CO at 1200 °C. Sen and co-workers managed to produce SWNTs via pyrolysis of CO and benzene in the presence of Fe.\textsuperscript{57} Large quantities of SWNT bundles were synthesized by Kong et al. by pyrolyzing methane in the presence of iron oxide at high temperature over 1000 °C.\textsuperscript{56} Nowadays, it is possible to generate SWNTs using pyrolysis of various carbon sources in the presence of metals and/or metal alloys.\textsuperscript{39,66,67} The differences between these three methods are the quality and purity of the obtained products. However, arc discharge and different types of CVD
are the most promising utilized techniques in large scale production of carbon nanotubes and related materials.

Figure 1.3 (a) Schematic diagrams of thermal CVD apparatus. (b) SEM of the well-aligned CNTs.68

1.2.2 Applications of CNTs

Graphite, carbonaceous materials and carbon fiber electrodes are commonly used in fuel cells, batteries and other electrochemical applications. Nowadays, single- and multi-walled CNTs were used in various prototype electronic devices, environmental remediation, energy conversion and storage related issues etc. due to their small dimensions, smooth surface topology and perfect surface specificity. In the following sections, I will briefly summarize some applications of this tubular structured carbon materials.

Environmental Remediation

Since there are many surface functional groups and high surface area of CNTs, they are spread quickly in environmental remediation applications.69, 70 CNTs show strong interactions with both heavy metal ions and organic compounds. The adsorption-related applications of CNTs to solve environmental pollution problems have received considerable attention in recent years. This is because compared with other methods (e.g., precipitation,71 ion-exchange,72 photodegradation73 etc.), adsorption is one of the most efficient and economical process used for the removal of both organic and inorganic contaminants from aquatic phase.10 Recent studies have reported the use of CNTs for adsorption. The removal of gases (ammonia,74 ozone,75, 76 methane77, 78 etc.), inorganic,79-82 organic pollutants (atrazine,83 trihalomethanes,84 benzene,85 toluene86 etc.) and biological contaminants87 have been
reported by CNTs. Apart from using as absorbents, CNTs/semiconductor composites were also synthesized and used as photocatalysts and quite a few studies concerning the photocatalytic activity of CNT-TiO\textsubscript{2} hybrids for the oxidation degradation of organic compounds, such as acetone,\textsuperscript{88} propene,\textsuperscript{89} and phenol,\textsuperscript{90, 91} as well as the inactivation of bacterium anthraxium have been reported.\textsuperscript{92} CNT-ZnO have been investigated for the decomposition of methylene blue,\textsuperscript{93} while the decomposition of indigo carmine with both CNT-ZnO and CNT-TiO\textsubscript{2} have also been tested.\textsuperscript{94} All of these studies observed superior photocatalytic performance by the hybrid over the individual component. For example, Lee et al. used CNT-ZnO composites for the decomposition of methylene blue, who observed a superior performance of CNT-ZnO hybrids over the mechanically mixed composite.\textsuperscript{93} The importance of the interface was further supported by the work of Yao et al. who compared MWCNT-TiO\textsubscript{2} hybrids with SWCNT-TiO\textsubscript{2} hybrids.\textsuperscript{91} In contrast to MWCNTs, the higher flexibility and resilience of SWCNTs caused them to wrap around the TiO\textsubscript{2} particles, thus increasing the interfacial area. The authors believed that this enhanced interface was the reason for the higher photocatalytic activity observed in SWCNT-TiO\textsubscript{2} hybrids for the decomposition of phenol.

![Figure 1.4](image_url)

**Figure 1.4** The proposed mechanisms for the photocatalysis of the hybrid CNT-TiO\textsubscript{2}. (a) The CNTs acts as a photosensitizer, where the electron is excited and then injects into the conduction band of TiO\textsubscript{2}. (b) The CNT serves as an electron sink, and scavenges away the electron hindering its recombination with a hole.\textsuperscript{96}

All these works clearly demonstrated a synergistic effect of CNTs in enhancing the performance of TiO\textsubscript{2} or ZnO. The mechanism of the degradation was proposed by different models. The first explanation is purely physical and can be described in terms of CNTs acting as a dispersing agent that prevents semiconductors from
agglomerating, thus providing a higher active surface area for the resulting catalyst compared with single-phase semiconductor.\textsuperscript{95}

The second model is the strong adsorption ability of CNTs which may act as additional adsorbents for organic compounds, and then diffuse to the TiO\textsubscript{2}-CNT phase boundary to undergo degradation.\textsuperscript{90, 97, 98} Finally, the CNTs may act as photosensitizers for n-type semiconductors like TiO\textsubscript{2}. This means the photoinduced electrons are easily transferred to the CNT-TiO\textsubscript{2} interface and injected into the TiO\textsubscript{2} conduction band (Figure 1.4).\textsuperscript{99}

**Energy Conversion Applications**

*Photovoltaic Devices and DSSCs*

In recent years, researchers have studied the application of CNTs in a range of fields in energy conversion systems, such as solar cells and fuel cells. CNTs have been used in both bilayer and bulk heterojunction polymer photovoltaic devices for enhanced charge separation and transportation. The first rectifying heterojunction between MWNTs and a commercially available soluble derivative was reported by Romero et al.\textsuperscript{100} Their results showed that the nonlinear current injection was enhanced by a local field created at the interface between the two materials upon exposure of the junction to light. For another example, using a bilayer photovoltaic device, Kuila et al. have investigated the charge transfer at the polymer-CNT interface by grafting CH\textsubscript{2}OH-terminated regioregular P3HT onto carboxylic groups of acid-oxidized CNTs via esterification reaction and showed an increase in the power conversion efficiency.\textsuperscript{101} Apart from using as bilayer and bulk heterojunction polymer photovoltaic devices, CNTs also used as counter electrode (CE) material in DSSCs, for example, Lee et al. reported the successful application of MCNTs as electrocatalysts for triiodide reduction in DSSCs. In their research, they argued that the defect-rich edge planes of bamboolike-structured MCNTs facilitated the electron-transfer kinetics at the CE-electrolyte interface, resulting in low charge-transfer resistance and an improved fill factor. In combination with a dye-sensitized TiO\textsubscript{2} photoanode and an organic liquid electrolyte, a multiwall CNT counter-electrode DSSCs shows 7.7\% energy conversion efficiency under 1 sun illumination.\textsuperscript{102} Another example was illustrated by Nam et al. In their study, they investigated the performance of DSSCs with CNTs on CE applied by two different methods. In one method, randomly dispersed multi-wall CNT paste was screen-printed. In the other
method, relatively well-aligned CNTs were directly grown by catalytic CVD. The results showed that when the highly purified and aligned CNTs were used as CEs, a conversion efficiency of DSSCs of over 10% was recorded. This CNT-deposited CE showed a higher photoconversion efficiency than CNT-printed and Pt-coated electrodes under the same experimental conditions. Moreover, other reports concerning CNT CE used in DSSCs were also reported.

_Fuel Cell_

**Figure 1.5 Summary of fuel-cell types.**

The fuel cell discovered in 1839 by Sir William Grove is a device in which the production of electricity is due to oxidation on a fuel reducer electrode coupled to the reduction of an oxidant on the other electrode (Figure 1.5). Therefore, oxygen reduction reaction (ORR) plays a key role in the performance of the cell. The traditional cell has many drawbacks including high fabrication costs and the spoilage of the Pt electrode with time. CNTs functionalized with electron-accepting nitrogen atoms prove to be a potential candidate to replace traditional Pt-electrodes. The use of CNTs as catalyst can potentially reduce Pt usage by 60% compared with carbon black, and heteroatoms-doped CNTs are enable to replace the require of Pt in fuel cells.

Apart from the above applications, CNTs were also used in water purification, hydrogen storage etc. Although CNTs were studied a lot, however, the lack of solubility and dispersion in most solvents compatible with the biological milieu (aqueous-based), and difficulty in maintaining high quality and minimal impurities have limited its application.
**Energy Storage**

*Lithium Ion Batteries (LIB)*

Due to its high energy density, high voltage, long cycling life and good environment compatibility, LIB is considered to be one of the most useful batteries in portable electronics.\(^{122}\) On the other hand, LIB is recognized as a rock-chair battery with Li\(^+\) insertion/excitation in the two electrodes during the charging/discharging processes. The performance of LIB strongly depends on the structures and properties of its electrodes. Commercially, the anode is composed of a carbon material (graphite) and the cathode is constructed by the lithium metal oxide.\(^ {123}\)

As a member of the carbon family, CNTs are widely used in LIB for computers and smart mobile phones.\(^ {124,125}\) Compare to other materials, CNT is an interesting intercalation host because of its special structure and chemical bonding. Compared with graphite, CNTs might have a higher saturation composition because the guest species can intercalate in the interstitial sites and between the nanotubes.\(^ {126}\) Therefore, CNTs are expected to be suitable high energy density anode materials for rechargeable LIB.\(^ {126}\) In these LIB, a tiny amounts of CNTs powders are blended with active materials and a polymer binder, such as 1 wt% CNTs loading in LiCoO\(_2\) cathodes and graphite anodes. The small amount of CNTs provides not only increased electrical connectivity but also mechanical integrity, which enhances rate capability and cycle life.\(^ {124,127,128}\)

*Electrical Double Layer Capacitors (EDLCs)*

EDLCs, often called supercapacitors, have steadily grown in importance as high-power electrochemical energy storage devices with ultra-long cycle-life.\(^ {129,130}\) Upon the application of a potential to one of the electrodes, the ions of the opposite sign accumulate on its surface in a quantity proportional to the applied voltage, forming a so-called electrical double layer. This double layer consists of an electrical space charge from the electrode side and an ion space charge from the electrolyte side.\(^ {131}\) It stores energy by charging electrical double layers through highly reversible ion adsorption on the surface of high-surface-area electrodes, generally made from porous carbon.\(^ {132,133}\) EDLCs represent today more than 80% of the commercially manufactured electrochemical capacitors by using carbon as the active material.\(^ {134}\) The active materials used in EDLCs are CNTs since they offer a combination of
electrical conductivity, high specific surface area, and electrochemical stability over a wide range of potentials in both aqueous and nonaqueous electrolytes. On the other hand, remarkable performance has been obtained for supercapacitors. Supercapacitors have several advantages over conventional batteries, including higher specific power (~2 orders of magnitude higher than batteries and fuel cells), higher cycle life (able to withstand millions of charge/discharge cycles), rapid charge/discharge times (seconds to minutes), high efficiencies (up to 98%), and unaltered performance in extreme heat and cold. As know that, in a supercapacitor, the CNTs surface area of the electrodes accessible to the solvated electrolyte ions determines the capacitance.

1.3 Carbon Quantum Dots (CQDs)/C-Dots

![Timeline showing recent activity regarding C-dots in the literatures.](image.png)

Figure 1.6 *Timeline showing recent activity regarding C-dots in the literatures.*

In the past few years, semiconductor quantum dots are emerged as a new class of fluorescent particulate materials for variety of applications in optical bioimaging and beyond. Among the two-photon fluorescence materials, semiconductor QDs such as CdSe and related core-shell nanoparticles exhibit the best performance. However, these popular QDs have serious toxicity even at relatively low concentrations. In addition, their superior photophysical features are usually observed in organic solvents, thus restricting tremendously their analytical potential. Although until recently, methods to make these luminescent QDs water-soluble and biocompatible have been reported, which includes surface passivation with protective layers, and coating of the QDs with protecting silicon oxide films. Nevertheless, these protocols are compromised by reducing their photoluminescence efficiency and time-consuming, complicated, expensive
Recently, a new class of carbon-based fluorescent materials, including carbon nanoparticles (CNPs) and CQDs as an alternative to QDs has received particular attention (Figure 1.6).\textsuperscript{146-150} Compared with conventional QDs, carbon-based fluorescent materials are superior in chemical stability and biocompatibility.\textsuperscript{151, 152} Moreover, some of these carbon nanostructured materials have been reported to emit efficiently in the visible range, which shows promise in the development of efficient carbon emitters.\textsuperscript{153, 154} The advances in this area are appearing frequently, with a number of significant breakthroughs taking place within the last couple of years. Several of the seminal advances are illustrated in Figure 1.6. The synthesis methods of CQDs are summarized in the following sections.

1.3.1 Synthetic Methods

The approaches to synthesize CQDs or C-dots can be generally classified into two main groups: top-down and bottom-up methods. In the top-down methods, arc discharge,\textsuperscript{155} laser ablation,\textsuperscript{151-153, 156} and electrochemical oxidation were conventionally used,\textsuperscript{157-159} where the C-dots are formed or “broken off” from a larger carbon structure. Bottom-up approaches consist of combustion,\textsuperscript{5, 160, 161} supported synthetic,\textsuperscript{162, 163} microwave\textsuperscript{164} and hydrothermal methods,\textsuperscript{6, 165, 166} where the C-dots are formed from molecular precursors.

Top-Down Approaches

*Electrochemical Synthesis*

![Figure 1.7](image)

\textbf{Figure 1.7} (a) Schematic device of electrochemical preparation and (b) the generated C-dots.\textsuperscript{158}

Carbon-dots were first demonstrated by Zhou et al by using the electrochemical synthesis method.\textsuperscript{159} In their study, they used CNTs as the working electrode in an electrochemical cell consisting of a Pt wire CE and Ag/AgClO$_4$ reference electrode with degassed acetonitrile solution containing tetrabutylammonium perchlorate as electrolyte. The solution changed from colorless to yellow then to dark brown when
cycling the applied potential between -2.0 and +2.0 V, which indicated the exfoliation of C-dots from the CNTs and their accumulation in solution. TEM shows that a uniform spherical shape and a narrow size distribution around 2.8 nm in diameter were formed. After purifying the C-dots, it emitted blue luminescence upon irradiation with an UV lamp. Similarly, Chi and co-workers also produced C-dots electrochemically from a graphite rod working electrode, a Pt mesh CE, and a Ag/AgCl reference electrode (Figure 1.7). The solution turned to yellow initially and eventually became dark brown when cycling between -3.0 and +3.0 V, as Zhou’s group has noted. High resolution transmission electron microscopy (HRTEM) results showed two modalities of spherical C-dots were produced with average sizes of about 20 nm and 2 nm. Apart from this, C-dots could also be generated by ionic liquid (IL) assisted electrooxidation of graphite using water-soluble 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] containing up to 90 wt.% water as the electrolyte. The oxidation occurred initially at graphite edge sites, grain boundaries, or defect sites, which resulted in an opening up of the edge sheets. This facilitated the second stage by providing a path for BF₄⁻ ions to intercalate into the anode, thereby causing a depolarization and expansion of the graphite anode. Increasing the water-to-IL ratio resulted in a more-efficient production of C-dots, while decreasing this ratio resulted in a larger fraction of nanoribbons.

**Laser-Ablation Method**

![Figure 1.8](a) The C-dots structure and (b) Luminescence image. More recently, C-dots have been purposefully produced by Sun and co-workers by laser ablation method (Figure 1.8). The C-dots were prepared by hot-pressing a mixture of graphite powder and cement, followed by stepwise baking, curing, and annealing under an argon flow. In this method, the C-dots were surface passivated
by polymeric agents such as diamine-terminated poly (ethylene glycol) (PEG<sub>1500N</sub>)<sup>153</sup> or poly (propionyl-ethylenimine-co-ethylenimine) (PPEI-EI).<sup>151</sup> Moreover, Hu et al. also reported fluorescent CNPs synthesized by laser irradiation of a suspension of carbon powders in organic solvent and the light emission could be tuned by selecting appropriate solvents.<sup>169</sup>

**Arc-Discharge Methods**

The first report of this method to generate carbon quantum dots was discovered by Xu et al. when they isolated an unknown fluorescent carbon nanomaterial.<sup>155</sup> Firstly, the soot was oxidized with HNO<sub>3</sub> to introduce carboxyl functional groups, which could improve the hydrophilicity of the carbon material. The sediment was then extracted with alkaline solution, and this resulted in a stable black suspension. Finally, the suspension was separated by gel electrophoresis into CNTs, and C-dots were obtained. FT-IR spectroscopy (FT-IR) indicated the presence of carboxyl functionality, and energy-dispersive x-ray spectroscopy (EDX) analysis showed that the fluorescent materials contain no metal residue from the catalysts used in the nanotube synthesis. Quantitatively, all of the fluorescent components make up only 10% of the mass of the CNT suspension. The generated materials fluoresced green-blue, yellow, and orange, in order of elution. Each of these three fluorescent bands were purified by dialysis to afford salt-free material.<sup>155</sup> Two years later, Bottini et al. once again isolated fluorescent nanoparticles from both pristine and nitric acid-oxidized commercially available carbon nanotubes that had been produced by the electric arc method which is similar to the method reported by Xu et al. by oxidation of soot using HNO<sub>3</sub>.<sup>170</sup>

**Bottom-Up Approaches**

Apart from the top-down methods mentioned above, another method called bottom-up approaches were also used to synthesize CQDs, for example, combustion/thermal<sup>5, 160-162, 171</sup> or microwave<sup>164</sup> methods during which the C-dots are formed from oxidation of the molecular precursors.

**Surface Oxidation Functionalization Method**

Recently, CQD have been successfully generated from graphene oxide, graphene, and which was called graphene quantum dots (GQDs). These edge-bound nanometer-sized graphene pieces have fascinating optical and electronic properties. They have been synthesized either by nanolithography<sup>172</sup> or from starting materials
such as GO or carbon fibers (CF) by chemical breakdown which have a resin-rich surface. For example, Peng et al. fabricated the GQDs by chemical oxidation and cutting of micrometer-sized pitch-based CF.⁴ The as-synthesized GQDs are highly soluble in water and other polar organic solvents, such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Moreover, the absorption properties of as-synthesized GQDs can be controlled by simply changing the temperature. Furthermore, Zhu et al. obtained CQD by dispersing GO into DMF and then transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave under higher temperatures. The oxidation state could be controlled by changing the amount of precursors (GO) ratios. The product consisted of a brown transparent suspension and black precipitates, and the black precipitates were wasted. The solid samples can be obtained by evaporating the solvents, and the GQDs have excellent solubility in many polar organic solvents or water with different PH levels.¹⁷³

Figure 1.9 (a) Representation scheme of oxidation cutting of CF into GQDs. (b) UV-vis spectra of GQDs.⁴

Combustion/Thermal Routes

This intriguing approach was first presented by Mao and co-workers.⁵ They collected soot by placing a piece of aluminum foil or a glass plate atop of a burning candle. The collected soot was then mixed with HNO₃ to oxidize the carbon particle surfaces. After cooling, the formed C-dots (<2 nm) were collected by centrifugation or dialysis. The C-dots photoluminescence spectra have a broad color range, with the emission-peak wavelengths ranging from 415 (violet) to 615 nm (orange-red) and both λₓₑ and pH dependent behaviour. The generated C-dots could soluble in both water and organic solvent such as methanol, DMF and dimethyl sulfoxide. The candle-burning approach was also followed by other groups.¹⁶⁰,¹⁷¹ Similarly, using this method, Giannelis and co-workers obtained surface-passivated C-dots that were either hydrophilic or organophilic in nature using a one-step thermal decomposition of low-temperature-melting molecular precursors and the monodispersed C-dots with
sizes less than 10 nm. The C-dots synthesized displayed $\lambda_{\text{ex}}$ dependent photoluminescence (PL) emission that is generally characteristic of C-dots as well.

**Figure 1.10** Processing diagram for the synthesis of photoluminescent carbon dots.$^{163}$

CQDs can also be synthesized using silica as carriers combined with high temperature thermal treatment of carbon precursors. For example, Liu et al. reported a novel and straightforward route towards nanosized (1.5-2.5 nm) carbon dots with amorphous structure by employing surfactant-modified silica spheres as carriers (Figure 1.10). First, satellite-like polymer/F127/silica composites were prepared as carriers and resols as carbon precursors. The subsequent high-temperature treatment and removal of silica carriers generated nanosized CQDs. Acid treatment and simple surface passivation finally resulted in water-soluble, multicolor photoluminescent CQDs. To make the CQDs soluble in water, the crude CQD suspension was mixed with a quarter volume of concentrated nitric acid, and the mixture was heated at reflux for 24 h. However, the suspension of such oxidized CQDs cannot emit luminescence under excitation at 365 nm. Therefore, a typical surface passivation process was further carried out using PEG$_{1500}$N. Strong photoluminescence was observed when this passivated suspension was irradiated by a 365 nm UV lamp.$^{163}$

**Hydrothermal Treatment**

In a recent study, a simple, low-cost, and green preparative strategy toward water-soluble, nitrogen-doped, carbon-rich, photoluminescent CQDs by hydrothermal treatment of grass has been reported by Liu et al.$^{166}$ The hydrothermal treatment of grass at 180 °C leads to a yellow dispersion. The TEM image of the products formed,
revealing that they consist of CQDs well separated from each other. The corresponding particle size distribution indicates that these CQDs have diameters ranging from 3 to 5 nm. However, the HRTEM image taken from one nanodot shows the dot possesses a crystalline structure with lattice spacing of 0.20 nm which is considerably smaller than the interlayer distance of 0.34-0.36 nm between graphene layers in graphite. Such observation also suggests the nanodot is not graphitic carbon. The dispersion shows a strong PL emission peak centered at 443 nm indicating the nanodots are fluorescent.

![Figure 1.11](image.png)

Figure 1.11 UV–vis absorption (red) and PL (at 320 nm excitation) spectra of the GQDs dispersed in water; (b) PL spectra of the GQDs at different excitation wavelengths. (c) PLE spectrum with the detection wavelength of 430 nm and PL spectrum excited at 257 nm. Inset: Photograph of the GQD aqueous solution taken under UV light in a fluorescence spectrophotometer. (d) pH-dependent PL spectra when pH is switched between 13 and 1.

On the other hand, Pan et al. have developed a simple hydrothermal route for cutting peroxidi zed graphene sheets into ultrafine GQDs with strong blue emission with diameters mainly distributed in the 5-13 nm range. The cutting mechanism may involve the complete breakup of mixed epoxy chains composed of fewer epoxy groups and more carbonyl groups under hydrothermal conditions. The process contains thermal deoxidization of GO sheets in a tube furnace at 200-300 °C and then oxidized using the mixture acid of concentrated H₂SO₄ and HNO₃. Finally, the
suspension after purified and diluted was transferred to a Teflon-lined autoclave and heated at 200 °C for 10 h. The functionalized GQDs were found to exhibit bright blue photoluminescence (PL). Following the hydrothermal deoxygenation process, more than 85% of the GQDs were found to consist of 1-3 layers and, intriguingly, the resulting GQDs showed $\lambda_{\text{ex}}$ dependent PL behaviour (Figure 1.11), a feature broadly shared by the C-dots.  

1.3.2 Applications of CQDs/C-Dots

Environmental Remediation

Detection of Cations and Anions

Selective and sensitive detection of heavy metal ions and anions in aqueous media are important since they play an active role in different biological and environmental processes. For example, Zhou et al\textsuperscript{174} reported an unmodified C-dots fluorescent sensor for label-free detection of Hg\textsuperscript{2+} and biothiols with high sensitivity and selectivity. The authors attribute the quenched fluorescence (FL) of C-dots through charge transfer process. Moreover, the FL of C-dots could be turned on due to the strong binding preference of biothiols toward Hg\textsuperscript{2+} by forming Hg\textsuperscript{2+}-S bond. Therefore, by taking advantage of the observed FL change, they can fabricate a facile FL sensor that allows detection of Hg\textsuperscript{2+} biothiols. On the other hand, Liu et al\textsuperscript{166} developed a simple, low-cost, and green preparative strategy toward water-soluble, nitrogen-doped, carbon-rich, photoluminescent polymer nanodots by hydrothermal. The increased reaction temperature leads to a decrease in size and an increase in quantum yield. Most importantly, they further demonstrated the proof of concept that such CQDs can serve as a very effective fluorescent sensing platform for label-free sensitive and selective detection of Cu (II) ions with detection limit as low as 1 nM. More recently, our group\textsuperscript{175} reported an analytical method for rapidly, sensitively, and selectively detecting iodide (I\textsuperscript{−}) in aqueous media using N-doped carbon quantum dots as the fluorophores. The experimental results demonstrated that the N-doped carbon quantum dot fluorophores possess high selectivity for I\textsuperscript{−} detection. The presence of nitrogen functional groups results in a positively charged carbon quantum dot surface, which is advantageous for the detection of I\textsuperscript{−} fluorescence because of the strong electrostatic interaction between carbon quantum dots and I\textsuperscript{−} (Figure 1.12).
Energy Conversion Applications

Sensitizers for Solar Cells

CQDs have broad absorption spectra, large absorption coefficients, and good solubility in polar solvents and these make carbon dots very attractive as alternatives to scarce and expensive heavy metals commonly used for photovoltaic and photocatalytic applications. Yan et al. have synthesized largest soluble GQDs with uniform size through a stepwise solution chemistry method. The GQDs have an absorption edge of 900 nm, the optimal value for single-junction solar cells under nonconcentrated sunlight, which means it may be a good candidature of sensitizer. It is known that in traditional DSSCs, the current state of the art Ru-complex sensitizers offer good performance but rely on expensive, scarce ruthenium, and are often time-consuming to synthesize. Therefore, to explore whether these issues can be surmounted, the CQDs functionalized as sensitizers were used on sensitized nanocrystalline TiO₂ solar cell. It is well known that the most effective Ru-based sensitizers contain a number of carboxylate ligands to enable coordination of the dye to the TiO₂, and the GQDs can be used as light absorbers for DSSCs. The GQDs synthesized by Yan absorbs a wide spectrum of light from visible to near IR. The absorption edge extends up to 900 nm, the optimal energy threshold that enables the...
thermodynamic limit of energy conversion efficiency in single-junction solar cells under nonconcentrated sunlight. The current-voltage characteristics of such a device under a simulated AM 1.5 Global light and in the dark, respectively. A short-circuit current density ($J_{sc}$) of 200 µA cm$^{-2}$ and an open-circuit voltage ($V_{oc}$) of 0.48 V were produced with a fill factor (FF) of 0.58.\textsuperscript{180}

Recently, Mirtchev et al. presented a new strategy for the synthesis of water-soluble, colloidal stable CQDs in solution phase and a preliminary exploration of their utilization as sensitizers in nanocrystalline TiO$_2$-based solar cells.\textsuperscript{181} The CQDs synthesized by Mirtchev et al. also have many functional groups on their surface. The absorption spectrum of a thin films of CQDs displays broad absorption throughout visible region. Under AM 1.5 illumination, the $V_{oc}$ and FF values reach 380 mV and 64% respectively, achieving a power conversion efficiency ($\eta$) of 0.13%. Moreover, recently, N-doped nanostructured carbon materials (graphene, nanotube etc.) have attracted much attention because doping can efficiently induce charge delocalization and tune the work function of carbon.\textsuperscript{182} As a result, the introduction of N into CQDs, namely N-CQDs, will be also expected to display enhanced performances for some given applications. Zhang et al. used N-CQDs evaluated as metal-free sensitizers for DSSCs and the CQDs-sensitized TiO$_2$-based solar cell exhibited a $J_{sc}$ of 0.33 mA cm$^{-2}$, a $V_{oc}$ of 0.37 V, a FF of 0.28, and overall power conversion efficiency of 0.03 %, while N-CQDs sensitized solar cell exhibited a $J_{sc}$ of 0.69 mA cm$^{-2}$, $V_{oc}$ of 0.46 V, FF of 0.43, and overall $\eta$ of 0.13%. The results showed that N-CQDs sensitized solar cell displayed better performance than N-free counterpart.\textsuperscript{183}

**Bioimaging**

Quantum dots such as CdS and related core-shell nanoparticles have been used in various optical imaging experiments.\textsuperscript{184} However, because heavy metals are the essential elements in such QDs, they have prompted serious health and environmental concerns. Therefore, CQDs become an attractive alternative for bioimaging applications because of their tunable PL properties and almost nontoxicity.

To determine whether GQDs that synthesized by Peng et al\textsuperscript{4} can be used for cellular imaging (Figure 1.13), they chose the green GQDs because the nucleus was stained with mounting medium with DAPI (blue color) under imaging. Then they performed in vitro cellular studies using human breast cancer cell lines T47D. The
cells were cultured and treated with green GQDs. The obtained images clearly visualize the phase contrast image of T47D cells, nucleus stained blue with DAPI, agglomerated high contrast fluorescent image of green GQDs around each nucleus and overlay image of cell with phase contrast, DAPI and green GQDs. Sun and co-workers reported their study on C-dots bioimaging capabilities. To demonstrate the potential of CQDs for cell imaging with two-photon luminescence microscopy, human breast cancer MCF-7 cells were cultured in terms of the established protocol. Upon incubation with the CQDs in an aqueous buffer at 37 °C, the MCF-7 cells became brightly illuminated when imaged on the fluorescence microscope with excitation.

Figure 1.13 Fluorescent images of human breast cancer cell T47D after incubation with green GQDs for 4 h (a) Phase contrast picture of T47D cells. (b) Individual nucleus stained blue with DAPI. (c) Agglomerated green GQDs surrounding each nucleus. (d) The overlay high contrast image of nucleolus stained with blue DAPI and GQDs (green) staining. Fluorescent images of human breast cancer cell T47D after incubation with green GQDs.
1.4 Graphene-based Materials

Upon recent years, graphene has attracted much attention of the scientists.\textsuperscript{186-188} Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two dimensional honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities.\textsuperscript{189} The reason why graphene received so much research interest is that it has a large theoretical specific surface area as high as 2630 m\textsuperscript{2} g\textsuperscript{-1},\textsuperscript{190} high intrinsic mobility (200 000 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}),\textsuperscript{191} high Young’s modulus (\textasciitilde 1.0 TPa),\textsuperscript{192} and thermal conductivity (\textasciitilde 5000 W m\textsuperscript{-1} K\textsuperscript{-1}),\textsuperscript{193} and its highly optical transmittance (\textasciitilde 97.7%),\textsuperscript{194} good electrical conductivity which merit attention for its applications for transparent conductive electrodes.\textsuperscript{195,196}

\textbf{Figure 1.14} Mother of all graphitic forms (fullerene, CNTs and graphite).

1.4.1 Synthetic Methods

Creating high-quality graphene in scalable, economical processes is the first step towards practical application of graphene. In the 1960s, Boehm speculated that reducing exfoliated graphite oxide would yield monolayers in solution.\textsuperscript{197} The first electronic measurements of ultrathin graphitic carbon around 2004 required samples sufficiently isolated from its substrate, (e.g., on SiO\textsubscript{2}) and ignited an explosion of interest in the fields.\textsuperscript{198,199} In general, these techniques can be divided into “bottom-up” and “top-down” methods. In the bottom-up method, graphene was epitaxial growth on single-crystal SiC and CVD on metal foil surfaces.\textsuperscript{200-203} To date, high-quality graphene with a well-defined molecular structure was usually prepared by
top-down methods such as chemical exfoliation of graphite, \textsuperscript{7} thermal exfoliation \textsuperscript{205} and electrostatic deposition. \textsuperscript{206} In the following paragraphs, some of the widely used methods to synthesize graphene will be demonstrated.

**Mechanical Cleavage**

Graphene was first exfoliated mechanically from graphite in 2004. \textsuperscript{191} Ever since the first graphene discovered using micromechanical cleavage of bulk graphite, this method has been widely used to prepare high-quality graphene single layers. This technique is quite simple, utilizing everyday adhesive tape to repeatedly peel layers off from highly oriented pyrolytic graphite and then pressing it onto an appropriate substrate, typically but not limited to oxidized silicon. \textsuperscript{207} Sizes of individual graphene crystals can reach millimeter, but production suffers from low output. The stamp technique offers not only high scalability but also easily controllability. This also make the possibility of stamp large-area complex graphene patterns at predetermined sites of substrates, paving the way for possible high-throughput synthesize of graphene-based integrated devices in the future.

![Figure 1.15 Schematic flowchart of electrostatic force assisted exfoliation of prepatterned few-layer graphene.\textsuperscript{208}](image)

Besides mechanical exfoliation, another stamp process based on electrostatic exfoliation was proposed by Liang et al (Figure 1.15). \textsuperscript{208} In their exfoliation process, a bias was applied between the pre-patterned highly oriented pyrolytic graphite stamp and SiO$_2$/Si substrate so as to generate an electrostatic attraction force between their surfaces. The electrostatic force then exfoliated the pre-patterned few layers graphene sheets and attached them onto the SiO$_2$ surface when the graphite stamp was vertically moved away from the substrate. The electrostatic force acted only onto the outmost graphene layers during each exfoliation/print cycle due to the thin screening depth in graphite. Finally, the very thin layers of graphene were obtained. By using this technique, few layers graphene nanoribbons with width as small as 18 nm were successfully produced. In the meantime, the exfoliated patterns also remain
in high quality. For example, Williams et al. transferred graphene patterns on a flexible, transparent polyethylene terephthalate substrate. These highly crystalline samples are best suited for the study of fundamental properties such as ballistic transport, carrier mobility, thermal conductivity and so on. Moreover, it should notice that it is still hard to fabricate uniform single-layer graphene patterns by the stamp technique, which requires better engineering of the stamp-preparation and stamping processes.

**Chemical Vapor Deposition**

![Graphene films transferred onto a SiO\textsubscript{2}/Si substrate and a glass plate, respectively.](image)

**Figure 1.16** (a,b) Graphene films transferred onto a SiO\textsubscript{2}/Si substrate and a glass plate, respectively. (c) Roll-to-roll transfer of graphene films from a thermal release tape to a PET film. (d) Transparent large-area graphene film transferred on a 35-inch PET sheet.

CVD method has emerged to be one of the most promising techniques for large-scale production of single and multiple layers graphene films. Large-area graphene films of the order of centimeters on copper substrates by CVD under high temperatures by pyrolysis of hydrocarbon precursors such as methane were reported. For example, Li et al. have reported the graphene synthesized by this CVD method which are predominantly single-layer graphene, with a small percentage of area having few layers, and are continuous across copper surface steps and grain boundaries. Furthermore, the as-grown graphene can be easily transferred to alternative substrates, such as SiO\textsubscript{2}/Si or glass (Figure 1.16), for further
evaluation and for various applications. Up to now, the largest continuous area of CVD graphene reported is 30-inch diagonal length, grown on copper foil in an 8-inch diameter quartz tube at low pressure obtained by Bae et al (Figure 1.16).\textsuperscript{213} The scalability and processability of CVD graphene and the roll-to-roll methods presented by Bae et al. are expected to enable continuous production of graphene-based electronic devices at large scales.

The number of graphene layers depends highly on the carbon solubility of the substrate, whilst the thickness and crystal ordering can be controlled by the cooling rate and hydrocarbon gas concentration. To illustrate, nickel-based substrate has relatively high carbon solubility.\textsuperscript{215, 216, 217} The carbon atoms can dissolve at high temperature then segregated at the surface and precipitate onto the metal surface and form single or multilayer graphitic films upon cooling. However, using this high carbon solubility of substrate, non-uniform films with a wide thickness ranging from 1 to around 10 layers with monolayer domain sizes up to several tens of micrometers in diameter were produced. An example of the coexistence of CVD and surface segregation processes can be found in the graphitization of Ni in a CH\textsubscript{4}-H\textsubscript{2} mixture at $\geq 1000$ °C.\textsuperscript{218} In this process, the production of carbon species at the Ni surface by the decomposition of CH\textsubscript{4} creates a concentration gradient between the bulk and surface, which finally will lead the carbon atoms to diffuse into the metal and form a solid solution. Once saturation, graphite forms on the metal surface. Upon cooling, the carbon atoms dissolved in the metal at high temperature precipitate out and segregate at the metal surface, forming multi-layers of graphene. The formed layers of graphene are highly dependent on the crystalline status of the metal substrate. In single crystal Ni substrate, the atomically smooth surface and the absence of grain boundaries produce more uniform and thinner few-layer graphene, while in polycrystalline Ni, grain boundaries serve as graphene nucleation sites favoring multilayer growth. Moreover, different cooling rates lead to different carbon segregation behaviours, affecting the thickness and quality of graphene films.\textsuperscript{219} Instead of using the hydrocarbon gases as carbon precursors, solid state carbon sources such as PMMA or even table sugar, is shown to produce graphene on select metal substrates at high enough temperature.\textsuperscript{220} By controlling the Ar/H\textsubscript{2} gas flow ratio, monolayer, bilayer, or few-layered graphene can be grown using a Cu thin film catalyst on SiO\textsubscript{2}/Si substrates with a 100 nm thick spin-coated PMMA film at temperatures as low as 800 °C.\textsuperscript{221}
Chemically Derived Graphene

At present, chemical oxidation of graphite to graphene oxide has emerged to be a viable route to afford graphene-based single sheets in considerable quantities.\textsuperscript{222-224} GO is usually synthesized through the oxidation of graphite using oxidants including concentrated H\textsubscript{2}SO\textsubscript{4}, HNO\textsubscript{3} and KMnO\textsubscript{4} chemicals based on Hummers method.\textsuperscript{225} Hence, GO is highly hydrophilic and readily exfoliated in water compared to pristine graphite because GO is heavily oxygenated bearing hydroxyl and epoxy groups on sp\textsuperscript{3} hybridized carbon on the basal plane, in addition to carbonyl and carboxyl groups located at the sheet edges on sp\textsuperscript{2} hybridized carbon. A monolayer, homogeneous and stable GO colloidal could simply obtained by sonication of GO. For example, Li et al. reported that the surface charges on GO are highly negative when dispersed in water by measuring the zeta potential due to the ionization of the carboxylic and the hydroxyl groups.\textsuperscript{7} Therefore, the formation of stable GO colloids in water was attributed to not only its hydrophilicity but also the electrostatic repulsion. Moreover, these functional groups provide reactive sites for a variety of surface-modification reactions to develop functionalized GO and graphene-based materials. On the other hand, GO was electrically insulating and contained large quantities of defects and disorders due to the disruption of the conjugated electronic structure by these functional groups.

Many methods of removing the oxygen from GO structure have been reported which includes chemical,\textsuperscript{204} thermal,\textsuperscript{226} electrochemical\textsuperscript{227} or electromagnetic flash\textsuperscript{228} and laser-scribe\textsuperscript{229} techniques, but generally resulted in inferior samples which are hence more precisely named reduced graphene oxide (rGO). The rGO can partly restore its graphitic structure as well as conductivity. Chemical reduction of GO sheets has been performed with several reducing agents including hydrazine,\textsuperscript{7,230,231} sodium borohydrate,\textsuperscript{232,233} and some green reducing chemicals including L-ascorbic acid,\textsuperscript{234} Escherichia coli (E. coli) bacteria\textsuperscript{235} and reducing sugars, such as glucose, fructose and sucrose.\textsuperscript{236} The formed rGO became less hydrophilic due to the removal of oxygen atoms and thus precipitated. However, Li and co-workers demonstrated the preparation of stable aqueous suspension of rGO nanosheets by adjusting the pH (with ammonia solution) of the aqueous solution during reduction with hydrazine. Electrochemical reduction is an ecofriendly and economical option, producing high-quality rGO in large scales.\textsuperscript{237,238} The reduction of GO films on graphite electrodes can be effectively tuned by varying the applied potential. Thermal treatment is
another way to reduce GO.\textsuperscript{226} Thermal reduction can be combined with chemical treatments to achieve more complete removal of oxygen.\textsuperscript{231, 239, 240}

1.4.2 Application of Graphene

**Graphene-based Semiconductor Photocatalysts**

Graphene has high conductivity, superior electron mobility and extremely high specific surface area, and more importantly the wet chemistry method can produce it on a large scale with low-cost. On the other hand, GO, the oxidized form of graphene which has large quantity of functional groups on it makes it superior candidate as an important component for making various functional composite materials. Especially, in recent years, graphene-based semiconductor photocatalysts have attracted extensive attention because of their usefulness in environmental and energy applications.

As we know, when a photon with energy of $h\nu$ matches or exceeds the band gap energy ($E_g$) of the semiconductor, an electron in the valence band (VB) is excited into the conduction band (CB), and will leaving a positive hole in the VB.\textsuperscript{241} The photogenerated holes and electrons play a very important role in pollutant degradation, photocatalytic disinfection, and solar energy conversion. However, the photogenerated holes and electrons are in their excited states which are unstable and easily recombined, which results in low efficiency of photocatalysis in real application process.\textsuperscript{241-243} To improve the efficiency of the photocatalysts, a variety of strategies have been employed including doping,\textsuperscript{244-246} combined with other semiconductors\textsuperscript{247, 248} and noble metal loading.\textsuperscript{249, 250} Because graphene has good electron conductivity, large specific surface area and high superior electron mobility, synthesis the composites of graphene and semiconductor photocatalysts have been widely studied by many researchers so as to enhance their photocatalytic performance.\textsuperscript{251-256} Different semiconductors including metal oxides, (e.g. TiO$_2$,\textsuperscript{257-260} ZnO,\textsuperscript{261-263} SnO$_2$,\textsuperscript{264-266} Cu$_2$O,\textsuperscript{266} Fe$_2$O$_3$,\textsuperscript{267} NiO,\textsuperscript{268} MnO$_2$,\textsuperscript{269} and ZrO$_2$\textsuperscript{264}) salts (e.g. ZnS,\textsuperscript{270} CdS,\textsuperscript{271-273} CdSe,\textsuperscript{274} Bi$_2$WO$_6$,\textsuperscript{275} BiVO$_4$,\textsuperscript{254} Sr$_2$Ta$_2$O$_7$,\textsuperscript{276} ZnFe$_2$O$_4$,\textsuperscript{277} InNbO$_4$,\textsuperscript{278} and g-Bi$_2$MoO$_6$\textsuperscript{279}) metal-free polymers (e.g. graphitic carbon nitride\textsuperscript{280, 281}). For instance, Kamat’s group has produced rGO-TiO$_2$/noble metal composites.\textsuperscript{251, 252, 282, 283} Under UV illumination ($\lambda<380$ nm), colloidal TiO$_2$ nanoparticles suspended in ethanol undergo charge separation, forming electron-hole pairs. The vast majority of these charge carriers recombine, leaving a fraction of holes are
scavenged by ethanol. The excess electrons can store for many days if the system is kept free from electron-scavenging species. Then, the stored electrons transferred to GO and reduce it to rGO. And the extra stored electrons finally transfer the noble metal ions to form the metal crystalline. Using this method, they demonstrated the feasibility of using graphene as an electron-transfer medium in the graphene/TiO$_2$/noble metal composite photocatalysts. Stimulated by this idea, an extensive research on the preparation, modification, and application of graphene-based semiconductor photocatalysts have been reported.$^{253, 254}$ Several graphene and semiconductor composites and their photocatalysis properties were summarized in Table 1.1.

**Dye Sensitized Solar Cells (DSSCs)**

![Figure 1.17](image)

**Figure 1.17 Working principle of dye-sensitized solar cells.**

As shown in Figure 1.17, typical DSSCs consists of a dye-sensitized nanocrystalline TiO$_2$ film as the photoanode, a CE and an electrolyte with a redox couple in the liquid or solid state.$^{284, 285}$ The CE plays a very important role in DSSCs. Its task is to reduce redox species in liquid solar cells, which are used as mediators in the regeneration of the sensitizer after electron injection, or to collect holes from the hole conducting material in solid-state DSSCs.$^{13}$ Normally, platinum-loaded conducting glass has been widely used as CE for DSSCs because the high catalytic activity and excellent conductivity against iodine in the electrolyte.$^{286, 287}$ However, the scarcity and expensive of Pt has limited its applications. Therefore, it is important to explore Pt-free materials to replace Pt CE for DSSCs.$^{288-291}$ Currently, the main drawback of carbon-based CEs is the requirement of a large amount of carbon to reach comparable efficiencies to Pt-based CEs. This makes the device bulkier and
more opaque. Graphene, since it has been large quantity fabricated, is being explored as a DSSCs CE to solve these issues. For example, Hu et al. synthesized a new type of graphene sheet with a 3D honeycomb-like structure. The 3D graphene sheets exhibited excellent catalytic performance as a CE for DSSCs with an energy conversion efficiency as high as 7.8%, which is comparable to that of an expensive Pt electrode.291

Figure 1.18 (a) Preparation route of the nitrogen-doped graphene foam CE. (b) Current density-voltage characteristics of the nitrogen doped graphene foam CE.292

The other successful example of using graphene as CE was demonstrated by Xue et al. who reported 3D N-doped graphene foams (N-GFs) with N content as high as 7.6% by annealing the freeze-dried graphene oxide foams as CE (Figure 1.18).292 The resultant DSSCs with foam-like N-doped graphene CE showed power conversion efficiency as high as 7.07%, and is comparable to that of DSSCs with a Pt CE (7.44%) constructed under the same condition. Apart from this, graphene/polymer composites,293, 294 graphene/metal composites,290, 295 graphene/CNT composites15, 296 were also used as CE in DSSCs. It was found that the defects and functional groups of the graphene sheets play a critical role in the electrocatalytic sites in DSSCs CEs. Therefore, tuning the defects and searching for effective functional groups for graphene sheets may be promising research directions for graphene-based or heteroatoms-doped graphene DSSCs.

Apart from above applications, the advantages of graphene or graphene-based composites are also used in fuel cells (such as the methanol oxidation cells,297, 298 and oxygen reduction cells299-301), photovoltaic devices etc.302
Chapter 1

Energy Storage

Graphene is a promising electrode material due to its high specific surface area, high conductivity and charge carrier mobility, high transparency and great mechanical strength. Thus, it is expected to be an ideal material for energy storage and conversion. There have been several reports on graphene-based electrodes for LIB, supercapacitors etc. (Table 1.2).

Lithium Ion Batteries (LIB)

Graphite is conventionally used as commercialized anode because of its good life cycle performance and high coulombic efficiency. However, the specific capacity of graphite is limited by forming an intercalation compound of LiC₆. In order to improve the specific capacities of the anode materials, a variety of carbon nanomaterials such as carbon nanofibers, CNT, and mesoporous carbons silicon, metals and oxides were used for this purpose. However, one of the main drawbacks of these materials is their huge volume variations during the lithium insertion/extraction processes. In recent years, graphene and its composites have been used as both anode and cathode materials on LIBs. Compared with graphite, graphene has a huge specific surface area, and more edge sites for anchoring other electroactive materials. Recently, Yang et al. reported the fabrication of graphene-encapsulated Co₃O₄ (rGO/Co₃O₄) by coassembly between negatively charged GO and positively charged oxide nanoparticles. The process is driven by the mutual electrostatic interactions of the two species, and is followed by chemical reduction. The rGO/Co₃O₄ nanoparticles exhibit a very high reversible capacity, thus holding great potential as an anode material for lithium storage. It is well known that LiFePO₄ has been widely explored as a cathode material for LIB. However, the practical application of LiFePO₄ has been limited by its low conductivity. Therefore, carbon based materials including carbon black or carbon nanotube were used to improve the conductivity of LiFeO₄. Recently, graphene has also been used for this purpose. Zhang et al. prepared a LiFePO₄/graphene composite by coprecipitation of both components. A similar composite was also prepared through a hydrothermal route.

Electrical Double Layer Capacitors (EDLCs)

The most important challenge EDLCs facing today in their widespread use is limited by their low energy storage density and relatively high effective series
resistance. To solve this problem, Zhu et al.\textsuperscript{318} reported a simple activation with KOH of microwave exfoliated graphene oxide and thermally exfoliated GO to achieve specific surface area values up to 3100 m\textsuperscript{2} g\textsuperscript{-1}. The surface specific area (SSA) of the activated MEGO (a-MEGO) could be readily controlled by the ratio of KOH versus MEGO. Two-electrode supercapacitor cells constructed with this carbon yielded high values of gravimetric capacitance and energy density with organic and ionic liquid electrolytes.

\textbf{Figure 1.19} Characterization of liquid electrolyte-mediated CCG (EM-CCG) films. (a) A photograph showing the flexibility of the film. (b and c) SEM images of cross sections of the obtained EM-CCG films containing (b) 78.9 volume percent (vol. \%) and (c) 27.2 vol. \% of H\textsubscript{2}SO\textsubscript{4}, respectively.\textsuperscript{319}

Recently, Yang et al. used chemically converted graphene (CCG) with two-dimensional configuration and formed graphene gel films by evaporation of the volatile electrolyte in the presence of a nonvolatile liquid electrolyte.\textsuperscript{319} The CCG hydrogel films obtained by filtration of CCG dispersion were exchanged with a miscible mixture of volatile and nonvolatile liquids and were then subjected to removal of the volatile liquid by vacuum evaporation. The packing density of CCG hydrogel films, with a metastable and adaptive pore structure, can be compressed irreversibly by capillary pressure through controlled removal of volatile solvent trapped in the gel. The graphene sheets in the films stacked in a nearly face-to-face fashion, so the packing density can be controlled from 0.13 to 1.33 g cm\textsuperscript{-3} by changing the ratio of volatile and nonvolatile liquids (Figure 1.19).

\section*{1.5 Heteroatom-doped Carbon Materials}

Heteroatom-doped carbon based materials represent one of the most prominent families of carbon materials that used in energy related applications, such as fuel cells, LIB, supercapacitors or hydrogen storage.\textsuperscript{331-333} Conventionally, N-doped
carbon has experienced great progress throughout past decades; however, many of other doping candidates also have gained researchers' interest in the last few years. Apart from this, heteroatoms co-doped carbon was also studied recently because which can probably create synergistic effects.

Basically, N-doped carbon material can be divided into two major groups with contrary properties: nitrogen rich carbon nitrides with C₃N₄ as a representative which exhibiting a rather stoichiometric composition on the one hand, and N-doped carbon materials in which only a small percentage of atoms in the carbon backbone are substituted by nitrogen atoms on the other hand. The graphitic allotrope g-C₃N₄ has been the subject of numerous synthetic approaches, based on the trimerisation of nitrile units, which actually dates back to 1834. These C₃N₄ represent a class of materials focusing on the photocatalytic and generally hetero-catalytic applications of carbon nitrides. The heteroatoms-doped carbons have advanced tremendously in the past few years, especially by proving their usefulness as electrocatalysts for oxygen reduction reaction in fuel cell cathodes, or as electrode materials in supercapacitors.

1.5.1 g-C₃N₄ and Heteroatom-doped Carbon Materials

**Synthesis of g-C₃N₄**

Graphitic nitride (g-C₃N₄) has attracted much attention in recent years because of their structure similarity to graphene. However, it consists of carbon, nitrogen, and some minor hydrogen content only. In contrast to graphene, g-C₃N₄ is a medium-band gap semiconductor (2.7 eV) and a good candidature as an effective photocatalyst and chemical catalyst for a broad variety of reactions. This allows its direct use in sustainable chemistry as a multifunctional heterogeneous metal-free catalyst, for example in oxidation of hydrocarbons and water splitting. For quite a long time, there is a prevailing discussion about the possible structure models for g-C₃N₄. At the beginning, inspired by the structure of graphite, triazine (C₃N₃) had been put forward as the elementary building blocks of g-C₃N₄ (Figure 1.20a and b). However, tri-s-triazine rings that are cross-linked by trigonal nitrogen atoms, another possible building block, which are structurally related to the hypothetical polymer melon, have recently been shown to be energetically favourable to the triazine-based modification. The synthesis and characterization of g-C₃N₄ is a challenging task by itself, and to date a large number
of different experimental attempts have been made.\textsuperscript{364-372} Until now, the most widely used method was the high temperature pyrolysis of cyanamide,\textsuperscript{373} dicyandiamide,\textsuperscript{374} melamine\textsuperscript{375} or urea\textsuperscript{376} which was seen as good synthetic strategies to generate slightly defect, polymeric species.

Figure 1.20 Two predicted structures of g-C\textsubscript{3}N\textsubscript{4} made up of (a) Condensed melamine subunits and (b) Condensed tri-s-triazine subunits.\textsuperscript{377} (c) Reaction path for the formation of g-C\textsubscript{3}N\textsubscript{4} starting from cyanamide.

The formation of g-C\textsubscript{3}N\textsubscript{4} using cyanamide as precursor was fabricated by pyrolysis it through a step by step elevated temperature process.\textsuperscript{378} The reaction is a combination of polyaddition and polycondensation scheme where the precursors are condensing towards melamine in the first step. The second step is a condensation process where ammonia is eliminated. Therefore, the products were different when performed in a closed and open reaction flasks. In the pyrolysis procedure, when the pyrolysis temperature increased to 350 °C, essentially melamine-based products are formed, while the tris-s-triazine forms via melamine rearrangements at round 390 °C. When the temperature increased to 520 °C, condensation of this unit to polymers, networks and potentially the final polymeric C\textsubscript{3}N\textsubscript{4} occurs. Above 600 °C, the material becomes unstable. Further heating the material to 700 °C leads the residue-free disappearance of the material via generation of N and cyano fragments. This process was demonstrated as in Figure 1.20c.
Synthesis of Heteroatom-doped Carbon Materials

The synthetic ways of heteroatoms-doped carbons are nevertheless incredibly manifold, and are thus not limited to a single standard procedure. Classically, heat treatment of crude carbons with reactive heteroatom sources is one way of obtaining heteroatoms-doped carbons. For example, N-doped carbon used nitrogen sources of such as urea, nitric acid or especially ammonia etc.\textsuperscript{379-383} Another doping approach is via the pyrolysis or chemical vapor deposition of heteroatoms contained and carbon containing precursors, for N-doping, such as heterocycles, melamine or aminated sugars, by which a direct incorporation of the nitrogen atoms into the forming carbon backbone becomes possible.\textsuperscript{24,384}

Heat Treatment of Crude Carbons with Heteroatom Sources

As we know, CVD is widely used to synthesize various carbon nanomaterials including CNTs,\textsuperscript{385} carbon nanofibers,\textsuperscript{386} graphene,\textsuperscript{387} and also for heteroatoms-doped carbon materials.\textsuperscript{388} For example, to synthesize N-doped graphene, a metal catalyst (Cu or Ni) is usually used as the substrate, and then at high temperature, a carbon source gas mixed with a N-containing gas is introduced.\textsuperscript{389,27,203} These precursors dissociate and recombine into N-graphene by means of precipitation on the surface of the catalyst.\textsuperscript{203,390} Apart from using gas mixture, liquid organic precursors such as acetonitrile or pyridine have also been used to form N-graphene.\textsuperscript{391,392} Moreover, in the CVD approach, the N content can be controlled by changing the flow rate and ratios between carbon source and nitrogen source.\textsuperscript{203} Moreover, for this method, synthesis of other N-doped carbon materials has revealed that the doping environment is also influenced by the flow rate, catalyst, and growth temperature.\textsuperscript{393-395} For boron doping, Yang et al.\textsuperscript{396} using CVD with benzene, triphenylborane (TPB), and ferrocene as precursors and catalyst, synthesized boron-doped CNTs with tunable boron content of 0-2.24 at% by using different TPB concentrations. Instead of CVD, arc discharge based synthetic procedure was also applied, in which elemental boron and graphite powder served as precursors, yielding a mixture of different boron-doped carbon nanostructures, such as graphitic sheet, nanotube etc.\textsuperscript{397} In comparison to B, N doping, S doping in carbon materials is still quite rare and represents an emerging field within carbon-based material research. Schmidt et al. used a microporous polymer network containing thienyl building
blocks as precursor for intrinsically microporous S-doped carbon with variable sulfur contents.\textsuperscript{398, 399}

**Postsynthesis Treatment**

Post treatment includes thermal treatment,\textsuperscript{400} plasma treatment,\textsuperscript{401} and NH\textsubscript{3} treatment.\textsuperscript{402} The widely used method of post treatment is thermal treatment. In this method, the already synthesized carbon materials and the wanted doped heteroatom precursors are mixed together, then, thermal treatment of the mixture will lead to the successful doping of the carbon. For example, it has been shown that heating graphene in NH\textsubscript{3} atmosphere at high temperature (\(\geq 800^\circ\text{C}\)) can produce N-graphene.\textsuperscript{403, 404} However, the N content in the N-graphene synthesized by this method is relatively low (less than 3.0 at.\%). The low doping level may be attributed to two reasons: one is the insufficient defects numbers in the high quality graphene; the other is the high annealing temperature, which will break the C-N bonds in N-graphene. Moreover, study also shows that nitrogen doping is more likely to occur at the defects and edges of graphene in the thermal treatment method.\textsuperscript{401}

![Figure 1.21](image)

**Figure 1.21 Schematic illustration of the fabrication of N and S-doped graphene.**\textsuperscript{405}

Apart from graphene, GO can also be used to synthesize N-doped graphene by thermal treatment in the presence of various nitrogen precursors.\textsuperscript{384} For sulfur doping, Yang et al. reported the blend of GO homogeneously with benzyl disulfide, followed by subsequent thermal treatment, the author proposed the amount of sulfur doped is 1.5 wt\% and homogeneously distributed throughout the sheet.\textsuperscript{406} For another S, or N-doping example, Yang et al. reported a similar approach in their S, or N-doped graphene synthesized by using GO as starting carbon and annealed in an atmosphere
of H₂S or NH₃. After this thermal treatment, S or N-doped graphene were obtained after removal of the silica template (Figure 1.21). Meanwhile, since the doped carbon materials have introduced active sites in the carbon, it shows significant potential compared with the undoped one. Nowadays, researchers begin to study their beneficial properties in energy related applications. In the following paragraphs, I would like to briefly introduce some of the applications of g-C₃N₄ and heteroatoms doped-carbon materials used as catalysts in environmental remediation and energy conversation and storage.

### 1.5.2 Applications of g-C₃N₄ and Heteroatom-doped Carbon Materials

#### g-C₃N₄ for Water Splitting and Organic Pollutant Degradation

Owing to its electronic and structural properties, g-C₃N₄ possesses all the prerequisites required for a heterogeneous photocatalysts. The bandgap of the condensed graphitic carbon nitride is estimated to be 2.7 eV from its ultraviolet-visible spectrum, corresponding to an optical wavelength of 460 nm. This bandgap is sufficiently large to overcome the endothermic character of water-splitting reaction, which normally requires four photons with an average energy of 1.23 eV. DFT calculation suggest that that the N atoms would be the preferred oxidation sites for H₂O to form O₂, whereas the carbon atoms provide the reduction sites for H⁺ to H₂. Most importantly, both the HOMO and the LUMO encompasses the oxidation and reduction potential of water. This means that the hole in the HOMO is sufficiently reactive to oxidize water to oxygen, whilst the electron in the LUMO has enough reduction potential to reduce water to hydrogen. However, pure g-C₃N₄ can only absorb blue light up to 450 nm, which limits the utilization of solar energy. To date, however, efficient and stable H₂ evolution could be achieved by modification of g-C₃N₄ either with a small amount of co-catalyst, such as Pt or Au etc. or doping. This is presumably due to kinetic effects, as splitting of a noble metal-H bond is much less kinetically hindered than splitting of an N-H bond. On the other hand, g-C₃N₄ can be used as photocatalysis photodegradation of organic pollutant. The details of its application will be further illustrated in Chapter 2.

#### Heteroatom-doped Carbon Materials for Energy Conversion and Storage

#### Heteroatoms-doped Carbon Materials as Catalyst in Energy Conversion

The origin of the development of heteroatom-doped carbons used as catalyst in fuel cell can be date back to 1964 when Jasinski et al. applied metal-phthalocyanine-
complexes to catalyze the reduction of oxygen electrochemically in the cathodic half-cell. They found thermal treatment of related catalysts could increase both activity and stability; so the concept of N-doped carbons as electrocatalysts was born.\footnote{414} From then on, metal and carbon complex mimicking catalysts was derived from an accordant review provided by Zhang et al. in 2008.\footnote{415} However, the necessity of metals in the ORR catalysts was more and more doubted. In 2006, completely metal free catalysts were proven to be good candidate catalysts for ORR.\footnote{416} It was not until 2009 when N-doped CNTs was used as metal-free catalysts for ORR presented by Dai et al. which showed remarkably property exceeding the activity of conventional Pt@C catalysts, that it triggered widely study by researchers worldwide.\footnote{24} Other than nitrogen, boron,\footnote{396,417} phosphorus,\footnote{418} sulfur\footnote{406} etc. and co-doping carbon materials were all used as catalysts in ORR.\footnote{337,419} For example, Yang et al. tailored the electronic arrangement of graphene by doping sulfur and the material using as ORR catalyst showed significantly improved behaviours.\footnote{406} On the other hand, Dai et al. using the heat treatment of crude carbons with heteroatom sources method synthesized B and N co-doped CNT catalyst for ORR. The authors believed that due to a synergetic effect arising from co-doping of CNTs with boron and nitrogen, the resultant B and N co-doped vertically aligned CNT electrode had higher electrocatalytic activity for ORR in alkaline medium than its counterparts doped with boron or nitrogen alone. Moreover, many other heteroatoms-doped carbon material were also studied for ORR and the principle of the highly activity towards ORR will be further demonstrated in Chapter 4.

**Heteroatom-doped Carbon Materials in Energy Storage**

As mentioned before, although graphene-based materials can reach a high reversible capacity at a low charge rate,\footnote{420} it is still rate-limited at a high charge/discharge rate.\footnote{421} Thus, heteroatom-doped graphene based device is proposed with the intent to achieve a high reversible capacity at high charge/discharge rate. In an earlier work reported by Reddy et al. they obtained N-doped graphene using CVD method.\footnote{391} The reversible discharge capacity of N-graphene was almost doubled compared with pristine graphene because of the enhanced Li ion intercalation with the introduction of N atoms. In another work, N-doped graphene with 2 at% N content was synthesized by heat treatment of GO in an NH\textsubscript{3} atmosphere.\footnote{422} N-graphene possessed a reversible capacity of around 900 mA h g\textsuperscript{-1} at a current density of 42 mA g\textsuperscript{-1} and a capacity of around 250 mA h g\textsuperscript{-1} at a high current density of 2.1 A
The excellent LIB performance of N-graphene can be ascribed to many factors, such as the introduction of N atoms, the defects and disordered surface morphology induced by doping, increased electrode/electrolyte wettability, and all of these finally improved their electrochemical performance.

For supercapacitors applications, a material with high specific surface is preferred. For example, Kanamori et al.\textsuperscript{423} have synthesized monolithic S-doped carbon material by using divinylbenzene as carbon precursor and polydimethylsiloxane as sulfur precursor. The obtained monolithic showed a complex trimodal porous structure, with a surface area $>2400$ m$^2$ g$^{-1}$. With this unique structure, the S-doped monolithic carbon showed significantly higher specific capacitances than crude activated carbon electrodes without sulfur functionalities.

### 1.6 Fabrication of High Performance Carbon-based Materials from Biomass

Nowadays, environmental problems such as global warming and dwindling energy resources are becoming increasingly critical issues. Utilization of biomass, especially inedible lignocelluloses and chitin to create fuels, energy, and a host of other products are highly desirable for construction of sustainable society.\textsuperscript{424,425} Therefore, integrated utilization and multi-product of biomass is becoming the significant issue and development tendency. From a general point of view, lignocellulose is firstly fractionated to three main components, that is, lignin, hemicelluloses, and cellulose.\textsuperscript{426} Whilst chitin, the second most abundant semi-crystalline polysaccharide,\textsuperscript{427} are also widely studied and used in environmental remediation and energy conversion applications.\textsuperscript{428,429} In this part, simple literature reviews regarding extraction of cellulose and chitin from grass and animal shells, respectively, will be summarized, the details of it will be demonstrated in Chapter 6. The obtained materials are used as ORR catalyst in fuel cells.

#### 1.6.1 Preparation of Cellulose Nanofibers

The conventional method to isolate cellulose nanofibers from the three sources was mainly performed by two ways: one is the chemical extraction method that undergoes several steps which was reported by Wise et al.\textsuperscript{430} Firstly, wood powder was sieved under different mesh and solvent extraction was performed with a mixture of toluene/ethanol for a period of time so as to remove the wax in the raw material. Secondly, lignin in the sample was removed using an acidified sodium chlorite solution at moderate temperature, and the process was repeated until the
product became white.\textsuperscript{430} Thirdly, the sample was treated in 6 wt\% potassium hydroxide over night at room temperature and then at the same concentration at 80 °C for 2 h in order to leach hemicelluloses. This resulted in whole cellulose being practically obtained.\textsuperscript{431} The other widely used method was using bacteria. The most studied species of bacteria that produces cellulose is generally called \textit{gluconacetobacterxylinus}.\textsuperscript{432} Under special culturing conditions the bacteria secrete cellulose microfibrils, producing a thick gel composed of cellulose microfibrils and around 97\% water, called pellicle, on the surface of the liquid medium.\textsuperscript{433, 434}

\textbf{1.6.2 Preparation of Chitin Nanofibers}

Various methods have been employed for preparation of chitin nanowhiskers or nanofibers including acid hydrolysis,\textsuperscript{435-437} TEMPO-mediated oxidation,\textsuperscript{438, 439} ultrasonication,\textsuperscript{440} electrospinning,\textsuperscript{441} mechanical treatment,\textsuperscript{442} and gelation.\textsuperscript{443} However, chitin nanofibers were normally obtained by a chemical extraction method from animal shells.\textsuperscript{444, 445} To make it simple, firstly, to remove the contaminating proteins from the raw animal shells, the refined shell powders were refluxed in potassium hydroxide for several hours under vigorous stirring. This suspension then filtered and washed with deionized water. Next, the chitin samples were treated with HCl solution to remove the mineral salts. After filtration and rinsing with deionized water, the treated samples were dispersed and boiled further in KOH solution to completely remove any residual proteins. The pigment was then removed from the samples using sodium chlorite in sodium acetate buffer, followed by filtration and washing with deionized water. The purified wet chitin from dry crab shell was dispersed in acetic acid solution.\textsuperscript{446} The other methods for preparing chitin fiber will be lists in Chapter 6 for details.

\textbf{1.6.3 Applications of Cellulose and Chitin}

Cellulose constitutes the most abundant and renewable polymer resource available worldwide. This molecular structure gives cellulose its characteristic properties of hydrophilicity, chirality and degradability. Chemical reactivity is largely a function of the high donor reactivity of the OH groups.\textsuperscript{447} Therefore, the widely known application of cellulose material is their adsorbent properties due to their special properties: hydrophilic, porous, many functional groups, high surface area etc. However, unmodified cellulose has a low adsorption capacity as well as variable physical stability. Therefore, chemical modification of cellulose can be carried out to
achieve adequate structural durability and efficient adsorption capacity. For example, Guo et al. used cellulose bead loaded with iron oxyhydroxide (BCF), and applied for the adsorption and removal of arsenate and arsenite from aqueous systems. The results show that the BCF had higher removal efficiency for arsenite than arsenate. The composites are stable and possess high removal efficiency of arsenic by BCF after regeneration. On the other hand, modified cellulose used as adsorbent was reviewed by Connell et al. Apart from this, cellulose was also widely used in drug delivery, digital display, biomedical etc. For chitin, the application of it in protein immobilization, bioengineering and as adsorbent were reported. For example, the poor solubility of chitin is the major limiting factor in its utilization. Despite this limitation, various applications of chitins have been reported, e.g. as raw material for man-made fibers. The fibers were used as adsorbents and wound-dressing materials. For instance, Ma et al. employed ultrafine chitin nanowhiskers with 5-10 nm diameters as barrier layers in a new class of thin-film nanocomposite membrane for water purification and the nanocomposite membranes presented high virus adsorption capacity as demonstrated by MS2 bacteriophage testing, due to the very high surface-to-volume ratio.

For energy conversion applications, the lignocellulosic materials have been mainly used in energy conversion application in biofuel. However, to achieve this conversion, it should undergo three key steps: (1) pre-treatment of raw material so as to acquire the specific material that wanted; (2) conversion of cellulose and hemicellulose into fermentable sugars; (3) fermentation of sugars into raw biofuels. For example, both dilute-acid and enzymatic hydrolysis of cellulose were used to generate biofuels. In terms of chitin, it has attracted attention in various scientific and engineering processes due to its excellent biocompatibility, non-toxicity, chemical and thermal stability. In this study, cellulose and chitin obtained from biomass will be used as catalysts in alkaline fuel cell towards oxygen reduction reactions (ORR) which will be shown in Chapter 6.
1.7 Scope of the Thesis

The superior properties of graphitic carbon-based materials and their significance for energy and environmental applications have attracted enormous research activities over the past decade or so. Despite significant progress, there are many unresolved issues requiring further research. This study intends to develop technological solutions for three important issues: (i) developing an effective means to tune bandgap structure for enhancement of light utilization efficiency and photocatalytic activity; (ii) demonstrating the feasibility of utilizing plentiful renewable biomass materials to replace petroleum-based synthetic chemicals for synthesis of high performance graphitic carbon materials; (iii) developing facile synthetic method to realize controllable doping and co-doping heteroatoms into graphitic carbon structures to produce high performance electrocatalysts.

Chapter 1 literature reviews current research activities related to the development of new carbon materials including nanotubes, graphitic carbons, carbon nanodots/quantum dots (CNDs/CQDs) and their derivatives.

Chapter 2 investigates the fabrication of g-C₃N₄/rGO with a tunable bandgap structure as an effective means to enhance the visible light utilization efficiency and photocatalytic activity.²²

Chapter 3 demonstrates the feasibility of fabricating graphitic carbon materials from raw biomass. Monkey Grass is directly transformed into high quality N-doped graphitic carbon nanoparticles (N-CNs) and nanodot/nanosheet aggregates (N-CNAs) via a facile hydrothermal process without the needs of any synthetic chemicals. The resultants N-CNs are innovatively used as an effective sensitizer for solar cells. A new anion (I⁻) fluorescent quenching principle is developed to enhance the overall conversion efficiency. The resultant N-CNAs are successfully applied as high performance electrocatalyst for oxygen reduction reaction (ORR).²³

Heteroatoms co-doped graphitic carbon materials are known to enhance the electrocatalytic activity for ORR, but doping of heteroatoms into graphitic carbon structures in a reproducibly and precisely controlled manner is highly challenging. Chapter 4 proposes and experimentally validates a self-sponsored co-doping approach for facile control doping of S and N into graphitic carbon network structures. The required carbon and dopant (S, N) sources are self-sponsored by a sole precursor (1-allyl-2-thiourea) without the need for catalysts. With this new approach, the controllable doping and graphitic carbon growth can be concurrently
achieved by simply controlling the thermolysis temperature. A high performance electrocatalyst should possess a surface atomistic structure that best matches the needed electrochemical properties of the target redox system. It also needs to possess an optimal pore-structure network that best meets the needs for electron and mass transport. Doping is effective for tailoring atomistic structures but ineffective for altering pore-structures. A long-ranged graphitic carbon network would provide superior electron pathway with improved electron collection efficiency. To facilitate mass transport, a larger pore size and shorter diffusion pathway would be favourable, but such structures often possess limited surface area. In general, a structure possessing high surface area often has small pore-size, unfavourable for mass transport. A structure with multi-sized pore structures would be rational for achieving high effective surface area without compromising mass transport. For this, a silica nanosphere template is employed in this study to create long-ranged graphitic carbon network that possesses a trimodal-pore structured (micro-, meso- and macro-pores) graphitic carbon network. The resultant S, N co-doped graphitic carbon network possesses high ORR catalytic activity.

Chapter 5 focuses on the development of high performance Pt-free counter electrode materials for dye-sensitised solar cells including S, N co-doped graphitic carbon network and the (0001) faceted single crystal NiS nanosheet film.

Chapter 6 explores the feasibility of fabricating high performance 3D N-doped carbon-based aerogel ORR electrocatalysts from abundant biomasses such as cellulose and chitin.

Chapter 7 provides a summary of research presented in this thesis and future works.
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CHAPTER 2 $\text{g-C}_3\text{N}_4/\text{rGO}$ NANOCOMPOSITES AND THEIR VISIBLE LIGHT PHOTOCATALYTIC ACTIVITY
2.1 Introduction

Graphitic carbon nitride (g-C$_3$N$_4$) has become an attractive candidate as visible light photocatalyst due to its excellent sunlight harvesting capability, superior physicochemical and photochemical stabilities, plentiful material sources and easy synthesis.$^1$ As we know, there are two prevailing structure models of g-C$_3$N$_4$, namely, triazine (C$_3$N$_3$)$_2$$^2$-$^4$ and tri-s-triazine rings.$^5$-$^7$ Moreover, the latter has recently shown to be energetically favored with respect to the triazine-based modification. This type of structure can be obtained by pyrolysis of cyanamide, dicyandiamide, or melamine which yields a melon polymer built up from melem units.$^7$-$^{12}$ Up to now, the condensation pathways of cyanamide to dicyandiamide to melamine and all of the other C/N materials were seen as suitable synthetic strategies to generate slightly defects, polymeric species, and it turned out in most of the catalytic experiments that defect-containing, polymeric g-C$_3$N$_4$ is more active. Apart from this, g-C$_3$N$_4$ is thermal stable as well. Thermal gravimetric analysis (TGA) on g-C$_3$N$_4$ reveals that this material is significantly robust and non-volatile up to 600 °C even in the air. A complete decomposition of carbon nitrides occurs at 750 °C resulting in no residue of the material.$^{13}$ However, the stacking with optimized van der Waals interactions between the single layers of carbon nitride makes it insoluble in most solvents.$^{13, 14}$

As a photocatalyst, the photocatalytic performance depends on preparation method, including precursors used and condensation temperature, the degree of condensation and packing between the layers. Generally speaking, ordinary polymeric carbon nitride exhibits strong blue photoluminescence at room temperature. The luminescence was observed over a wide range (430-550 nm) with the strongest luminescence peak at about 470 nm.$^{15}$-$^{17}$ In comparison with other g-C$_3$N$_4$ allotropes, the small bandgap (ca. 2.70 eV) of g-C$_3$N$_4$ is a result of sp$^2$ hybridization of the carbon and nitrogen that form the π-conjugated graphitic planes with comparable graphite structure.$^1, 18$ It is well known that the materials with delocalized conjugated π structures have been confirmed to have high charge separation efficiency and low charge recombination rate. Nowadays, g-C$_3$N$_4$ materials have been widely used in many photo-related applications such as photoelectrochemical,$^{19, 20}$ water splitting,$^{21}$ oxidation reaction$^{22, 24}$ etc. However, the obtained visible light photocatalytic activity of pure g-C$_3$N$_4$ is rather low due to the marginal visible light absorption and grain boundary effects.$^{25}$ Moreover, the weak van der Waals interaction between
adjacent conjugated planes also limits the electron coupling between the planes, which negatively affects the electron transfer and photocatalytic activity.\textsuperscript{26} Aiming to improve the visible light photocatalytic efficiency of the g-C\textsubscript{3}N\textsubscript{4}-based photocatalyst, a new strategy of doping\textsuperscript{24, 27-29} or compositing g-C\textsubscript{3}N\textsubscript{4} with other semiconductors has been widely investigated.\textsuperscript{29, 30}

As the thinnest material, graphene has received considerable attention due to its unique optical, electronic and mechanical properties, promising for a range of applications such as solar energy conversion, photocatalysis, sensing and fuel cells.\textsuperscript{31-37} Graphene and g-C\textsubscript{3}N\textsubscript{4} possess similar carbon network structure and sp\textsuperscript{2} conjugated π structure, which make them the most compatible materials to form composites. Importantly, the resultant composites could possess an enhanced photocatalytic activity because of the superior electronic properties introduced by the graphene component facilitating electron transfer and charge separation processes. For example, using graphene oxide modified g-C\textsubscript{3}N\textsubscript{4} composite fabricated via a sonochemical, an enhanced visible light photocatalytic activity toward the degradation of rhodamine B and 2, 4-dichlorophenol was reported.\textsuperscript{38} Instead of graphene oxide, Zhang and co-workers used rGO to form non-covalently composite with g-C\textsubscript{3}N\textsubscript{4}, leading to an enhanced optoelectronic conversion property.\textsuperscript{25} However, their work did not provide detailed information regarding the actual weight ratio of g-C\textsubscript{3}N\textsubscript{4} to rGO in the resultant nanocomposites. Moreover, in their study, the bandgap of the fabricated composite was found to be almost constant with different rGO to g-C\textsubscript{3}N\textsubscript{4} ratios. Generally, for a composite semiconductor photocatalyst containing rGO, the altered band structure originated from the composited rGO is responsible for the enhanced visible light photocatalytic activity as demonstrated by a number of reports where they use rGO as mediator to narrow the photocatalyst bandgap to achieve high photocatalytic activities under visible light irradiation.\textsuperscript{39-41}

In this chapter, we report a thermal conversion method to fabricate high visible light active g-C\textsubscript{3}N\textsubscript{4}/rGO (CN/rGO) nanocomposites formed by cross-linked approach. The band structure of the resulting nanocomposites can be readily tuned by simply controlling the weight ratio of cyanamide to GO in precursor materials. The conduction and valence band positions of the obtained nanocomposites with different CN/rGO weight ratios have been investigated in detail using optical and electrochemical techniques. The fabricated CN/rGO nanocomposites with different band structures as photocatalysts have been systematically evaluated for
photocatalytic degradation of rhodamine B (RhB) and 4-nitrophenol under visible light irradiation (λ > 400 nm).

2.2 Experimental Section

2.2.1 Chemicals and Materials

Natural graphite powder (325 meshes) was purchased from Chem Supply (Australia), and all of other reagents with analytical grade purity were purchased from Sigma Aldrich and used without further purification.

2.2.2 Synthetic Method

Preparation of GO:

GO was synthesized by modified Hummers method through oxidation of graphite powder.\textsuperscript{42, 43} Typically, the graphite powder (5.0 g) was added into an 80 °C solution composed of concentrated H\textsubscript{2}SO\textsubscript{4} (30 mL), K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} (3.0 g) and P\textsubscript{2}O\textsubscript{5} (3.0 g), and then reacted for 6.0 h. The resultant dark blue mixture was cooled down to room temperature, then washed adequately with deionized water until pH of the filtrate was close to 7.0 and dried in an oven at 80 °C overnight. Then, 2.5 g of pre-oxidized graphite was placed into 115 mL of cold (0 °C) concentrated H\textsubscript{2}SO\textsubscript{4} solution. KMnO\textsubscript{4} (7.5 g) was added gradually into the above solution under stirring, and the temperature of the mixture was kept below 20 °C for 2.0 h. The mixture was then stirred at 35 °C for 3.5 h. After that, 230 mL of water was slowly added into the above mixture, and then reacted for another 1.5 h at room temperature. More water (300 mL) and 30% H\textsubscript{2}O\textsubscript{2} (6.5 mL) were then added into the above solution to terminate the reaction. The mixture was subsequently washed with diluted HCl solution and centrifuged. The resulting product was further washed and dialyzed for one week.

Preparation of CN/rGO nanocomposites:

GO aqueous solution (1.0 mg mL\textsuperscript{-1}) was mixed with cyanamide (99%, Sigma Aldrich) with different weight ratios, and then was concentrated into a paste at 100 °C on a hot plate. After that, the synthesized product was grinded into fine powders and put into a crucible, and then heated to 550 °C for 4.0 h in Ar atmosphere. Pure g-C\textsubscript{3}N\textsubscript{4} was prepared by heating only cyanamide under the same preparation conditions as CN/rGO nanocomposites. The rGO modified g-C\textsubscript{3}N\textsubscript{4} nanocomposite was denoted as CN/rGO-x%, where x% is the initial weight ratio of GO to cyanamide.
2.2.3 Characterizations

Transmission electron microscopy (TEM) (Philips F20) and X-ray Diffraction (XRD) (Shimadzu XRD-6000 diffractometer, equipped with a graphite monochromator) were employed for characterising the sample structure. Chemical compositions of the samples were analysed by X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyser). All binding energies were carefully aligned by reference to the C1s peak (284.6 eV) arising from surface hydrocarbons or possible adventitious hydrocarbon. UV-Vis diffuse reflectance spectra of the nanocomposites were recorded on a Varian Cary 5E UV-Vis-NIR spectrophotometer. Fourier transform infrared spectroscopy (FT-IR) analysis of the samples was performed using Perkin Elmer spectrum 1000 FT-IR spectrophotometer with KBr as the reference sample. Photoluminescence spectra (PL) of the samples were obtained using a fluorescence spectrometer (Hitachi F-7000) at 293 K. The excitation wavelength was 315 nm, the scanning rate was 1200 nm min\(^{-1}\), and the PMT voltage was 700 V. The widths of the excitation slit and emission slit were both 2.5 nm. Mott–Schottky curves were measured by a Princeton Applied Research PARSTAT 2273, using a three-electrode system. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (\(S_{\text{BET}}\)) using nitrogen adsorption-desorption isotherms of the samples on a Quantachrome Autosorb-1 equipment. The thermal processes of the precursor was heated from 100 °C to 1000 °C with a ramp rate of 5 °C min\(^{-1}\) in an inert (Ar) atmosphere with simultaneous TG/DSC (TG/DSC, Netzsch STA 449F3 equipment).

2.2.4 Measurements

The photocatalytic activity was evaluated in a XPAII reactor (Nanjing Xujiang Machineelectronic Plant, China). 8.0 mg of nanocomposite photocatalyst was put into 10 mL of quartz test tube containing 5.0 mL of 5.0 mg L\(^{-1}\) RhB and 10 mg L\(^{-1}\) 4-nitrophenol, and then stirred in dark for 0.5 h to achieve adsorption equilibrium before light irradiation. After that, a 1000 W Xe lamp (the UV light was cut off by 2.0 M sodium nitrite\(^{44, 45}\)) was used as the visible light source to perform the photocatalytic experiment at 25 °C. The remaining concentration of RhB and 4-nitrophenol in reaction solution was determined using UV-Vis spectrophotometer (UV-1800, Shimadu). The dispersion ability of the fabricated nanocomposites in
aqueous medium is relatively low and the reaction solution was therefore constantly stirred during photocatalytic reaction process.

2.3 Results and Discussion

2.3.1 Structure and Morphology

![DSC / a.u.](attachment:image.png)

**Figure 2.1** TG (black line) and DSC (blue line) curves of cyanamide from 100 to 1000 °C, respectively. It indicates that excellent thermal stability of g-C_3N_4 can be formed under the pyrolysis temperature of 550 °C.

CN/rGO nanocomposites with different rGO ratios were obtained by thermally treating the precursor materials consisted of cyanamide and GO with different weight ratios at 550 °C for 4.0 h in Ar. Table 2.1 summarizes the reaction condition, mass product yield, and composition of the fabricated nanocomposites with different weight ratios of rGO to g-C_3N_4. It was found that an increase in the added amount of GO in the reaction solution results in a slight increase in the product yield. This may be due to the effect of the increased amount of GO that interacted with cyanamide under higher temperature and formed chemical bond in the final composites which will be illustrated in the following sections. The weight ratios of rGO to g-C_3N_4 in nanocomposites were estimated based on the product yield by assuming that the rGO weight in the nanocomposite equals the initial GO amount. The resultant nanocomposites are denoted as CN/rGO-x% (x% is the weight ratio of rGO to g-C_3N_4 in the nanocomposite). The reason why we chose 550 °C as the pyrolysis temperature is that according to the TG/MS curve shown in Figure 2.1, excellent thermal stability of g-C_3N_4 will only be formed in the range of 400-700 °C. However,
heating the material to 700 °C will result in the residue-free disappearance of the material via generation of N and cyano fragments.

Figure 2.2 (a) Photographs of pure g-C₃N₄ and CN/rGO nanocomposites, in which, from left to right, weight ratio of rGO to g-C₃N₄ in the final product are 0.0%, 1.6%, 2.5%, 5.1% and 19.6%, respectively. (b) XRD patterns of the pure g-C₃N₄, rGO and CN/rGO nanocomposites.

Figure 2.2a shows the photographs of pure g-C₃N₄ and CN/rGO nanocomposites. As shown, the color of the pure g-C₃N₄ is bright yellow. With increasing rGO ratio, the color of the resulting nanocomposites changes from slight gray for CN/rGO-1.6%, gray for CN/rGO-5.1% to dark gray for CN/rGO-19.6%. A similar phenomenon has also been observed for other carbon/semiconductor composite materials.⁴⁶-⁴⁸ Figure 2.2b shows the XRD patterns of pure g-C₃N₄, rGO and CN/rGO nanocomposites with different rGO ratios. As shown, a broad diffraction peak at around 24.3° was observed for the rGO, meaning that the rGO sheets were loosely stacked.⁴⁹ However, both of the pure g-C₃N₄ and CN/rGO nanocomposites show a strong characteristic (002) peak at 27.4°, corresponding to the interlayer-stacking of the conjugated aromatic system with a stacking distance of 0.326 nm, indicating that the formed nanocomposites possess layered structures. The peak at 13.0° corresponding to d
value of 0.676 nm is related to the in-plane ordering of tri-s-triazine units (Figure 2.3).  

![Molecular structure of the formed pure g-C₃N₄ structure.](image)

**Figure 2.3** *Molecular structure of the formed pure g-C₃N₄ structure.*

It was also found that with increasing rGO ratio in nanocomposites, the relative intensity of (002) peak increased. This could be due to an increase in structural correlation length introduced by large size rGO sheets. On the other hand, the XRD pattern recorded for CN/rGO nanocomposites did not differ significantly from those of pure g-C₃N₄, which also strongly suggested the successful intercalation of rGO into g-C₃N₄ and the intercalation did not disturb the structure of g-C₃N₄.

![TEM images and SAED patterns](image)

**Figure 2.4** *(a), (b)* TEM images and *(c), (d)* their corresponding SAED patterns of pure g-C₃N₄ and CN/rGO-2.5%, respectively.
Figures 2.4a and b show the TEM images of pure g-C₃N₄ and CN/rGO nanocomposite (take CN/rGO-2.5% as an example). As shown, the TEM images clearly show g-C₃N₄ and CN/rGO-2.5% with lamellar structures. The TEM image of pure g-C₃N₄ also indicates that numerous mesoporous structures with several tens of nanometres exist in the layers which are folded at the edges of the sample. For the CN/rGO-2.5%, it exhibits platelet-like textures similar with pure g-C₃N₄ but forming multiple corrugated layers buckled together. The similar SAED patterns (Figures 2.4c and d) of pure g-C₃N₄ and CN/rGO-2.5% demonstrate the homogeneous distribution of monolayer rGO sheets in the layered g-C₃N₄ structure, implying an ignorable effect of rGO modification on the layered structure of g-C₃N₄. This can be supported by their similar XRD patterns of pure g-C₃N₄ and CN/rGO-2.5% (Figure 2.2b).

Table 2.1 Reaction condition, mass product yield and composition of the products.

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2.3.2 Optical Property

![Graph showing UV-Vis diffuse reflectance spectra and Kubelka-Munk plots]

**Figure 2.5** (a) UV-Vis diffuse reflectance spectrum of the pure g-C₃N₄, rGO, and CN/rGO nanocomposites. (b) The plots of transformed Kubelka-Munk function versus the light energy.

UV-Vis diffuse reflectance spectrum of pure g-C₃N₄, rGO, and CN/rGO nanocomposites are shown in Figure 2.5a. Clearly, rGO modification importantly affects the optical property of the CN/rGO nanocomposites. As shown, all investigated samples exhibit strong visible light absorption. Moreover, with increasing rGO ratio in CN/rGO nanocomposite, a red shift to longer wavelength was observed in the absorption edge of nanocomposite. Importantly, the red shift of the absorption band edge means the bandgap narrowing of the CN/rGO nanocomposite.³⁹,⁵² Figure 2.5b shows the plots of the transformed Kubelka-Munk function as a function of light energy of all investigated samples. Based on Figure 2.5, the estimated bandgaps are 2.50, 2.40, 2.34, 2.23 and 1.55 eV, corresponding to
pure g-C$_3$N$_4$, CN/rGO-1.6%, CN/rGO-2.5%, CN/rGO-5.1% and CN/rGO-19.6%, respectively. This supports the observation of a red shift in the absorption band edge of CN/rGO nanocomposite as compared to pure g-C$_3$N$_4$. Similar phenomenon has also been observed in the case of the TiO$_2$/rGO composite materials, which can be attributed to the formation of chemical bonding between TiO$_2$ and the specific sites of rGO (e.g., Ti-O-C bonding) that can form localized occupied states in the bandgap of TiO$_2$, leading to a red shift of the absorption band edge, as reported by other groups.$^{39,53}$

In the case of CN/rGO nanocomposites in our work, the reason of the bandgap narrowing has never been addressed in literatures. However, similar to the TiO$_2$/rGO composite, the oxygen-rich active sites on the GO surface (e.g., -OH, -COOH) can play key role of cross-linkers to form C-O-C covalent bonding between rGO and g-C$_3$N$_4$ during thermal conversion, which could be the reason for the bandgap narrowing and enhanced visible light absorption of the nanocomposites.$^{54}$ The above results imply that the combination of rGO with g-C$_3$N$_4$ is not simply through π-π stacking interaction.$^{25}$ Recently, Afroze et al. found that C-O-C covalent bonding can be easily formed owing to oxygen rearrangement under high temperature through thermal treatment of plasma polymerized 1, 1, 3, 3-tetramethoxy-propane (PPTMP) thin films.$^{54}$ The formation of C-O-C covalent bonding results in a red shift in the absorption band edge of the resulting material.$^{54}$ Further, theoretical calculations illustrated that oxygen near the conduction and valence bands originated from the C-O-C covalent bonding which introduces extra $p$ states can also decrease the bandgap of a semiconductor.$^{55}$ It can be also seen from Figure 2.5a that the rGO modification can not only narrow the bandgap of the nanocomposite, but also improve visible light utilization (stronger absorption intensity of the CN/rGO nanocomposites than that of the pure g-C$_3$N$_4$), which can be advantageous to enhance the visible light photocatalytic activity of the nanocomposite. However, too high rGO ratio in nanocomposite is also disadvantageous because most of the incident light will be absorbed by rGO, resulting in a decreased light utilization of g-C$_3$N$_4$. Therefore, an apt rGO ratio in nanocomposite could be critically important for improving the light utilization, thus photocatalytic efficiency.

It is well known that the performance of semiconductor photocatalysts is highly dependent on their band structures.$^{27}$ To further investigate the effect of rGO ratio on the band structure of the CN/rGO nanocomposite, flat band potentials ($E_{fb}$) of the
CN/rGO nanocomposites have been measured by electrochemical technique, which can be used to approximately estimate the conduction band edge potentials ($E_{cb}$) of the CN/rGO nanocomposites. Figure 2.6a shows the Mott-Schottky plots of pure g-C$_3$N$_4$ and CN/rGO nanocomposites with different rGO ratios in dark, revealing typical n-type characteristics for these CN/rGO nanocomposites.

### 2.3.3 Bandgap Structure Characterization

#### Figure 2.6 (a) Mott-Schottky plots of pure g-C$_3$N$_4$ and CN/rGO nanocomposites at a fixed frequency of 800 Hz. (b) Schematic illustration of band structures (CB: conduction band, VB: valence band) of pure g-C$_3$N$_4$ and CN/rGO nanocomposites.

The $E_{cb}$ potentials derived from Mott-Schottky plots are about -1.27, -1.16, -0.96, -0.95 and -0.74 V for pure g-C$_3$N$_4$, CN/rGO-1.6%, CN/rGO-2.5%, CN/rGO-5.1% and CN/rGO-19.6%, respectively (Figure 2.6b). Obviously, the conduction band edge potentials of the CN/rGO nanocomposites occur to positive-shift compared to pure g-C$_3$N$_4$, and CN/rGO-19.6% exhibits the biggest positive-shift of $E_{cb}$. Based on the bandgap data of the nanocomposites obtained by UV-vis diffuse reflectance spectra, the calculated valence band potentials ($E_{vb}$) for all investigated photocatalysts are ca. 1.23, 1.24, 1.38, 1.28 and 0.81 V for pure g-C$_3$N$_4$, CN/rGO-
1.6%, CN/rGO-2.5%, CN/rGO-5.1% and CN/rGO-19.6%, respectively, as shown in Figure 2.6b. Compared to pure g-C₃N₄, the $E_{\text{vb}}$ of the CN/rGO-1.6%, CN/rGO-2.5% and CN/rGO-5.1% apparently happens to positive-shift, while a negative-shift of $E_{\text{vb}}$ occurs for the CN/rGO-19.6%. Among all samples, the CN/rGO-2.5% displays the most positive valence band potential, meaning higher oxidation power in comparison with other samples. The above results indicate that an apt rGO ratio can significantly adjust the band structure of the nanocomposite, and thus the photocatalytic performance.

![Figure 2.7](image_url)  
**Figure 2.7** FT-IR spectra of GO, rGO, g-C₃N₄ and CN/rGO nanocomposites.

Figure 2.7 shows the FT-IR spectra of GO, rGO, pure g-C₃N₄ and CN/rGO nanocomposites. The FT-IR spectrum of GO shows C=O (1725 cm⁻¹), aromatic C=C (1621 cm⁻¹), carboxyl C-O (1382 cm⁻¹), epoxide/ether C-O-C (1231 cm⁻¹), and alkoxy/alkoxide C-OH stretches (1027 cm⁻¹). However, almost all of these non-sp² carbon bonds are disappeared after thermal treatment at 550 °C, indicating GO reduction to form rGO. It is known for GO that carboxylic and lactone groups begin to decompose at ~250 °C, and -COOH and carbonyl groups are reduced at ca. 450 °C. Phenol and quinone groups decompose almost entirely between 500 and 900 °C. Above 900 °C, -OH groups start to decrease and oxygen-containing groups in GO are completely eliminated at ~1100 °C. As shown in Figure 2.7, except for -OH group, almost all the other oxygen-containing functional groups on the GO surface were removed at 550 °C (see the rGO curve in Figure 2.7), which means that the non-removed -OH groups could act as cross linkers to connect rGO and g-C₃N₄ by forming C-O-C bonds in the nanocomposites during thermal conversion.
Obviously, the C-O-C peak at ~1231 cm\(^{-1}\) can be observed for all investigated CN/rGO nanocomposites (Figure 2.7), further indicating that the non-removed -OH groups on the rGO surface can be used as cross-linkers to link rGO and g-C\(_3\)N\(_4\), resulting in bandgap narrowing of the nanocomposite.\(^{55}\)

**Figure 2.8** (a) XPS survey spectra of the synthesized g-C\(_3\)N\(_4\) sample. High resolution C1s (b) and N1s (c) spectra of pure g-C\(_3\)N\(_4\).
Figure 2.9 (a) XPS survey spectra of the CN/rGO-2.5% samples. High resolution C1s (b), N1s (e) and O1s (c) spectra of CN/rGO-2.5%.

XPS technique was further employed to characterize the elemental composition and oxygen bonding configurations in CN/rGO nanocomposites. As shown in Figure 2.8a, the XPS survey spectra of pure g-C₃N₄ shows only carbon and nitrogen elements. However, the CN/rGO nanocomposite (take CN/rGO-2.5% as an example) clearly shows the presence of carbon, nitrogen and oxygen elements, indicating the incorporation of oxygen into the framework of CN/rGO nanocomposite (Figure 2.8a).
Similar results can also be obtained for other CN/rGO nanocomposites. The O/C atomic ratio is calculated to be around 0.095 for CN/rGO-2.5%. It is also found that oxygen content in CN/rGO nanocomposites can be tuned by simply controlling the GO ratio in reaction precursors (e.g., O/C atomic ratio of 0.55 for CN/rGO-19.6%). Figure 2.8b shows the high resolution C1s XPS spectra of pure g-C$_3$N$_4$. As shown, three fitted peaks at 284.8, 286.9 and 287.8 eV can be observed. The peaks located at about 284.8 and 286.9 eV are corresponding to bulk graphitic sites in a CN matrix and sp$^2$C bonded to N in an aromatic ring.$^{61}$ Moreover, the smaller peak centred at 284.8 eV also illustrates that pure g-C$_3$N$_4$ has a lower graphitic degree, meaning low conductivity.$^{62}$ The peak located at 287.8 eV is corresponding to sp$^3$-bonded C in C-N. $^{61}$ Different from pure g-C$_3$N$_4$, the C1s XPS spectra of CN/rGO-2.5% exhibits a new peak at \(\sim\)287.5 eV, which is attributed to the formation of C-O-C bonding configurations during thermal treatment (Figure 2.9a and Figure 2.10),$^{63}$ and the high resolution O1s XPS spectra of CN/rGO-2.5% further confirms the presence of oxygen in the nanocomposite (Figure 2.9c). For comparison, the high resolution XPS of CN/rGO-19.6% was also characterized. Figure 2.11 show that when more rGO was used, the C-O-C peak and oxygen peaks increased significantly due to more oxygen functional groups on the surface of GO (especially the -OH groups). Therefore, the C-O-C bond intensity could be easily tuned by only controlling the amount of graphene oxide used before calcination.

![Schematic illustration of the reaction process and the CN/rGO nanocomposite structure.](image)

**Figure 2.10** Schematic illustration of the reaction process and the CN/rGO nanocomposite structure. Gray, blue and red spheres represent carbon, nitrogen and oxygen atoms in CN/rGO, respectively.

Similarly, the bonding configurations of nitrogen atoms in g-C$_3$N$_4$ (Figure 2.8c) and CN/rGO-2.5% (Figure 2.9b) were also investigated by high resolution N1s XPS spectra. The N1s XPS spectra of pure g-C$_3$N$_4$ and CN/rGO-2.5% can be fitted into three peaks centred at 398.3, 399.5, and 400.2 eV, respectively. The peaks with lower binding energy located at about 398.2 and 399.5 eV, corresponding to
pyridinic-like (N-sp$^2$C) and pyrrolic-like (N-sp$^3$C) nitrogen, respectively, while the peak centred at 400.2 eV corresponds to graphitic-like nitrogen.$^{64}$ Further, the peak at 399.5 eV corresponding to N-sp$^3$C confirms the formation of g-C$_3$N$_4$, which is in agreement with the XRD results of pure g-C$_3$N$_4$. Based on the above investigations, some conclusions can be drawn that most of oxygen functional groups in GO can be removed at 550 °C. However, the non-removed -OH groups during thermal treatment can act as the cross-linker role for forming C-O-C bonds responsible for the narrowed bandgap of the nanocomposites (Figure 2.10).

![Graph showing binding energy and intensity for C-N, C=O, C=O, C=N, and CN/rGO-19.6 %](image)

**Figure 2.11 (a)** High resolution C1s and (b) O1s spectrum of CN/rGO-19.6%.

### 2.3.4 Surface Area Measurement

As we know, the surface area of a catalyst also plays an important role in the photocatalytic activities. Therefore, the BET method was used to test the surface areas of the samples. Figure 2.12 shows the N$_2$ adsorption-desorption isotherm of the CN/rGO samples. According to Figure 2.12, the calculated surface areas of the
fabricated photocatalysts are 9.86 m$^2$ g$^{-1}$ for g-C$_3$N$_4$, 4.69 m$^2$ g$^{-1}$ for CN/rGO-1.6%, 3.95 m$^2$ g$^{-1}$ for CN/rGO-2.5%, 3.86 m$^2$ g$^{-1}$ for CN/rGO-5.1%, and 1.20 m$^2$ g$^{-1}$ for CN/rGO-19.6%, respectively. The fabricated nanocomposites including pure g-C$_3$N$_4$ have low surface areas (< 10 m$^2$ g$^{-1}$). Therefore, the surface area of the nanocomposite is not an influencing factor for the resulting photocatalytic performance. This further confirms that the improved photocatalytic activity of the nanocomposite can be due to the significantly narrowed bandgap, positively shifted valence band edge potential and enhanced electronic conductivity.

**Figure 2.12** Nitrogen adsorption-desorption isotherms of g-C$_3$N$_4$ and CN/rGO nanocomposites.

### 2.3.5 Photocatalytic Performance

Owing to its excellent visible light activity, g-C$_3$N$_4$ based photocatalysts have been widely investigated for environmental remediation and photocatalytic production of hydrogen.$^{29, 30, 50}$ Before degradation, we characterized the transmittance property of 2 M NaNO$_2$ solution which as UV filter to effectively cut off UV light ($\lambda<$ 400 nm), as shown in Figure 2.13. The NaNO$_2$ solution as UV filter has the same role with the conventional UV filter. Many studies also employed NaNO$_2$ solution as UV filter for visible light photocatalytic reaction.$^{44, 45}$ In this work, the fabricated CN/rGO nanocomposites with tunable band structures as photocatalysts were evaluated by photocatalytic degradation of RhB and 4-nitrophenol under visible light irradiation ($\lambda>$ 400 nm) and the possible mechanism of the degradation was demonstrated in
Figure 2.14. As shown, rGO in nanocomposites was used as superior electron transfer media, reducing the recombination of the photoholes and electrons.

Figure 2.13. *UV-vis* transmittance spectrum of 2 M NaNO₂ solution.

For comparison, pure g-C₃N₄ was also measured. Prior to light irradiation, 5.0 mg L⁻¹ RhB (or 10 mg/L 4-nitrophenol) solutions containing photocatalysts were maintained in dark for 0.5 h to achieve adsorption equilibrium. Figure 2.15a shows the photocatalytic degradation curves of RhB with light irradiation time for different photocatalysts. As shown, under visible light irradiation (λ>400 nm), no noticeable degradation of RhB (curve a) was observed with direct photolysis without photocatalyst. Without visible light irradiation, no degradation of RhB can be observed in the presence of CN/rGO photocatalyst (take CN/rGO-2.5% as an example, curve b). Under visible light irradiation, it was found that the degradation efficiency of RhB initially increases, then decreases with increasing rGO ratio in CN/rGO nanocomposites. The best degradation efficiency was obtained with CN/rGO-2.5% photocatalyst (curve i), as shown in Figure 2.15a. After 75 min of visible light irradiation, 84%, 100%, 52%, 36% and 80% of RhB were degraded using CN/rGO-1.6%, CN/rGO-2.5%, CN/rGO-5.1%, CN/rGO-19.6%, and pure g-C₃N₄, respectively. Obviously, an apt rGO ratio in CN/rGO nanocomposite (e.g., rGO ratio of 2.5% in nanocomposite) can significantly improve the resulting photocatalytic activity compared to pure g-C₃N₄. This improved photocatalytic activity of the nanocomposite with an apt rGO ratio could be due to some advantages: (1) narrowed bandgap of the nanocomposite, responsible for the improved visible light utilization; (2) very positive valence band potential, resulting in high oxidation
power of the nanocomposite; (3) superior electron transport property owing to rGO acting as electron collectors, and therefore decreasing the charge recombination.

Figure 2.14. Photo-oxidation mechanism of the CN/rGO nanocomposites towards the degradation of dyes.

These advantages of rGO in nanocomposites can dramatically increase their photocatalytic performance. However, the nanocomposites with too high rGO ratio (e.g., CN/rGO-5.1% and CN/rGO-19.6%) will be disadvantageous for improving the photocatalytic activity because most of incident visible light will be absorbed by rGO, resulting in a decreased light utilization of g-C₃N₄. Therefore, an apt rGO ratio in nanocomposite is critically important for improving the resultant photocatalytic performance. Also, using all investigated photocatalysts, it was found that the photocatalytic degradation of RhB follows first-order reaction dynamics under our experimental conditions. Based on the first-order Equation:

$$\ln\left(\frac{C_0}{C_t}\right) = Kt$$

where $k$ is the rate constant (min⁻¹), $C_0$ is the initial concentration of RhB, and $C_t$ is the actual concentration of RhB at time $t$. The linear relationships between $\ln\left(\frac{C_0}{C_t}\right)$ and the light irradiation time of the photocatalysts are given in Figure 2.15b. As shown, the photocatalytic degradation rate of CN/rGO-2.5% toward RhB is almost 3.0 times of pure g-C₃N₄, and 2.3, 6.8 and 11.3 times of CN/rGO-1.6%, CN/rGO-5.1% and CN/rGO-19.6% under the same experimental conditions, respectively. Apparently, CN/rGO-2.5% displays the best photocatalytic activity toward RhB degradation among all investigated photocatalysts.
Figure 2.15 (a) Photocatalytic activities and (b) The degradation efficiency for the g-C$_3$N$_4$ and CN/rGO photocatalysis system. (c) Photocatalytic activities for g-C$_3$N$_4$ and CN/rGO photocatalysis system towards 4-nitrophenol degradation for 150 min.

Further, the photocatalytic degradation mechanisms of RhB using CN/rGO nanocomposites were also investigated in this work. CN/rGO-2.5% was chose to use as photocatalyst for this purpose. As we know, the triethanolamine (TEOA) is an effective hole scavenger for photocatalytic reaction. In this work, it was found that the photocatalytic degradation efficiency significantly decreased when 10 vol%
TEOA was introduced into the reaction system (curve c in Figure 2.15a). However, when TBA (a radical scavenger) was added to the reaction solution, the photocatalytic degradation was hardly suppressed (curve h in Figure 2.15a). The results indicate that the photocatalytic degradation of RhB using CN/rGO nanocomposite can be due to a direct photohole oxidation under visible light irradiation.

![Bar chart showing photocatalytic degradation efficiency](image)

**Figure 2.16** *Recycle test of CN/rGO-2.5% catalyst towards RhB degradation for 75 min.*

In this work, the photocatalytic degradation of 4-nitrophenol was also performed using the fabricated photocatalysts. As shown in Figure 2.15c, the CN/rGO-2.5% exhibits the best photocatalytic activity toward photocatalytic degradation of 4-nitrophenol, which is almost 2.7, 2.0, 3.5 and 4.3 times of g-C₃N₄, CN/rGO-1.6%, CN/rGO-5.1% and CN/rGO-19.6%, respectively, after 150 min of visible light irradiation. When TEOA (10 vol%) was added into the reaction system, only 0.8% 4-nitrophenol was degraded, which further proved the photocatalytic degradation was due to a direct photoholes oxidation under visible light irradiation. The above results further confirm that the fabricated CN/rGO nanocomposite with an apt rGO ratio possesses excellent visible light activity.

It is worth pointing out that the stability of a given photocatalyst during photocatalytic reaction is a crucial factor for its practical application. Stability tests were therefore evaluated by carrying out repeatedly photocatalytic reaction using CN/rGO-2.5% photocatalyst under visible light irradiation. The results demonstrate that after repeating use of five times, only 1.1% decrease in photocatalytic
degradation efficiency can be achieved, indicating a high stability of the fabricated CN/rGO photocatalyst, as shown in Figure 2.16. It is well known that PL analysis is usually used to investigate the carrier separation efficiency of semiconductor photocatalyst.\(^{65}\) Figure 2.17 shows the PL spectra of pure g-C\(_3\)N\(_4\), rGO, and CN/rGO nanocomposites. As shown, the PL spectrum of the pure g-C\(_3\)N\(_4\) shows a strong PL emission band at 450 nm that is equivalent to 2.7 eV. This strong peak can be attributed to the band-band PL phenomenon, resulting from the n-\(\pi^*\) electronic transitions in g-C\(_3\)N\(_4\).\(^{66}\) Apparently, rGO modification leads to significant fluorescence quenching of the CN/rGO nanocomposites. Moreover, the extent of the fluorescence quenching was found to be noticeably increased with increasing rGO ratio, indicating a decreased recombination of photogenerated electrons and holes in nanocomposites because rGO acting as an electron collector. Overall, an apt rGO ratio could significantly improve the photogenerated carrier separation efficiency, thus enhancing light utilization and photocatalytic performance.

![Figure 2.17 Photoluminescence spectra of the g-C\(_3\)N\(_4\), rGO, and CN/rGO nanocomposites.](image)

2.4 Conclusion

In summary, we have successfully prepared the g-C\(_3\)N\(_4\)/rGO (CN/rGO) nanocomposites with different rGO ratios by a facile thermal conversion method. It was found that the CN/rGO nanocomposites were formed by cross-linked C–O–C bonds during thermal conversion. The influence of rGO ratio on the resulting photocatalytic activity of CN/rGO nanocomposites has been investigated in detail by photocatalytic degradation of RhB and 4-nitrophenol under visible light irradiation. It
was found that CN/rGO-2.5% exhibited the best photocatalytic activity toward photocatalytic degradation of RbH and 4-nitrophenol. This importantly improved photocatalytic activity of the nanocomposite is mainly due to an apt rGO ratio resulting in improved light utilization, high oxidation capability, and superior electron transport property ascribing to narrowed bandgap, positively shifted valence band edge potential, and enhanced electronic conductivity, respectively. The approach used in this work can be extended to synthesize other rGO modified semiconductor materials for applications in photocatalysis, solar energy conversion and fuel cells.

2.5 References

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CHAPTER 3 HYDROTHERMAL TRANSFORMATION OF 
BIOMASS INTO NITROGEN-DOPED CARBON 
MATERIALS AND THEIR APPLICATIONS FOR 
ENERGY CONVERSION
3.1 Introduction

Carbon nanodots (CNDs), especially heteroatoms-doped ones, are receiving great research attention due to their cost-effective, environmentally friendly, and have been promising candidates for energy conversion applications, such as sensitizer used in solar cells and fuel cells. Until now, varieties of synthetic methods have been investigated to synthesize doped or undoped CNDs, as briefly summarized in Chapter 1. The conventional approaches to synthesize CNDs can be generally classified into two main groups, namely, top-down and bottom-up methods. In the top-down methods, arc discharge, laser ablation, and electrochemical oxidation have been developed and widely used. The bottom-up approaches include combustion/thermal or microwave and hydrothermal methods etc. Generally, these approaches either involve tedious and complex experimental procedures or use harsh reaction conditions, or possess low yield production. Moreover, to achieve heteroatom-doped CNDs, the reported approaches almost exclusively require the use of synthetic chemicals as carbon and heteroatom sources. It is therefore highly desirable to realize heteroatom doping by simple, low-cost, high yield and environmentally benign synthetic methods for fabrication of commercially viable CNDs-based materials for applications in solar cells and fuel cells.

Biomass is a class of ideal starting materials for green synthesis of carbon-based materials because they are earth-abundant, readily available and cheap to obtain. Biomasses and their derivatives are generally N-containing materials that can be used to produce N-containing carbon materials. In this regard, the majority of the reported works employ the biomass derivatives to produce N-containing carbon materials, only few reports directly utilize the crude biomasses ( e.g., grass, soy milk, rice and soy bean etc.) to produce N-containing carbon materials, due to the lack of satisfactory synthetic methods for the production of valuable carbon materials. Recently, N-doped carbon nanodots have been successfully fabricated under hydrothermal conditions using grass as precursor, and used for analytical determination of heavy metal and iodide ions in water, demonstrating a feasibility of using crude biomass to produce valuable carbon materials.

It is well known that most of CNDs are fluorophores. When these CNDs are used as sensitizers in solar cells, the fluorescent emission has been an effective way of charge recombination that significantly reduces the utilization efficiency of
photo-excited electrons for solar cells, resulting in decreased light conversion efficiency. We therefore propose that the light conversion efficiency of CNDs sensitized solar cells could be significantly enhanced via a suitable fluorescent quenching mechanism to dramatically improve the utilization efficiency of photo-excited electrons. To achieve this goal, recent studies have revealed that the fluorescent emission of CNDs can be effectively and efficiently quenched by cations (e.g., Cu$^{2+}$ and Hg$^{2+}$).\textsuperscript{15, 56-58} Such quenching phenomena have been successfully utilized for sensitive and selective detection of Cu$^{2+}$ and Hg$^{2+}$. We recently confirmed that the fluorescent emission of nitrogen-doped graphitic CNDs could also be effectively quenched by anions such as iodide (I$^-$), and used for sensitive and selective I$^-$ determination in aqueous solution.\textsuperscript{53} Additionally, the GQDs with uniform size (around 5 nm) have recently been synthesized, and used as the sensitizer for quantum dot-sensitized solar cells, achieving an overall light conversion efficiency of 0.056%.\textsuperscript{59} The conversion efficiency was further improved to 0.13% in subsequent studies using carbon nanodots as sensitizers.\textsuperscript{60-62} On these bases, we choose N-doped CNDs in this chapter as the testing sensitizer to validate the proposed fluorescent quenching performance enhancement principle. We think the validation of such a generically applicable efficiency enhancement principle would be high valuable for design and development of high performance CQD sensitized DSSCs.

On the other hand, the synthesized N-doped carbon nanodot/nanosheet and nanodot/nanosheet aggregates from hydrothermal reactions of grass were also used as electrocatalyst for oxygen reduction reaction, exhibiting superior electrocatalytic activity with good operational stability and high resistance to fuel molecules (e.g., methanol). Experimental and theoretical studies further indicate that the doped pyridinic-N plays a key role for an excellent four-electron ORR electrocatalytic process. The developed carbon-based materials are promising as ORR electrocatalysts to replace Pt-based electrocatalysts with inherent disadvantages of high cost, source scarcity and serious cross-over effect.

\textbf{3.2 Experimental Section}

\textbf{3.2.1 Chemicals and Materials}

The Monkey Grass (Ophiopogon Japonicus) was obtained from various places in Gold Cost, Australia. It was washed with deionized water and sonicated for 30 mins
thoroughly to remove the impurities adsorbed on the surface and dried in the oven overnight.

3.2.2 Preparation of N-doped Carbon Nanodot (N-CNDs) for Solar Cell

N-doped CNDs were synthesized by a facile hydrothermal method. In a typical synthesis, 30 g fresh Monkey Grass (*Ophiopogon Japonicus*) was firstly cut into pieces and added into 60 mL of deionized water (Millipore Corp., 18 MΩ), and then the mixture was transferred into a 100 mL of Teflon lined autoclave. The hydrothermal reaction was kept at 180 °C for 6 h. After hydrothermal reaction, the obtained product was collected by filtration (0.2 µm cellulose membrane) and centrifugation at 4,500 rpm and 14,000 rpm for 15 min, respectively. The obtained nanodot solution was collected for further characterization and use. In this work, the fabricated N-doped CNDs solution possesses a concentration of ca. 35 mg mL$^{-1}$ with a production yield of around 7.0%.

3.2.3 Preparation N-doped Carbon Nanodot/Nanosheet (N-CN) and Nanodot/Nanosheet Aggregates (N-CNAs) for Oxygen Reduction Reaction

In a typical synthesis, N-CN was firstly prepared by a facile, one-step hydrothermal method using dried Monkey Grass as the sole starting material without any synthetic chemicals. In a typical preparation, fresh grass was firstly washed, and then dried at 100 °C for 10 h. The dried grass was subsequently ground into powder form and used as the starting material. The powder form dried grass (5.0 g) was mixed with 60 mL of deionized water. The mixture was then transferred into a 100 mL of Teflon lined autoclave and kept at 180 °C for 10 h. After hydrothermal reaction, the N-CN was collected by centrifugation at 4,500 rpm for 15 min to remove large size products. The concentration of the as-prepared N-CN is ca. 21 mg mL$^{-1}$. The obtained N-CN was preserved for further characterization and use. Pure N-CNDs were obtained by centrifugation of the hydrothermal product at a centrifugal rate of 14,000 rpm for 20 min. N-CNAs were obtained by evaporation of N-CN solution at 70 °C for 6 h. The resulting N-CNAs (ca. 52 mg mL$^{-1}$) were collected and preserved for further characterization and use.

3.2.4 Characterization

TEM analysis was performed using a Philips F20 electron microscopy. XRD patterns were obtained using a Shimadzu XRD-6000 diffractometer, equipped with a graphite monochromator. Chemical compositions of the samples were analyzed using
XPS (Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer). All binding energies were carefully aligned by reference to the C 1s peak (284.6 eV) arising from surface hydrocarbons or possible adventitious hydrocarbon. FT-IR spectra of the samples were analyzed by a Perkin Elmer spectrum 1000 FT-IR spectrophotometer using KBr pellets. PL spectra of the N-CNs and N-CNAs in water were recorded by a F7000 Fluorescence Spectrophotometer (Hitachi, Japan) with slit width of 0.5 mm. The excitation wavelength was 360 nm. UV-vis absorption spectra of the samples were recorded on a Varian Cary 4500. The PL spectra of carbon nanodot samples were measured on F-7000 Fluorescence Spectrophotometer (Hitachi). Carbon nanodot loading amount on nanocrystalline TiO$_2$ film was measured by carefully calculating the weight of TiO$_2$ film samples before and after sensitization.

### 3.2.5 Sensitization

For more meaningful comparison, the commercially available nanocrystalline TiO$_2$ films with a thickness of ca. 10 µm (DYESOL, Australia) were used as photoanode material and firstly treated at 500 °C for 30 min prior to sensitizing with N-doped carbon nanodot solution at room temperature for 24 h. The carbon nanodot-sensitized TiO$_2$ films were then dried in a nitrogen stream for further use in solar cell measurements. The TiO$_2$ film sensitized with N-doped carbon nanodot solution was denoted as CND-TiO$_2$. CND-TiO$_2$ film was further treated in 100 mM I$^{-}$ aqueous solution (NaI, Sigma-Aldrich) for 30 min to form I$^{-}$ modified TONC film (denoted as CND-TiO$_2$-I). After that, the CND-TiO$_2$-I film was adequately rinsed using deionized water and then dried at room temperature in a nitrogen stream for 12 h. All photoanodes were preserved for further measurement in solar cells.

### 3.2.6 Solar Cell Measurement

All investigated solar cells were fabricated with traditional sandwich type configuration by using a carbon nanodot-sensitized TiO$_2$ film and a platinum counter electrode deposited on FTO conducting glass (DYESOL, Australia). The organic solvent-based electrolyte (OSBE) for the investigated cells was DYESOL high efficiency electrolyte (EL-HPE, the solvent is primary Acetonitrile, and iodine content is about 340 mM). The aqueous electrolyte (AE) was prepared by mixing 0.1 M NaI and 0.01 M I$_2$ in deionized water. A mask with a window area of 0.15 cm$^2$ was applied on the TiO$_2$ photoanode film side to define the active area of the cells. A
500 W Xe lamp (Trusttech Co., Beijing) with an AM 1.5G filter (Sciencetech, Canada) was used as the light source. The Light intensity was measured by a radiant power meter (Newport, 70260) coupled with a broadband probe (Newport, 70268). The photovoltaic measurements of solar cells were recorded by a scanning potentiostat (Model 362, Princeton Applied Research, US). The IPCE as a function of wavelength was measured with a QE/IPCE measurement kit (NewSpec). The Mott-Schottky experiments of the investigated photoelectrodes were measured on an electrochemical working station (PAR 2273). The fluorescent quantum yield (QY) of the fabricated N-doped carbon nanodot solution was measured according to the reported method using F-7000 Fluorescence Spectrophotometer (Hitachi).

3.2.7 Electrochemical Measurements

All electrochemical measurements were carried out using a three-electrode system consisting of a working electrode, an Ag/AgCl reference electrode (3.0 M) and a platinum mesh counter electrode. CV measurements were carried out using a computer-controlled potentiostat (CHI 760D, CH Instruments, USA) in a standard three-electrode cell at a scan rate of 100 mV s\(^{-1}\). Prior to measurements, RDE (GC, 5.0 mm in diameter, Pine Instrument) was firstly polished using 1.0, 0.3 and 0.05 µm alumina slurry sequentially, and then rinsed adequately using deionized water and ethanol in ultrasonic bath. The cleaned RDE was then dried in a N\(_2\) stream for immobilization of N-CNDs, N-CN, N-CNA and commercial Pt/C (Vulcan, 20 wt. %) catalysts. 1.5 mg mL\(^{-1}\) N-CNDs, N-CN, N-CNA and Pt/C solutions (in 0.2% Nafion aqueous solutions) were firstly prepared. 10 µL of the prepared catalyst solution was cast on the cleaned RDE, then dried in air. Subsequently, another 5.0 µL of 1.0% Nafion aqueous solution was coated on the electrode surface, and dried at 60 °C. The loading amount of catalyst on the RDE was ca. 76 µg cm\(^{-2}\). The catalyst coated GC electrode was placed in an electrochemical cell containing 60 mL of N-saturated or O-saturated 0.1 M KOH solution with or without 3 M methanol. All measurements were performed using RDE or RRDE (Pine Modulated Speed Rotator with CE Mark (Pine Instrument) controlled by a CHI 760D electrochemical potentiostat).

3.2.8 Theoretical Calculations

All computations are performed using the Vienna ab initio simulation package (VASP) based on all-electron projected augmented wave (PAW) method.\(^{63-65}\) A
plane-wave basis set is employed to expand the smooth part of wave functions with a kinetic energy cut-off of 500 eV. For the electron-electron exchange and correlation interactions, the functional of PBE, a form of the general gradient approximation (GGA), is used throughout with the spin-polarization calculation. The Brillouin-zone integrations were performed using Monkhorst-Pack grids of special points, with gamma-point centered \((4 \times 4 \times 1)\) \(k\)-points meshes used for the \((5 \times 5)\) graphene cell. When the geometry is optimized, all atoms are allowed to relax. And the geometric structures are optimized until the residual forces were below 0.001 eV Å\(^{-1}\).

3.3 Results and Discussion

3.3.1 N-CNDs as Sensitizer in Solar Cells

![Schematic illustration of photo-excited electron transfer path from excited state of carbon nanodots.](image)

Figure 3.1 *Schematic illustration of photo-excited electron transfer path from excited state of carbon nanodots.*

As shown in Figure 3.1, upon a light excitation, an electron can be promoted from the ground-state \((\text{C}^0)\) to the excited-state \((\text{C}^*)\) of CNDs, leaving a positive charge carrier \((h^+)\) at the \(\text{C}^0\). The fate of the photo-excited electrons determines whether they could be converted to useful electricity. Without quenching, there is a high probability that the photo-excited electron would return to \(\text{C}^0\) and recombine with \(h^+\) to generate fluorescent emission (Route I) rather than extract to the external circuit to generate electricity. It can be envisaged that the probability for a photo-excited electron to be utilized for generating electricity would be dramatically increased if Route I can be effectively inhibited. In this regard, the fluorescent quenching can be an effective means to inhibit the charge recombination. It is known that the photo-excited electrons can be quenched via different mechanisms. Figure 3.1 shows two simplistic quenching mechanisms that are directly relevant to this work. A photo-excited electron could be directly consumed by a suitable electron acceptor to achieve the fluorescent quenching (Route II). However, quenching in such a fashion
prohibits the light-to-electricity conversion. It is known that the positive charge carriers \((h^+)_i\) in the \(C^0\) of excited CNDs possess strong oxidative power that can be neutralized by extracting electron from a suitable electron donor to quench the fluorescent emission (Route III). Under such a circumstance and in absence of electron acceptor, the probability of injecting the photo-excited electrons into the conduction band of the TiO\(_2\) then to the external circuit would be significantly increased, which would lead to a dramatically improved utilization efficiency of the photo-excited electrons for electricity generation. This work will therefore focus on investigating the effectiveness of the fluorescent quenching via Route III for performance enhancement of the CNDs-sensitized solar cells. Considering majority of inorganic QDs or NDs are fluorophores, the proof of the proposed concept would have a broad implication for performance improvement of other QDs or NDs sensitized solar cells. In this Chapter, the aqueous solar cells (ASCs) were assembled by a CNDs-sensitized TiO\(_2\) photoanode and a commercial Pt counter electrode with aqueous I\(^-\) being used to serve a dual-function as the redox mediator and fluorescent quencher (denoted as CND-ASCs). An overall conversion efficiency of 0.529% can be achieved from a CND-ASC, significantly higher than the reported conversion efficiency (0.13%) obtained from the CNDs-sensitized solar cells with organic solvent I/I\(_3^-\) electrolyte.\(^{59-62}\)

**Morphology and Optical Property**

![Figure 3.2](image)

*Figure 3.2* (a) Size distribution of carbon nanodots; the insets of TEM image and photograph of the nanodot sample. (b) UV-vis absorption and PL emission spectra of carbon nanodot solution; excitation wavelength of 360 nm.
In this chapter, CNDs were synthesized through hydrothermal treatment of fresh grass at 180 °C for 6 h, similar to the reported methods by Liu et al.\textsuperscript{15} The TEM analysis indicates that the fabricated CNDs with graphitic structure are uniformly dispersed with diameters ranging from 2 to 6 nm (Figure 3.2a). Figure 3.2b shows the UV-vis absorption (black curve) and PL emission (blue curve) spectra of CNDs suspension solution. The UV-vis absorption spectrum confirms the visible absorption property, implying that the CNDs could be used as light absorbers. The PL spectra are peaked at ca. 495 nm for the CNDs at excitation wavelength of 360.

**Figure 3.3** (a) XPS survey spectra of carbon nanodot sample. (b) C1s, (c) N1s and (d) O1s high resolution XPS spectra of the nanodot sample.

**Figure 3.4** FT-IR spectra of N-doped carbon nanodot sample.
Figure 3.3a shows XPS survey spectra of the CNDs, confirming the presence of C, N and O elements with N/C atomic ratio of ca. 3.35%. The high resolution C1s, N1s and O1s spectra of the CNDs (Figure 3.3b-d) reveal that the existence of O- and N-rich surface functional groups and three types of doped N atoms (namely, pyridinic-N, pyrrolic-N and graphitic-N), consistent with the corresponding FT-IR results (Figure 3.4).

Table 3.1 Photovoltaic properties of the solar cells assembled with CND-TiO$_2$ photoanodes using organic solvent (OSE) and aqueous (AE) electrolytes.

<table>
<thead>
<tr>
<th>Photoanodes</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>Adsorbed Amount (mg cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TONC + OSBE</td>
<td>514</td>
<td>0.548</td>
<td>65.3</td>
<td>0.184</td>
<td>0.88 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>515 ± 9</td>
<td>0.551 ± 0.020</td>
<td>65.5 ± 1.6</td>
<td>0.185 ± 0.014</td>
<td></td>
</tr>
<tr>
<td>TONC + AE</td>
<td>498</td>
<td>1.92</td>
<td>55.3</td>
<td>0.529</td>
<td>0.88 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>497 ± 11</td>
<td>1.93 ± 0.07</td>
<td>55.0 ± 2.3</td>
<td>0.530 ± 0.053</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.5 (a) PL spectra of N-doped carbon nanodot solution in the presence of different I$^-$ concentrations (from top to bottom: 0, 1, 3, 5, 10, 30, 50, 100, 300, 500 mM). (b) Dependence of normalized PL intensity of the carbon nanodot solution on I$^-$ concentration within the range of 0-500 mM. The data were derived from Figure 3.5a. The excitation wavelength is 360 nm.
The doping of N into CNDs introduces positively charged surfaces, facilitating the interactions between I and graphitic carbon structure for effective quenching. The PL experiments were further performed to validate the quenching ability of I. It was found that the PL intensity of CNDs decreases with the increased I concentration up to 500 mM, and is very sensitive to I in low concentration range (e.g., 0-100 mM), indicating that I is an effective quencher for CNDs-based fluorophores. The CNDs-sensitized TiO$_2$ photoanodes used in this work were prepared by sensitizing an anatase dominated nanocrystalline TiO$_2$ film electrode with N-doped CNDs (denoted as CND-TiO$_2$). The resultant CND-TiO$_2$ shows a dark brown appearance (insets in Figure 3.6a) with no noticeable change in TiO$_2$ crystal phase (Figure 3.6b). XPS survey spectra further confirm the loading of CNDs onto TiO$_2$ films (Figure 3.7).

**Figure 3.6** (a) Surface and cross-sectional SEM images of nanocrystalline TiO$_2$ film; the insets of photographs of TiO$_2$ and CND-TiO$_2$ films. (b) XRD patterns of TiO$_2$ and TONC films. (c) High resolution I-XPS spectra of TONC film after adsorption of I. (d) PL of CND-TiO$_2$ and CND-TiO$_2$-I films; the excitation wavelength of 350 nm.
Chapter 3

Figure 3.7 XPS survey spectra of TiO₂, CND-TiO₂ and CND-TiO₂-I films.

To verify the interactions between CNDs and I, the CND-TiO₂ photoanode was immersed in an aqueous solution containing 100 mM I for 30 min, then rinsed adequately with deionized water. After dried at room temperature in a nitrogen stream for 12 h, the presence of I are confirmed by XPS analysis (Figure 3.7 and Figure 3.6c). This indicates a strong interaction between CNDs and I, which is critically important in determining the practicality of I as a quencher to improve the conversion efficiency of aqueous solar cells. PL experiments were therefore performed to directly validate the quenching ability of the adsorbed I. A dramatically decreased PL emission intensity observed from the CND-TiO₂-I confirms that the adsorbed I can be used as an effective quencher in aqueous media (Figure 3.6d).

DSSCs Full-Cell Characterization

The performance of the CND-ASCs were evaluated under the standard AM 1.5 simulated sunlight (100 mW/cm²). The red curve 1# in Figure 3.8a shows a typical photocurrent-voltage profile with a CND-ASC assembled using 0.1 M I/0.01 M I₂ aqueous electrolyte (AE). The data reveals a short-circuit current density (Jsc) of 1.92 mA/cm², an open-circuit voltage (Voc) of 498 mV and a fill factor (FF) of 55.3% with an overall conversion efficiency (η) of 0.529% (Table 3.1), which is over 4 times of the highest efficiency (0.13%) obtained to date from CNDs-sensitized solar cells with organic solvent I/I₃⁻ electrolyte (OSE). The performance of a solar cell assembled using an identical CND-TiO₂ but replacing the aqueous electrolyte (AE) with organic solvent (acetonitrile) electrolyte (OSE) containing ca. 0.68 M I /0.34 M I₂ was also investigated (curve 2# in Figure 3.8a). It reveals a Jsc of 0.548
mA/cm², a $V_{oc}$ of 514 mV and a $FF$ of 65.3% with a $\eta$ of 0.184% (Table 3.1), which is slightly higher than the efficiency (0.13%) reported by other groups.\textsuperscript{60-62} Obviously, the significantly improved $J_{sc}$ is the major factor for the higher $\eta$ achieved from the aqueous electrolyte cell. This could be directly resulted from the effective $\Gamma$ quenching in aqueous media, which is supported by the measured quenching efficiency shown in Figure 3.9, where a 55% decrease in the PL emission intensity can be resulted from an aqueous solution containing 100 mM $\Gamma$ in comparison to only 18% PL emission intensity decrease with the acetonitrile solution containing the same $\Gamma$ concentration. The higher quenching efficiency leads to a higher utilization efficiency of the photo-excited electrons for electricity generation, which is supported by the observed incident photon-to-current conversion efficiency (IPCE) spectra from the cells assembled using aqueous and acetonitrile electrolytes (Figure 3.8b).

![Figure 3.8](image)

**Figure 3.8** (a) Photocurrent as a function of photovoltage for solar cells assembled with CND-TiO$_2$ photoanodes, and (b) IPCE spectra of solar cells assembled with CND-TiO$_2$ photoanodes using organic solvent-based and aqueous $I/I_3^-$ electrolytes, respectively.

The above results demonstrate that $\Gamma$ quenching can play a key role to enhance the utilization efficiency of the photo-excited electrons for electricity generation. It is known that for a given quencher, the quenching performance can be highly dependent on its concentration. The effect of $\Gamma$ concentration on light conversion efficiency of the aqueous solar cells was therefore investigated. The results indicate that $J_{sc}$ dramatically decreased with a low $\Gamma$ concentration of 0.05 M, leading to a lower overall efficiency (0.237%, Figure 3.10). A high $\Gamma$ concentration of 0.5 M enables a high $J_{sc}$ but low $V_{oc}$, and $FF$, resulting a decrease in overall conversion.
efficiency to 0.506% (Figure 3.10). The decreased $V_{oc}$ and $FF$ at high $I$ concentration might be due to the formation of large number of I-induced trapping energy states.\textsuperscript{67}

**Figure 3.9** PL spectra of CNDs and CNDs + 100 mM I in (a) acetonitrile and (b) water. The excitation wavelength is 360 nm. The concentrations of CNDs in acetonitrile and water are around 15 mg mL\textsuperscript{-1} and 35 mg mL\textsuperscript{-1}, respectively.

Although the quenching approach presented in this work has demonstrated to dramatically improve the conversion efficiency of CND-ASCs to a level that is over 4 times of the best performed CNDs-sensitized solar cells reported to date, the achieved 0.529\% is still low compared to inorganic QD-SSCs.\textsuperscript{68-72} This could be due to lower fluorescent quantum yield (ca. 5.3\%) of the N-doped CNDs used in this work, which greatly limits the photo-excited electron utilization efficiency for photovoltaic application.\textsuperscript{73} It is envisaged that the quenching performance
enhancement principle could be more effective for QDs or NDs with higher fluorescent quantum yields. The above results have demonstrated the effectiveness of the proposed fluorescent quenching performance enhancement principle. We have assumed that I\textsuperscript{-} quenching is achieved via Route III (Figure 3.1). It is well known that upon the CNDs absorbing a photon (Equation 1), an electron can be promoted to the C\textsuperscript{*} of CNDs (C\textsuperscript{*}(e\textsuperscript{-})), creating a positive charge carrier at the C\textsuperscript{0} (C\textsuperscript{0}(h\textsuperscript{+})):\[ \text{CNDs} \rightarrow h\nu \rightarrow \text{C}\textsuperscript{*}(e\textsuperscript{-}) + \text{C}\textsuperscript{0}(h\textsuperscript{+}) \] (1)

If the quenching is via Route III, then I\textsuperscript{-} quencher will lose an electron to neutralize h\textsuperscript{+} (C\textsuperscript{0}(h\textsuperscript{+})) and produce I\textsubscript{3}\textsuperscript{-} (Equation 2):\[ 3I\textsuperscript{-} + \text{C}\textsuperscript{0}(2h\textsuperscript{+}) \rightarrow \text{C}\textsuperscript{0}[0] + I\textsubscript{3}\textsuperscript{-} \] (2)

Figure 3.11 (a) UV-vis absorption spectra of CNDs containing 1.0 mM I\textsuperscript{-} solutions under visible light illumination; inset of plots of UV-vis absorption peak intensities at 288 nm and 350 nm versus visible light illumination time. (b) UV-vis absorption spectrum of 1.0 mM I\textsuperscript{-} solution after visible light illumination of 15 min.

If this is true, then I\textsubscript{3}\textsuperscript{-} should be detected when a CNDs suspension solution containing I is illuminated. Figure 3.11a shows the UV-vis absorption spectra of CNDs suspension solution containing 1.0 mM I or in absence of I, under different illumination times (AM 1.5G simulated sunlight, 100 mW cm\textsuperscript{-2}). In order to eliminate the influence of O\textsubscript{2} on I oxidation, all solutions were purged with N\textsubscript{2} during experiments. In absence of I, with or without illumination, only one absorption band centered at ca. 275 nm can be observed, which is consistent with the reported CNDs spectra.\textsuperscript{15,53,66} In absence of CNDs, the UV-vis absorption spectrum obtained from a 1.0 mM I aqueous solution after 10 min illumination only displays a single absorption band centered at ca. 226 nm that is the characteristic absorption
spectrum of I (Figure 3.11b). The UV-vis absorption spectra obtained from the illuminated CNDs suspension solution containing 1.0 mM I shows two distinctive I$_3^-$ absorption bands centered at 288 and 350 nm, respectively (Figure 3.11a), deferring obviously from that observed from CNDs suspension or I solution in absence of CNDs. Moreover, the intensity of these peaks increase with illumination time (inset in Figure 3.11a), indicating the increased production of I$_3^-$. These experimental evidences confirm that I quenching does occur and is via Route III in accordance with Equation 2.

$$I_3^- + 2e^- \rightarrow 3I^-$$  \hspace{1cm} (3)

In this work, I serves a dual-function as a fluorescent quencher and redox mediator. This means that I in the quenching process must be regenerated at the counter electrode (commercial Pt catalyst in this work, Equation 3) before the utilization of photo-excited electrons for electricity generation can be realized.

Figure 3.12 (a) UV-vis diffuse reflection spectra of TiO$_2$, CND-TiO$_2$ and CND-TiO$_2$-I films. (b) Plots of $(ahv)^2$ versus photon energy (hv) of TiO$_2$, CND-TiO$_2$ and CND TiO$_2$-I films.
The above results validate that I can be effectively and efficiently oxidized and then transformed into I$_3^-$ in the presence of carbon nanodots under simulated light illumination, indicating that the redox process of I/I$_3^-$ couples is realizable in carbon nanodot-sensitized solar cells. However, the above evidences only demonstrate the feasibility of half carbon nanodot-sensitized solar cell. The matching of the energy band structures of photoanode material (e.g., TiO$_2$ in this work) and sensitizer (carbon nanodots in this work) is also critically important for the operation of a whole solar cell. For this, a further investigation is highly desirable. Many studies have demonstrated that carbon nanostructures can exhibit tunable bandgaps dependent on size, oxygen content, shape, and surface functionalization.$^{55, 76, 77}$ In this work, the UV-vis diffuse reflection spectrum of CND-TiO$_2$ and CND-TiO$_2$-I films exhibit superior visible light absorption property owing to the sensitization of carbon nanodots (Figure 3.12a). The bandgaps of CND-TiO$_2$ and CND-TiO$_2$-I have been calculated to be almost identical (ca. 1.59 eV) (Figure 3.12b). I modification has no obvious influence on the energy band structure of carbon nanodots under the investigated I concentration. Further, CND-TiO$_2$ as photoelectrode was also characterized by electrochemical technique.

![Graph showing Mott-Schottky plots](image)

**Figure 3.13** Mott-Schottky plots of TiO$_2$ and CND-TiO$_2$ film photoelectrodes.

Figure 3.13 shows the Mott-Schottky plots of CND-TiO$_2$ and TiO$_2$ photoelectrodes under standard AM 1.5 simulated sunlight (100 mW $cm^{-2}$). Based on Mott-Schottky plots, the flat band potential of CND-TiO$_2$ and nanocrystalline TiO$_2$ films is approximate -496 and -328 mV ($vs$ Ag/AgCl), respectively. Obviously, the carbon nanodot-sensitized TiO$_2$ photoelectrode possesses more negative flat band potential,
meaning the matching of the conduction band energies of TiO$_2$ and carbon nanodots, as shown schematically in Figure 3.14. After simulated light illumination, the photo-excited electrons from the carbon nanodots can effectively inject into the conduction band of TiO$_2$ owing to their matched energy band structures. Introduction can not only effectively quench the fluorescence of carbon nanodots to improve the photo-excited electron utilization efficiency for solar cell, but also act as redox mediator in solar cell. The matching of the energy band structures of photoanode material (e.g., TiO$_2$), carbon nanodots and I/I$_3^-$ couples is critically important for carbon nanodot-sensitized solar cells.

![Figure 3.14](image)

**Figure 3.14** Schematic illumination of photo-excited electron transfer in carbon nanodot-sensitized solar cell.

**Section Summarization**

In summary, N-doped carbon nanodots with O- and N-rich surface functional groups were successfully fabricated using fresh grass as the sole starting material by a simple, cost-effective and environmentally benign method. As sensitizer, the resulting solar cells made of carbon nanodot-sensitized TiO$_2$ photoanodes displayed excellent visible light harvesting capability and an overall light conversion efficiency of 0.184% using organic solvent I/I$_3^-$ electrolyte. Owing to high stability of carbon nanodots in aqueous solution, the solar cells assembled with carbon nanodot-sensitized TiO$_2$ photoanodes exhibited an overall light conversion efficiency of 0.529% using aqueous I/I$_3^-$ electrolyte. This study demonstrates a possibility of developing carbon nanodot-sensitized aqueous solar cells by a fluorescent quenching principle.
3.3.2 N-doped Carbon Nanodot/Nanosheet (N-CNs) and Nanodot/Nanosheet Aggregates (N-CNAS) for Oxygen Reduction Reaction

Morphology, XRD and Optical Properties

![Fabrication procedure of the N-CNs and N-CNAS. (b) and (c) TEM images of the N-CNs and N-CNAS; insets are corresponding TEM and HRTEM images.](image)

**Figure 3.15** (a) Fabrication procedure of the N-CNs and N-CNAS. (b) and (c) TEM images of the N-CNs and N-CNAS; insets are corresponding TEM and HRTEM images.

Hydrothermally treating dried grass at 180 °C for 10 h yielded a brown colored N-CNs with a concentration of 21 mg mL⁻¹ (photo (1) in Figure 3.15a). The mass yield of N-CNs is ca. 25.2%, which is significantly higher than that of carbon nanodot-based materials fabricated by other methods. The concentrated solution via evaporation resulted in a dark brown colored solution containing 52 mg mL⁻¹ N-CNAS (photo (2) in Figure 3.15a). Detailed characterizations confirm that the as-synthesized N-CNs (Figure 3.15b) in the diluted solution was self-assembled into N-CNAS in the concentrated solution (Figure 3.15c). As shown in Figure 3.15b, the TEM image of the diluted solution is a mixture of 2-6 nm nanodots and 10-50 nm nanosheets (top inset in Figure 3.15b). The high resolution TEM image of the resultant nanodot shows a lattice spacing of ca. 0.32 nm (bottom inset in Figure 3.15b), which is in agreement with the <002> spacing of graphitic carbon. This can be further confirmed by XRD results (Figure 3.16). Shown in Figure 3.15c is TEM image of the N-CNAS in the concentrated solution. These aggregates display a particle-like shape, assembled by aggregating the nanodots anchored nanosheets (top...
inset in Figure 3.15c). TEM image indicates uniformly dispersed nanodots on the nanosheet aggregates (top inset in Figure 3.15c), having a graphitic carbon lattice spacing of \( \text{ca.} \ 0.32 \ \text{nm} \) (bottom inset in Figure 3.15c), suggesting that the aggregation occurred during the concentrating process under low temperature. Evaporation only changes the size and shape of the products rather than their graphitic structures. Many studies have demonstrated that carbon materials synthesized by hydrothermal methods possess oxygen-rich surface functional groups, which may play a key role to facilitate the self-assembly aggregation during the concentrating process.

![XRD patterns of the as-synthesized N-CNAs and N-CNs.](image)

**Figure 3.16 XRD patterns of the as-synthesized N-CNAs and N-CNs.**

Figure 3.17a shows XPS survey spectra of the N-CNs and N-CNAs, confirming the presence of C, N and O elements with similar N/C atomic ratios of 3.37% and 3.41%, respectively. Similar N/C ratios observed from N-CNs and N-CNAs further indicate that no significant graphitic structure changes occurred during the aggregation process. The high resolution C1s spectrum of the N-CNAs (Figure 3.17b) indicates the existence of functional groups such as C-C (284.4 eV), C-N (285.2 eV), C-O (286.6 eV), and C=O (288.3 eV), confirming the presence of doped N and O-rich functional groups. The high resolution N1s spectrum of the N-CNAs (Figure 3.17c) reveals the presence of three types of N atoms, namely, pyridinic-N (398.9 eV), pyrrolic-N (399.8 eV) and graphitic-N (401.2 eV). The relative atomic ratios of the three types of N in N-CNAs were found to be 2.6 (pyridinic):1.7 (pyrrolic):1 (graphitic). The C 1s and N 1s spectra of N-CNAs reveal very similar findings (Figure 3.18).
Figure 3.17 (a) XPS survey spectra of the N-CNs and N-CNAs. (b) and (c) High resolution XPS spectra of C1s and N1s of N-CNAs. (d) FT-IR spectra of the fabricated N-CNs and N-CNAs samples.

Figure 3.18 High resolution C1s (a) and N1s (b) XPS spectra of the as-synthesized N-CNs.

Figure 3.17d shows FT-IR spectra of the as-synthesized N-CNs and N-CNAs samples. After concentrating at 70 °C, the obtained N-CNAs exhibit very similar FT-IR spectra with the N-CNs. This indicates that the surface functional groups of the N-CNAs remain the same before and after preconcentration via evaporation. Both the N-CNs and N-CNAs exhibit characteristic absorption bands of O-H and N-H stretching vibrations at 3404 and 3285 cm\(^{-1}\), and C-H stretching vibration at 2934 cm\(^{-1}\). The characteristic absorption bands of aromatic CN heterocycles at 1280 to 1605 cm\(^{-1}\) were also observed, implying that the local structure of these carbon...
materials is consisted of CN units. These FT-IR data are in an agreement with XPS analysis. It has been a consensus that N doping into carbon structures can lead to significantly enhanced ORR performance. However, the relationship between the ORR electrocatalytic activity and the doped N types is still unclear and sometimes controversial, which deserves a clarification.

![Figure 3.19](image)

**Figure 3.19** (a) PL spectra of the N-CNs and N-CNAs in water with excitation wavelength of 360 nm; the insets are the photos of the N-CNs and N-CNAs aqueous solutions under 365 nm UV illumination. (b) PL spectra of the N-CNAs aqueous solutions with air, O$_2$-saturated, and N$_2$-saturated situations. Excitation wavelength is 360 nm.

N-doping improves the oxygen adsorption at the catalyst surface, which is one of the proposed ORR electrocatalytic activity enhancement mechanisms. An experimental demonstration of surface oxygen adsorption would provide evidence to support such a speculation. It is known that the dissolved O$_2$ can be detected via a fluorescent quenching concept. It is also known that carbon nanodots possess PL properties. These could be used to our advantage to investigate the surface oxygen adsorption properties. The measured PL emission spectra are peaked at 450 nm and 485 nm for N-CNs and N-CNAs, respectively (Figure 3.19a). The red-shifted PL emission peak position of N-CNAs could be due to the size-dependent trap sites. The effect of dissolved O$_2$ concentration on N-CNAs’ PL intensity is shown in Figure 3.19b. The measured decrease in PL intensity as O$_2$ concentration increased is due to the quenching effect occurred at the surface of N-CNAs. Similar phenomenon can also be observed from N-CNs (Figure 3.20a). This is a direct evidence of strong O$_2$ interaction with the surface of N-doped carbon material, implying a strong O$_2$ adsorption at the surface of N-CNAs, beneficial for electrocatalytic ORR. In addition,
the UV-vis absorption spectra of the N-CNs and N-CNAs indicate that the absorption bands of both materials are located at around 270 nm, consistent with the reported results (Figure 3.20b). The absorption band edge of the N-CNAs is slightly red-shifted when compared to that of the N-CNs, further confirming the formation of large sized aggregates (Figure 3.20b).

Figure 3.20 (a) PL spectra of the N-CNs aqueous solutions with air, O$_2$-saturated, and N$_2$-saturated situations. Excitation wavelength: 360 nm. (b) UV-vis absorption spectra of the N-CNs and N-CNAs. It should be noted that the samples for UV-vis measurements were diluted 100 times from original N-CNs and N-CNAs solutions to obtain the absorption bands at ca. 270 nm.

Electrochemical Performance

The above results indicate that the obtained N-CNAs possess the required characteristics for a high performance carbon-based ORR electrocatalyst. Electrocatalytic ORR performances of the N-CNAs were subsequently evaluated. To make the evaluation meaningful and comparative, where appropriate, the measurements of bare glassy carbon (GC) and N-CNs coated GC electrodes are performed under identical conditions as that for the N-CNAs coated GC electrode. Figure 3.21a shows the cyclic voltammetric (CV) responses of a bare GC electrode in 0.1 M KOH solutions saturated with N$_2$ or O$_2$. The CV curve obtained from the O$_2$-saturated solution exhibits distinctive characteristics for a two-electron transfer process (reducing O$_2$ to H$_2$O$_2$) with a cathodic current peak at ca. -0.44 V. The CV curve obtained from N-CNs coated GC electrode reveals similar characteristics as that of the bare GC electrode, with an increased cathodic current and slightly positively shifted peak potential to ca. -0.42 V (Figure 3.21b). Although the electrocatalytic activity of N-CNs is observable, the process is dominated by a two-
electron transfer reduction process. A careful investigation reveals that the measured response is largely contributed by the bare GC rather than N-CNs.

![Cyclic voltammograms of (a) bare GC electrode and (b) N-CNs electrode in N₂-,O₂-saturated 0.1 M KOH electrolyte with scan rate of 100 mV s⁻¹.](image)

**Figure 3.21** Cyclic voltammograms of (a) bare GC electrode and (b) N-CNs electrode in N₂-,O₂-saturated 0.1 M KOH electrolyte with scan rate of 100 mV s⁻¹.

![Photos of bare GC electrode (a) and N-CNs coated (b, e), N-CNDs coated (c, f) and N-CNAs coated (d, g) electrodes before and after electrocatalytic measurements.](image)

**Figure 3.22** Photos of bare GC electrode (a) and N-CNs coated (b, e), N-CNDs coated (c, f) and N-CNAs coated (d, g) electrodes before and after electrocatalytic measurements.

This is due to the difficulties to form a uniform and stable N-CNs film that completely covers the GC substrate and the formed film easily felling off the substrate during the measurement (Figure 3.22b, e). Different immobilization
approaches were hence attempted to improve the coverage, uniformity and stability of the coated film, but failed due to the extremely high water adsorption property of N-CNAs. Similar issue has also been experienced by Qu and co-workers in their recent study on the N-GQDs. They failed to directly use the as-synthesized N-GQDs as ORR electrocatalyst because of the difficulties to form a stable and continuous N-GQD film onto GC electrode. For carbon-based electrocatalysts, the coverage and stability of the catalyst film on the conducting substrate largely determine their applicability, but the key factors affecting the film quality are not yet understood. Available evidences to us suggest that the quality of the immobilized film is size dependent.

![Figure 3.23](image)

**Figure 3.23** TEM and HRTEM images (a), and high resolution C1s (b) and N1s (c) XPS spectra of the fabricated N-CNDs.

A smaller size leads to a larger volume expansion after water adsorption, hence a deceased stability. To confirm this, we fabricated well dispersed pure N-CNDs, (Figure 3.23), that possess even higher hydration volume expansion than N-CNAs. The cyclic voltammetric responses obtained from the N-CNDs coated GC electrode are found to be almost identical to that obtained from the bare GC electrode, because the immobilized N-CNDs film was rapidly displaced from GC surface (Figure 3.22c, f). The above results suggest that to obtain high quality catalyst film, the size and the interactive force among the individual carbon structure unit and the substrate must be carefully managed. In this work, an appropriate degree of aggregation of N-CNAs would be a viable means to increase the size and the interactive forces amongst the carbon materials and the substrate. For N-CNAs, the formed catalyst film onto GC can maintain high stability (e.g., 20,000 s, Figure 3.22g), while the N-CNAs and N-CNDs films quickly dissolve during measurement (e.g., 2 min).

Figure 3.24a shows the CV responses of the N-CNAs coated GC electrode in 0.1 M KOH solutions saturated with N₂ or O₂. The obtained O₂ reduction peak potential
Chapter 3

at ca. -0.21 V is very close to that of the commercial Pt/C electrocatalyst (ca. -0.18 V, Figure 3.24b) and 230 or 210 mV anodically shifted when compared to the bare GC or N-CNAs coated GC electrodes, respectively. It is well known that a Pt/C electrocatalyst often suffered from the crossover effects of fuel molecules such as methanol (Figure 3.24b). In strong contrast, the N-CNAs electrocatalyst exhibits a superior resistance to the crossover effects (Figure 3.24a) in presence of 3 M methanol. Figure 3.24c shows the linear sweep Voltametric (LSV) responses of N-CNAs and Pt/C coated GC rotating disc electrodes (RDE) under a rotation rate of 1000 rpm. It was found that the N-CNAs and the commercial Pt/C electrocatalysts possess almost identical onset potential of -0.08 V, indicating an intrinsic characteristic of low overpotential for ORR. Similar to the commercial Pt/C electrocatalyst, a wide current plateau can be observed for N-CNAs within a wide potential range, highly desirable for a high performance electrocatalyst. Moreover, the current density of the N-CNAs electrocatalyst resulting from ORR is comparable to that of the Pt/C electrocatalyst, indicating a superior electrocatalytic activity of the N-CNAs. The number of transferred electron (ideally, four electrons) involved in an ORR is an important parameter to evaluate the performance of an ORR electrocatalyst.

\[ \frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \]  
(1)

where \( J \) is the measured current density, \( J_L \) and \( J_K \) are the diffusion limiting and kinetic current densities, respectively. \( \omega \) is the angular velocity of the disk (\( \omega = 2\pi N \), \( N \) is the linear rotation speed). \( B \) is Levich slope that is expressed by:

\[ B = 0.2nFC_0(D_0)^{2/3}v^{-1/6} \]  
(2)

where \( n \) is the overall number of electrons transferred in an oxygen reduction process. Based on Eqs. (1) and (2), the transferred electron number (\( n \)) and \( J_K \) can be obtained from the slope and intercept of the Koutecky-Levich plots, respectively. \( F \) is the Faraday constant (\( F = 96485 \) C mol\(^{-1}\)), \( C_0 \) is the bulk concentration of O\(_2\) in electrolyte solution (\( C_0 = 1.2\times10^{-3} \) mol L\(^{-1}\)), \( v \) is the kinetic viscosity of the electrolyte (\( v = 0.01 \) cm\(^2\) s\(^{-1}\) in 0.1 M KOH). \( D_0 \) is the diffusion coefficient of O\(_2\) in 0.1 M KOH (\( D_0 = 1.9 \times 10^{-5} \) cm\(^2\) s\(^{-1}\)). A constant value of 0.2 is adopted when the rotating speed is expressed in rpm.
Figure 3.24 (a) and (b) CV responses of the N-CNAs and Pt/C electrocatalysts in N$_2$-saturated 0.1 M KOH, O$_2$-saturated 0.1 M KOH, and O$_2$-saturated 3 M methanol solutions. (c) LSV responses of N-CNAs and Pt/C electrocatalysts using a RDE at 1000 rpm and 10 mV s$^{-1}$. (d) LSV responses of N-CNAs in an O$_2$-saturated 0.1 M KOH solution measured on a RDE for different rotation rates. (e) Koutecky-Levich plots derived from the RDE measurements for N-CNAs. (f) The dependence of electron transfer number on the potential (the data were derived from Figure 3.24e).

Based on Figure 3.24d, the corresponding Koutecky-Levich curves were plotted for various potentials, as shown in Figure 3.24e. The excellent linear relationships for all plots obtained under various rotation rates for the potential range investigated suggest a first-order reaction with respect to the dissolved O$_2$. The transferred
electron number per O\textsubscript{2} molecule involved in the ORR process can be determined by the slope and intercept of the Koutecky-Levich plots as shown in Figure 3.24e. The transferred electron number (n) for the N-CNAs calculated from Figure 3.24e are found to be between 3.80 and 4.08 over the potential range of -0.3 V to -0.7 V (Figure 3.24f), implying a four-electron ORR process. This is further validated by the negligible anodic current measured at a Pt ring of a rotating ring-disk electrode (Figure 3.25a). The operational stability is also an important parameter for an ORR electrocatalyst. As shown in Figure 3.25b, the stability test indicates that the N-CNAs exhibit only 5.5% decrease in current density over 20,000 s of continuous operation at a rotation rate of 1000 rpm, under an applied potential of -0.4 V, whereas almost 27% decrease in current density was observed from the Pt/C, suggesting the N-CNAs possess a superior operational stability over the commercial Pt/C electrocatalyst.

**Figure 3.25** (a) LSV responses of RRDE in O\textsubscript{2}-saturated 0.1 M KOH for the N-CNAs at 1000 rpm; the ring electrode was polarized at 0.5 V. (b) Current-time responses of the N-CNAs and Pt/C electrocatalysts in O\textsubscript{2}-saturated 0.1 M KOH solution with a rotation rate of 1000 rpm.

**DFT Calculations**

It has been accepted that doping N into carbon materials creates electrocatalytic active sites. However, the effect of doped N types on ORR electrocatalytic activity remains unclear. A better understanding of the issue will benefit future design and development of such type of electrocatalysts. In this work, three identified N-doped types (pyridinic-N, pyrrolic-N and graphitic-N) in N-CNAs are investigated using density functional theory (DFT) calculations. The DFT calculations indicate that the doped N atom is highly negatively charged (ca. -2.70), regardless of doped N types (Figure 3.26). Compared to pyrrolic-N and graphitic-N, the carbon atoms around...
pyridinic-N possess higher positive charge (+1.21), beneficial to improving O₂ adsorption at the catalyst, hence the ORR performance. The DFT calculations in this work further confirm that O₂ adsorption for pyridinic-N ($\Delta E_{\text{ad}} = -0.82 \text{ eV}$) is stronger than that for pyrrolic-N ($\Delta E_{\text{ad}} = -0.05 \text{ eV}$) and graphitic-N ($\Delta E_{\text{ad}} = -0.15 \text{ eV}$), indicating a better ORR catalytic activity of the pyridinic-N (Figure 3.27). The calculated charge distribution indicates that the carbon atoms around pyridinic-N possess more positive charges and stronger O₂ adsorption. The experimentally confirmed four-electron ORR process at N-CNAs could be due to the mechanism of dissociative adsorption of O₂ molecules. Our theoretical calculations reveal that pyridinic-N and pyrrolic-N exhibit stronger dissociative adsorption ($\Delta E_{\text{dis}} = -2.69 \text{ eV}$ for pyridinic-N and $\Delta E_{\text{dis}} = -3.02 \text{ eV}$ for pyrrolic-N), while the dissociative adsorption is energetically unfavourable for undoped carbon and graphitic-N products, as shown in Figure 3.28.

Figure 3.26 Charge distributions of undoped (a) and N-doped (b-d) carbon product in its optimized structure. (b) Pyridinic-N; (c) Pyrrolic-N; (d) Graphitic-N.
Figure 3.27 $O_2$ molecule adsorption in optimized structures (minus denotes exothermic reaction). (a), (b) Undoped carbon structure; (c), (d) Pyridinic-N; (e), (f) Pyrrolic-N; (g), (h) Graphitic-N.

Considering $O_2$ adsorption on electrocatalyst being first-step for the ORR, although pyrrolic-N has stronger dissociative adsorption than that of pyridinic-N, the relatively weak $O_2$ adsorption of pyrrolic-N makes pyridinic-N more efficient for the ORR, which is in agreement with our experimental results (pyridinic-N is dominant in $N$-
In this work, we present only one possible situation of the influence of N doping species on the resulting ORR activity. The study on synergistic effect of three types of doped N species for the N-CNAs’ performance may be more close to a real situation, which deserves a further investigation in the future.

**Figure 3.28** Dissociative adsorption energy (minus denotes exothermic reaction) in optimized structures. (a) Undoped carbon; (b) Pyridinic-N; (c) Pyrrolic-N; (d) Graphitic-N.

**Section Summarization**

In summary, a facile and low-cost hydrothermal method to produce high quality N-CNAs at a yield as high as 25.2% for ORR catalysts was synthesized. This is an environmentally benign method using grass as the sole starting material without any synthetic chemicals. The obtained N-CNAs exhibit outstanding electrocatalytic activity, operational stability and high resistance to methanol crossover oxidation reaction. The theoretical studies indicate that the doped pyridinic-N plays an important role for N-CNAs’ excellent four-electron ORR electrocatalytic activity. The concept validated in this work demonstrates the feasibility using biomass as the starting material to produce high quality and high performance carbon-based electrocatalysts in a high-yield, cost-effective and environmentally friendly manner.
3.4 Conclusion

In this chapter, N-doped carbon nanodots with rich surface functional groups were successfully fabricated using fresh grass as the sole starting material by a simple, cost-effective and environmentally benign method. As sensitizer, the resulting solar cells made of carbon nanodot-sensitized TiO$_2$ photoanodes displayed excellent visible light harvesting capability and an overall light conversion efficiency of 0.184%. Owing to high stability of carbon nanodots in aqueous solution, the solar cells assembled with carbon nanodot-sensitized TiO$_2$ photoanodes exhibited an overall light conversion efficiency of 0.529% using aqueous I$_3^-$ electrolyte. The improved efficiency was due to the stronger affinity between CNDs and I$^-$ in aqueous media.

On the other hand, the obtained N-CNAs exhibit outstanding electrocatalytic activity towards ORR. Theoretical studies indicate that the doped pyridinic-N plays an important role for N-CNAs’ excellent four-electron ORR electrocatalytic activity. The concept validated in this chapter demonstrates the feasibility of using biomass as the starting material to produce high quality and high performance carbon-based sensitizer and electrocatalysts in a high-yield, cost-effective and environmentally friendly manner.

3.5 References

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CHAPTER 4 TEMPLATE-ASSISTED SYNTHESIS OF S, N CO-DOPED TRIMODAL-POROUS STRUCTURED GRAPHITIC CARBON ELECTROCATALYST AND ITS APPLICATION FOR OXYGEN REDUCTION REACTION
4.1 Introduction

As a key component, electrocatalyst determines electron transfer property in the process of oxygen reduction reaction (ORR), thus the performance of a fuel cell.\(^1\)\(^-\)\(^3\) The ORR can undergo either through a four-electron transfer process to directly combine \(O_2\) with electrons and protons into \(H_2O\) as the final product, or a less efficient two-step, two-electron transfer pathway involving the formation of \(H_2O_2\) as intermediate.\(^4\) Conventionally, Pt-based materials are the most efficient ORR electrocatalyst catalysts, but the high cost and scarcity of Pt hamper further development of fuel cell technologies based on these materials. More importantly, Pt-based electrocatalysts generally suffers from multiple drawbacks for ORR, such as susceptibility to fuel cross-over from the anode, deactivation by CO, and poor stability under electrochemical conditions.\(^5\)\(^-\)\(^20\) In this respect, a broad range of alternative catalysts based on nonprecious metals (e.g., Fe, Co etc.),\(^21\)-\(^26\) metal oxides (e.g. Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), Co\(_3\)O\(_4\), IrO\(_2\) etc.),\(^27\)-\(^34\) carbon-based materials and metal/metal oxide compositied materials,\(^35\)-\(^47\) as well as metal-free heteroatoms-doped carbon materials, have been widely and actively pursued as electrocatalysts for ORR.\(^48\)\(^-\)\(^79\) Among them, heteroatoms-doped (e.g. N,\(^48\),\(^59\),\(^62\),\(^64\),\(^71\) B,\(^80\),\(^81\) S,\(^49\),\(^54\) P\(^58\),\(^74\),\(^78\),\(^82\)) and co-doped\(^52\),\(^53\),\(^68\),\(^69\),\(^76\),\(^77\),\(^79\) graphitic carbon materials have shown great potential as promising metal-free electrocatalysts for ORR. For these heteroatom-doped carbon materials, it has been generally accepted that the electrocatalytic activities of such materials are originated from the changes in charge and spin densities of carbon atoms adjacent to the doped heteroatoms.\(^83\) Theoretical studies also have shown that the changes in charge and spin densities are strongly influenced by the kind of doped heteroatoms, doping levels and types of bonds formed between dopants and graphitic carbon atoms.\(^83\)-\(^85\) For example, DFT calculation results carried out by Dai’s group show that the carbon atoms with positive spin or charge density larger than 0.15 are most likely to serve as catalytic active sites.\(^50\) Thus, the number of atoms with large positive spin or charge density is another measure of its catalytic capability. In other words, this means that the electrocatalytic activity can be tailored by controlling these key factors during the synthesis. However, doping of heteroatoms into graphitic carbon structures in a reproducibly and precisely controlled manner is highly challenging. Although various doping approaches have been reported, the thermolysis-based methods are the most effective means. The reported thermolysis-based methods achieve the heteroatom doping by two common strategies. One is via...
thermal treatment of pre-synthesized carbon structures (e.g., graphene or graphene oxide etc.) in presence of heteroatom dopant precursors. Recently reported synthesis of heteroatoms-doped and co-doped graphene electrocatalysts are typical successful examples of such a strategy. Nevertheless, with this strategy, some chemical bonds of the pre-synthesized carbon structures must be thermally wrecked to enable the dopant to form chemical bonds with carbon atoms, which unavoidably causes damages to the graphitic carbon structures and allows limited options to achieve controllable doping. Another strategy is through a single thermolysis process to simultaneously achieve the graphitic carbon structure growth and doping. The effectiveness and impressive capability of this strategy have been demonstrated by Dai’s group in their series studies. However, a metal catalyst is necessary for control growth of desired graphitic carbon structures and separate precursors are required to provide the needed carbon and dopant sources. Furthermore, it is also difficult to distinguish whether the catalytic activity of a carbon catalyst is caused by its unique electronic properties or by some metal residues. As such, multiple parameters need to be well controlled before a desirable doping product can be obtained. All reported methods to date experience difficulties to reproducibly and precisely control the level of doping, and the type of bonds formed between dopant and graphitic carbon atoms.

In this chapter, we demonstrate a self-sponsored co-doping approach to control the doping of N and S into graphitic carbon network structures, which means, the doping level and type, heteroatom-carbon bonds, surface area, porous structures, could be easily controlled by this approach. The required carbon and dopant (S, N) sources are self-sponsored by a sole precursor, 1-allyl-2-thiourea, without the need for any other metal catalysts or precursors. Therefore, the electrocatalyst property was exactly sprout out from the S, N-doped carbon materials and not to others. With this new approach, the controllable doping and graphitic carbon growth can be concurrently achieved by simply controlling the thermolysis temperature. As we know, a high performance electrocatalyst should possess a surface atomistic structure that best matches the needed electrochemical properties of the target redox system. It also needs to possess an optimal pore-structure network that best meets the needs for electron and mass transport. Doping is effective for tailoring atomistic structures but ineffective for altering pore-structures. A long-ranged graphitic carbon network would provide superior electron pathway with improved electron collection.
efficiency. To facilitate mass transport, a larger pore size and shorter diffusion pathway would be favorable, but such structures often possess limited surface area. In general, a structure possessing high surface area often has small pore-size, unfavorable for mass transport. A structure with multi-sized pore structures would be rational for achieving high effective surface area without compromising the mass transport. For this, a silica nanosphere template is therefore employed in this work to create long-ranged graphitic carbon network that possesses a trimodal-pore structure (micro-, meso- and macro-pores). The resulting S, N co-doped graphitic carbon materials were further characterized, and used as electrocatalysts for ORR application. The ORR electrocatalytic activities of the prepared S, N co-doped graphitic carbon materials were discussed in detail based on theoretical and experimental results.

4.2 Experimental Section

4.2.1 Chemicals and Materials

All of the reagents with analytical grade purity were purchased from Sigma Aldrich unless special stated and used without further purification.

4.2.2 Preparation of Porous SN/C

Silica spheres were prepared by Stober’s method. In a typical synthesis, 200 mL of absolute ethanol was mixed with 20 mL of deionized water and 10 mL of 25 wt.% ammonia aqueous solution. The mixture was stirred vigorously for half an hour followed by quick addition of 15 mL of tetraethylorthosilicate (TEOS). The solution was stirred for another 4 h at room temperature; Silica was separated by centrifugation at 10,000 rpm for 10 min, followed by washing with ethanol and deionized water and finally kept at 70 °C in vacuum until dried. Then, the white solid was heated to 550 °C with a ramp rate of 5 °C min⁻¹ and further calcinated at 550 °C in air for 4 h. The preparation of sulfur and nitrogen co-doped graphitic carbon sheets catalysts was as follows: the fabricated ordered silica nanospheres were used as hard templates; 500 mg silica was mixed with 500 mg 1-allyl-2-thiourea (melting point ~70-72 °C) in 5 mL of deionized water at 80 °C under stirring in an open crucible. At this temperature, the 1-allyl-2-thiourea was dissolved well and a clear solution was formed, facilitating 1-allyl-2-thiourea to adsorb onto the silica surface. After evaporation of deionized water, the obtained 1-allyl-2-thiourea/silica composites were dried overnight at 60 °C in an oven and subsequently calcinated at 900 °C for 2
h with a ramp rate of 5 °C min\(^{-1}\) under Ar atmosphere, respectively. After removal of the silica template by HF etching, S and N co-doped carbon materials was obtained for further characterization and use.

### 4.2.3 Characterization and Calculation

SEM and energy-dispersive X-ray spectroscopy (EDXS) (JSM-6300F), TEM (Philips F20) and XRD (Shimadzu XRD-6000 diffractometer, equipped with a graphite monochromator) were employed for characterizing the structures and morphology of the obtained samples. Chemical compositions of the samples were analyzed by X-ray photoelectron spectroscopy (Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer). All binding energies were carefully aligned by reference to the C1s peak (284.7 eV) arising from surface hydrocarbons or possible adventitious hydrocarbon. Fourier transform infrared spectroscopy (FT-IR) analysis of the samples was performed using Perkin Elmer spectrum 1000 FT-IR spectrophotometer with KBr as the reference sample. The Brunauer-Emmet-Teller (BET) method was utilized to calculate the specific surface areas (\(S_{BET}\)) using nitrogen adsorption-desorption isotherms of the samples on a Quantachrome Autosorb-1 equipment. The thermolysis processes of the precursor was further analyzed by TG/DSC-MS technique, and heated from 100 °C to 1000 °C with a ramp rate of 5 °C min\(^{-1}\) in an inert (Ar) atmosphere with simultaneous TG/DSC and online evolved gas analysis (TG/DSC-MS, Netzsch STA 449F3 equipment).

### 4.2.4 Electrochemical Measurements

The pre-treatment was as follows: prior to use, the electrodes were polished mechanically with aluminitie powder under an abrasive paper to obtain a mirror-like surface, washed with ethanol and deionized water by sonication for 5 min and allowed to dry in a desiccator. 2 mg of each grinded sample was dispersed in 1000 µL of solvent mixture of Nafion (5 %), absolute ethanol, deionized water (V:V:V=1:1:8) by sonication, respectively. 12.0 µL suspension of each catalyst was pipetted onto the glassy carbon (GC) electrode surface. The electrode was allowed to dry at 60 °C for 10 min in a desiccator before use.

Electrochemical measurements were subsequently performed using a computer-controlled potentiostat (CHI 760D, CH Instrument, USA) with a typical three-electrode cell, incorporating a working GC rotating disk electrode (RDE, 5.0 mm in diameter) for the examination in the cyclic voltammograms and linear sweep
voltammetry, an Ag/AgCl, (3 M KCl) electrode as reference electrode, and a Pt electrode as counter electrode. The cyclic voltammogram experiments were conducted in O₂-saturated 0.1 M KOH solution for oxygen reduction reaction with scan rate of 100 mV s⁻¹ from -1.2 to +0.2 V at room temperature. Linear sweep voltammetry measurements were performed on RDE in the oxygen-saturated 0.1 M KOH solution at rotation rates varying from 600 to 2000 rpm with the scan rate of 10 mV s⁻¹. The exact kinetic parameters including electron transfer number (n) was analyzed on the basis of Koutecky–Levich equations shown in Equations. (1)-(3).

\[
\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}
\]  

(1)

\[
B = 0.2nFC_0(D_0)^{2/3}ν^{-1/6}
\]

(2)

\[
J_K = nFkC_0
\]

(3)

In which \(J\) is the measured current density, \(J_K\) and \(J_L\) are the kinetic and diffusion limiting current densities, \(\omega\) is the angular velocity of the disk (\(\omega=2\pi N\), \(N\) is the linear rotation speed), \(n\) is the overall number of electrons transferred in oxygen reduction. According to Equations (1) and (3), the number of electrons transferred \((n)\) can be obtained from the slope and intercept of the Koutecky–Levich plots, respectively. \(F\) is the Faraday constant \((F=96485 \text{ C mol}^{-1})\), \(C_0\) is the bulk concentration of \(O_2\) \((C_0=1.2\times10^{-3} \text{ mol L}^{-1})\), \(ν\) is the kinematic viscosity of the electrolyte \((ν=0.1 \text{ m}^2 \text{ s}^{-1} \text{ in 0.1 M KOH})\), and \(k\) is the electron transfer rate constant. \(D_0\) is the diffusion coefficient of \(O_2\) in 0.1 M KOH \((D_0=1.9\times10^{-5} \text{ cm s}^{-1})\). The constant 0.2 is adopted when the rotating speed is expressed in rpm, and it should change to 0.62 when the rotating speed is expressed in rps.

4.2.5 Theoretical Calculations

All computations were performed using the Vienna *ab initio* simulation package (VASP) based on the all-electron projected augmented wave (PAW) method with the consideration of spin-polarization. A plane-wave basis set was employed to expand the smooth part of wave functions with a kinetic energy cut-off of 500 eV. For the electron-electron exchange and correlation interactions, the functional of PBE, a form of the general gradient approximation (GGA), was used throughout. The Brillouin-zone integrations were performed using Monkhorst-Pack grids of special points, with gamma-point centered \((2\times2\times1)\) \(k\)-points meshes for the \((8\times8)\) graphene
cell. When the geometry was optimized, all atoms were allowed to relax. And the geometric structures were optimized until the residual forces were below 0.001 eV Å⁻¹. The charge density was analyzed using the Bader method.

4.3 Results and Discussion

4.3.1 Morphology, Structure and Composition

![SEM images and corresponding EDX spectra](image)

**Figure 4.1** SEM images and corresponding EDX spectra of the samples obtained at different synthesize stages. (a, e) silica spheres; (b, f) the silica has adsorbed the 1-allyl-2-thiourea outside the sphere; (c, g) the sample obtained after pyrolysis at 900 °C under the Ar atmosphere; (d, h) the morphology of the final product obtained after the removal of silica by 24 % HF and washed with deionized water at room temperature.
As shown in the experimental section, for a typical synthesis, 1.0 g of silica nanospheres were mixed with 10 mL water containing 1.0 g of 1-allyl-2-thiourea at 80 °C, followed by a slow evaporation process to dry the sample at 60 °C, allowing not only a uniform 1-allyl-2-thiourea coating layer on the nanospheres but also self-assembled into highly ordered structures. To approve the formation of the porous structure and successful S and N co-doping, a step by step synthesis process was characterized by SEM and EDX. The coated nanospheres were calcinated under different temperatures in a tubular furnace for 2 h in Ar to ensure the complete pyrolysis process. Take the SN/C-900 as an example, as shown in Figure 4.1, the synthesized silica nanospheres have a diameter of 80-100 nm and the EDX has clearly shown the existence of Si and O peaks. However, after mixing silica and 1-allyl-2-thiourea together at 80 °C using a lower evaporation procedure, the appearance of C, N and S peaks demonstrates successful adsorption of the precursor onto silica nanospheres. After pyrolysis at 900 °C, the existence of S and N illustrates successful doping of the heteroatoms into the product. After treated with HF, silica nanosphere templates were dissolved and porous structured carbon morphology was observed. The existence of N and S elements further demonstrates the successful doping by this simple one-pot pyrolysis process. Figure 4.1c shows a SEM image of the calcinated sample (SN/C-900), and it clearly shows highly ordered 3D structure. For comparison, the SN/C sample without using silica template was also synthesized. As seen in Figure 4.2a and b, the sample without using silica nanosphers template shows sheet-like morphology with a thickness of around 300-400 nm. To demonstrate the inner structure of the SN/C sample, TEM characterization was carried out. As seen from Figure 4.3, the TEM image of the sample synthesized with silica nanospheres template reveals that the 3D-network structure was constructed by very thin spherical carbon sheets originally formed on the surface of the highly ordered silica nanospheres (Figure 4.3b). However, the sample obtained without silica nanospheres template shows graphene sheet-shaped and multilayered structure (Figure 4.3c and d). According to the SEM and TEM images shown in Figure 4.1 and 4.3, we can conclude that the macro-pore structures are resulted from the removal of silica nanospheres, the micro-pore structures are the spherical thin layer graphitic carbon formed on the surface of the nanospheres and the meso-pore structures are formed by the cavities of neighborhood template nanospheres.
Figure 4.2 (a) and (b) SEM images of SN/C synthesized without using silica template.

Figure 4.3 TEM images of SN/C-900 sample with (a), (b) and without (c), (d) using silica template. The inset in Figure 4.3b and d show the HRTEM image of the sample and both samples show multi-layered structure.

The XRD patterns of SN/C-X samples are shown in Figure 4.4. As can be seen, with the increase of pyrolysis temperature, the graphitic degree is improved,
which means higher heating temperature is favorable for the carbonization process. We could also see from Figure 4.4 that the SN/C-900 shows a typical graphitic carbon peak at 2θ=24.6°, confirming the formed carbon sheets are graphitic carbon. The HRTEM image (inset in Figure 4.3b) indicates the graphitic carbon sheets consist of several graphitic layers. Compared to graphite carbon (~0.34 nm), a slightly larger d spacing (~0.36 nm) of (002) calculated by Bragg equation could be due to S and N doping.

Figure 4.4 Wide-angle XRD patterns of the SN/C-X samples.

It is known that for a given dopant, the doping level and the type of bonds formed between dopant and graphitic carbon atoms are important factors affecting the electrocatalytic activity. Figure 4.5 shows the high resolution XPS of N spectra for SN/C-X catalysts. The N1s spectra can be fitted into three peaks at 398.3±0.2 eV, 400.1±0.3 eV and 401.1±0.4 eV. The peaks with lower binding energy located at about 398.3 and 400.1 eV, respectively, corresponding to pyridinic-like and pyrrolic-like N, which can contribute to the π-conjugated system with a pair of p-electrons in the graphitic carbon layers. The higher binding energy located at about 401.1 eV is corresponding to “graphitic” nitrogen, that is, the carbon atoms within the graphitic layers are substituted by nitrogen atoms. It can be seen at lower pyrolysis temperatures, only pyridinic- and pyrrolic-N were formed. After 600 °C of pyrolysis, graphitic-N was formed. Pyridinic-N was the dominated peak below 800 °C until then it was overtaken by the graphitic-N. However, in higher pyrolysis temperatures, pyridinic- and graphitic-N were the dominate defects forms whereas pyrrolic-N defects type are less abundant. This is in accordance with expectations due to the
higher diffusion rate of carbon at high temperatures leading to the formation of the more stable graphitic-N defect. This means that the chemical state of N in doped graphitic carbon layers can be easily modulated by changing the pyrolysis temperature.

![Graph showing high resolution N XPS spectra of SN/C-X samples and the corresponding different peaks.](image)

**Figure 4.5** High resolution N XPS spectra of SN/C-X samples and the corresponding different peaks.

Figure 4.6 gives further details of the N and S high resolution XPS change with increasing pyrolysis temperature. As shown in Figure 4.6a, pyridinic-N is overtaken by the graphitic-N at higher temperature; However, in comparison, all high resolution S2p peaks of the SN/C samples prepared at different temperatures show...
one main peak at the binding energies of ∼164.0 eV, in agreement with the reported positions of -C-S-C- bond owing to their spin-orbit coupling. Moreover, the amount of the doping level was calculated by using N/C and S/C atomic ratios and the surface area is also given in Table 4.1.

To give a specific detail of the doping level changes, we once again use the SN/C-900 as an example; The XPS survey spectrum confirms the presence of N and S elements (Figure 4.6c). The presence of an O1s peak in the SN/C-900 graphitic carbon sheets could be due to the adsorbed oxygen, which can be an additional advantage for an ORR electrocatalyst. The amounts of doped N and S are calculated (in terms of N/C and S/C atomic ratios) to be 7.2% and 1.6%, respectively (Table 4.1). The high resolution N1s spectra (Figure 4.6d) suggest the presence of three types of N-C bonds, with 35.5%, 21.6% and 42.6% of the doped N being pyridinic-, pyrrolic- and graphitic-N, respectively (Table 4.1). The high resolution S2p spectrum shows a distinct peak at ∼164.0 eV that could be assigned to -C-S-C- bonds, which is further confirmed by the FT-IR spectrum (Figure 4.7). As shown in Figure 4.6, after calcination. Some characteristic bonds were observed and assigned to the stretching of carbonyl aromatic C≡C bonds (1624 cm⁻¹), 753 cm⁻¹, which is assigned to the stretching of C-S-C bonds. The broadened band in the range of 1200-1400 cm⁻¹ is attributed to the stretching mode of C-N heterocycles. The broad bands in the range of the 3000-3700 cm⁻¹ region can be attributed to the adsorbed H₂O molecules or N-H vibration possibly due to uncondensed amine groups.

**Table 4.1** Surface area, atomic ratios and atomic percentage of various N chemical states in SN/C-X samples of SN/C-X samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface Area (m²/g)</th>
<th>N/C (%)</th>
<th>S/C (%)</th>
<th>Pyridinic-N (%)</th>
<th>Pyrrolic-N (%)</th>
<th>Graphitic-N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN/C-400</td>
<td>56.9±3.7</td>
<td>26.3±0.6</td>
<td>3.1±0.3</td>
<td>58.0±0.9</td>
<td>42.0±1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>SN/C-500</td>
<td>372.7±3.5</td>
<td>24.9±0.3</td>
<td>2.8±0.4</td>
<td>57.5±0.8</td>
<td>42.5±0.7</td>
<td>0.0</td>
</tr>
<tr>
<td>SN/C-600</td>
<td>425.0±3.3</td>
<td>20.8±0.3</td>
<td>2.7±0.2</td>
<td>50.3±2.3</td>
<td>22.4±1.8</td>
<td>26.1±3.7</td>
</tr>
<tr>
<td>SN/C-700</td>
<td>481.4±3.6</td>
<td>11.6±0.5</td>
<td>2.1±0.3</td>
<td>48.0±1.4</td>
<td>22.1±2.3</td>
<td>30.0±2.5</td>
</tr>
<tr>
<td>SN/C-800</td>
<td>547.7±3.2</td>
<td>8.9±0.5</td>
<td>1.9±0.2</td>
<td>39.3±2.4</td>
<td>21.6±3.8</td>
<td>39.0±3.3</td>
</tr>
<tr>
<td>SN/C-900</td>
<td>571.9±3.0</td>
<td>7.2±0.4</td>
<td>1.6±0.2</td>
<td>35.5±2.5</td>
<td>21.6±1.8</td>
<td>42.6±0.9</td>
</tr>
<tr>
<td>SN/C-1000</td>
<td>860.4±3.9</td>
<td>2.5±0.4</td>
<td>0.7±0.3</td>
<td>23.2±1.8</td>
<td>19.1±2.1</td>
<td>57.7±2.7</td>
</tr>
</tbody>
</table>
Figure 4.6 (a) High resolution N and (b) S XPS spectra of SN/C-X. (c) Survey spectrum of and. (d) High resolution N XPS spectrum of SN/C-900.

The surface areas and pore size distribution of the synthesized porous structured samples were characterized further. As we known that large surface area is critically important for a high performance electrocatalyst. However, the effectiveness of a surface utilization is largely determined by the porous structure of the material because a surface is useful only when the reactant could readily reach it.

Figure 4.7 FT-IR spectra of the SN/C-X samples synthesized at lower and higher temperatures.
As shown in Figure 4.8, with the increase in pyrolysis temperature, the microporous zone is also increased. Figure 4.8 also shows the N\textsubscript{2} adsorption-desorption isotherm (Type 1B) for SN/C-X sample. A high BET surface area of 860 m\textsuperscript{2} g\textsuperscript{-1} (Table 4.1) can be obtained when the temperature is as high as 1000 °C. However, a very low calcination temperature, SN/C-400 for example, could not form good porous structure even using silica nanosphere as template, which means not only the template but also the carbonization degrees all play a vital role on the formation of the porous structures. As seen from Figure 4.8a, all the BET curves show a steeply increased adsorption at low relative pressures, indicating the presence of substantial micropores structures (<2 nm). It is the micropores existed in these carbon materials that contribute to the larger surface area of the sample. The micropores structures are the spherical thin layer graphitic carbon formed on the surface of the nanospheres. The sharply increased adsorption at high relative pressure region suggests the presence of large percentage of macropores structures (50-100 nm). The macropores are not good for the observer high surface areas, but it is the very reason for the formation of the large quantities of porous volume. The macropores structures are resulted from the removal of silica nanospheres which have a diameter around 80-100 nm.

![Figure 4.8](image)

Figure 4.8 (a) The N\textsubscript{2} adsorption/desorption isotherm of SN/C-X and (b) Pore size distribution curves of SN/C-X samples.

Moreover, according to the SEM and TEM images shown in Figure 4.1 and 4.3, the mesoporous structures are formed by the cavities of neighborhood template nanospheres. The pore size distribution was fitted by non-local density functional theory (NLDFT) which confirms that the resultant graphitic carbon network does possesses a trimodal-pore structure covering pore sizes ranging from micro- to meso- and macro-pores (Figure 4.8b). Importantly, the BET results indicate that the micro-
and macro-pore structures are dominant in determining the surface area and pore volume, respectively. In an electrocatalysis process, the presence of the macro-pores enables rapid mass transport to fully utilize the high surface area of micro- and meso-pore structures. Also, such a network structure provides sophisticated electron pass way and superior structural stability for the electrocatalyst.

4.3.2 TG/DSC-MS Studies

![Figure 4.9](image)

**Figure 4.9** TG/DSC and MS curves of (a), (b) 1-allyl-2-thiourea and (c), (d) Thiourea under Ar protection from 100 to 1000 °C with a temperature increase rate of 5° C min⁻¹ under Ar protection, respectively.

The formation process of these carbon-based materials using sole precursor synthesis approach deserves further characterization. For a thermolysis process, the concurrent growth of graphitic carbon and doping depend heavily on the precursors’ thermal decomposition characteristics. This might mean that a reproducibly controlled doping can be achieved with the self-sponsored sole precursor approach as the decomposition products of a given compound under a given temperature and atmosphere would be fixed. As seen from Figure 4.9a and b, the obtained TG/DSC-MS data suggest that the decomposition of 1-allyl-2-thiourea starts at 180 °C and completes at ~400 °C to emit H₂, N₂, CH₄, NH₃, H₂S and CS₂ (Figures 4.9). The major breakdown occurs at ~210 °C, as indicated by the endothermic DSC responses.
and online MS peaked emissions of gaseous products. Further decompositions occur at 265 and 315 °C to produce CS₂ and H₂S. These results suggest that the carbonization and doping occur below 400 °C, concurrent with decomposition of 1-allyl-2-thiourea. Since only a sole precursor is presence, the chemical composition of the carbonized products should be fixed. This is confirmed by the highly reproducible measurement data of carbonized products from 6 batches of 400 °C treated samples, showing ~2% and ~10% variations for the doped N and S contents, respectively (Table 4.1). The doped N forms are also reproducible, having a variation of ~1.5%, 2.8% for pyridinic and pyrrolic, respectively (Table 4.1). The dramatically reduced mass loss rate beyond 400 °C suggests that the bonds rearrangements and structural confirmation of the carbonized products are dominant reactions at higher temperatures. As such, the higher temperature treated samples should possess reproducible chemical compositions (including doping level and type) because the carbonized products formed at lower temperature with the fixed chemical compositions serve as the ‘precursors’ at a higher reaction temperature. The data obtained from the higher temperature treated samples (6 batches for each temperature) show highly reproducible N and S doping levels and the types of C-N bonds (Tables 4.1), demonstrating N and S doping level and type can be well controlled by simply optimizing the treatment temperature. For comparison, we also used thiourea as the precursor. However, as seen from Figure 4.9c and d, it completely decomposed around the temperature of 740 °C. From the XPS and XRD results mentioned above, we know that when the pyrolysis temperature is below 800 °C, it is hard to obtain high graphitic carbon structures. More importantly, less carbonization degrees will significantly influence the electron transfer ability of the electrocatalyst. Therefore, from this point of view, thiourea is not a good candidate as precursors to synthesize heteroatoms-doped graphitic carbon catalyst. On the other hand, these results also demonstrate selection of appropriate precursor is also important for the successful fabrication of electrocatalysts.

4.3.3 Electrochemical Performance

Since the structure, doping level and doping state were determined, the resultant S and N co-doped materials were evaluated as catalyst for ORR. To achieve this, CV was firstly characterized, for example, Figure 4.10a show the SN/C-900 electrode in a N₂ saturated KOH solution which exhibits a typical pseudo-capacitive behavior of heteroatom-doped graphitic carbon. As seen from it, a well-defined cathodic current
peaked at -0.30 V resulting from O₂ reduction (OR) was observed from the O₂ saturated solution, indicating a pronounced ORR electrocatalytic activity. On the other hand, CVs of other SN/C-X (X=400-1000 °C) electrodes in O₂ saturated KOH solution were also characterized and shown in Figure 4.10b.

![Cyclic voltammograms](image)

**Figure 4.10** (a) Cyclic voltammograms of the ORR at SN/C-900 electrode in N₂ or O₂ saturated KOH solution and (b) Cyclic voltammograms of SN/C-X samples obtained at different temperatures in O₂ with a scan rate of 100 mV s⁻¹ in the potential range from -1.2 to +0.2 V at room temperature, respectively.

From Figure 4.10b, increasing in cathodic current responses and shifting cathodic peak potentials towards the anodic direction can be observed with higher temperature (up to 900 °C) treated electrodes, indicating an improved catalytic performance. However, a reversed trend was observed for the SN/C-1000 electrode. Linear sweep voltammograms of SN/C-X coated rotating disk electrodes show OR currents increasing with increased rotation rates for all cases investigated (Figure 4.11).
Figure 4.11 (a)–(n) Linear sweep voltammograms and the corresponding Koutecky–Levich plots for ORR within the potential range of -0.4 to -1.0 V for SN/C-X electrode. All the tests were conducted from 0.2 V to -1.2 V with a scan rate of 10 mV s\(^{-1}\) in an \(\text{O}_2\) saturated 0.1 M KOH aqueous electrolyte.

The corresponding Koutecky-Levich plots of SN/C-X electrodes at different electrode potentials exhibit high linearity between -0.40 to -1.0 V (Figure 4.11), which suggest that the electron transfer numbers are similar for oxygen reduction at different electrode potentials. The number of transferred electrons (calculated from Equations (1)-(3)) determined from the Koutecky-Levich plots increases with a more cathodic potential (Figure 4.12). For a given potential, the number of transferred electrons increases with the treatment temperature up to 900 °C (Figure 4.12 and Figure 4.13).
Figure 4.12 Transferred electrons deduced from Koutecky–Levich plots in Figure 4.11. The calculation results obtained from the Koutecky–Levich plot slope shows that SN/C-400 to SN/C-700 and SN/C-1000 show a two-electron reduction process, whilst SN/C-800 and SN/C-900 catalysts show a direct four-electron process.

Again, a reversed trend was observed for the SN/C-1000 electrode. The SN/C-900 electrode exhibits the best performance among all SN/C-X electrodes that investigated, having 3.52 to 3.81 transferred electrons within the potential range of -0.4 to -1.0 V, signifying a 4-electron OR process (Figure 4.13). However, the samples obtained at lower pyrolysis temperatures show a distinct two steps process for ORR and an overall two-electron process. Figure 4.13b shows OR current...
responses of different SN/C-X electrodes obtained under comparable conditions. It is known that a less cathodic onset potential indicates a lower ORR overpotential. In this regard, SN/C-900 electrode possesses an onset-potential of ~35 mV, almost identical to that of commercial Pt/C electrode. The onset-potentials of other SN/C electrodes are cathodically shifted, including SN/C-1000 electrode. Noticeably, the OR current obtained from the SN/C-900 electrode is the highest among all electrodes investigated, including the Pt/C electrode. The excellent performance of the SN/C-900 electrode could be attributed to the optimal S, N doping level and doping form, and the superior electron and mass transport properties of the trimodal-porous structured graphitic carbon network. The OR current obtained from other SN/C electrodes are found to increase as the treatment temperature is increased, except SN/C-1000 electrode.

Figure 4.13 (a) Transferred electrons and the corresponding Koutecky–Levich plots (inset) for ORR within the potential range of -0.4 to -1.0 V for SN/C-900 electrode; (b) Linear sweep voltammograms of SN/C-X and Pt/C RDE electrodes at 1600 rpm and 10 mV s⁻¹.

4.3.4 Charge and Spin Densities Calculations

The changes in charge and spin densities introduced by sole-doping of N or S, and co-doping of S and N were studied by density functional theory (DFT) calculations (Figures 4.14 and Figure 4.15). The results indicate that except the spin density for pyridinic-N, for all other cases studied, the obtained changes in both charge and spin densities, and the numbers of positively charged C atoms from the S and N co-doped models are greater than that of the sole-doped models by either N or S. This could be due to the fact that the co-doping of S and N introduces the asymmetrical spin and charge densities, leading to the charge delocalisation as shown by Figures 4.14 and
Figure 4.15. For the contribution of the different forms of C-heteroatoms bonds, especially the high-resolution N1s which can divide into three forms, that is, pyridinic-, pyrrolic-N and graphitic-N. Both of them have been shown to serve as catalytically active sites for oxygen reduction.84, 90

Figure 4.14 Charge and spin density of graphitic-N (a, b), pyrrolic-N (c, d) and pyridinic-N (e, f) doped graphitic carbon sheets, respectively; (g, h) charge and spin density of only S-doped graphitic carbon sheet, respectively. Dark brown, gray, yellow and pink spheres represent C, N, S and H atoms in Figure 4.14a, c, e and g, respectively. The blue and yellow contours indicate the spin densities of the samples with the spin density value of ±2.0×10⁻⁷ electron Å⁻³.
In this case, although quantitatively confirming one doping model is more active than the other by DFT calculations is arguable, it is certain that the co-doping of S and N does introduce larger number of active C atoms, favorable for ORR which can be seen from the calculation results from Figure 4.14 and Figure 4.15 and this results also provides us the effective of the co-doping strategy introduced by the aim that proposed at the beginning of this chapter. When correlating the observed OR current and onset-potential of SN/C-X electrodes with S, N doping levels and the surface area, except for the SN/C-1000 electrode, all other electrodes follow a trend that an increase in the surface area and decrease in the S and N doping levels lead to an increased OR current and anodically shifted onset-potential, indicating an improved electrocatalytic activities (Figure 4.12 and Figure 4.13). A better performance resulting from the increased surface area is easy to be understood due to the easy attachment of the electrolyte to the active site on the doped carbon. Nevertheless, the decreased doping levels accompanied by the increased surface areas could lead to enhanced performances contradict the general perception of the doping effect on ORR catalytic activities. To the best of our knowledge, the effect of doping density (level) on the ORR electrocatalytic activity has not yet been investigated. We hypothesized that the best catalytic activity could only be achieved with an optimal doping level. DFT calculations were therefore further performed to investigate the effect of doping level on the charge and spin densities (Figure 4.15). The selection of the pyridinic-N doped graphitic carbons for DFT calculations is because the form of pyridinic-N doping introduces the highest charge and spin density changes into the doped graphitic carbons (Figures 4.14e, f). The DFT results shown in Figure 4.15a and b indicate that a maximized overall doping effect can be achieved with optimal N, S doping levels (e.g., C:N:S=112:8:2), which explains the best ORR catalytic performance obtained from the SN/C-900 electrode. Low doping levels (e.g., C: N: S=120:4:1) can introduce significant charge and spin density changes to individual doping sites (Figures 4.15c, d). However, under such conditions, the overall doping effect is limited due to the presence of fewer active doping sites, which could be a reason for the observed low catalytic activity from the SN/C-1000 electrode with similar S, N doping levels. With excessively high doping levels (e.g., C: N: S=91:23:3), a dramatically reduced doping effect to individual doping sites is observed (Figures 4.15e, f). That is, high doping levels can introduce large numbers of ‘active’ sites but the overall catalytic activity is reduced due to the dramatically
reduced doping effect to individual sites. This explains our experimental observations that a decrease in N and S doping levels (for treatment temperatures up to 900 °C) leads to an increased ORR catalytic activity but it started to deficiency under 1000 °C.

**Figure 4.15** Effect of doping level on charge and spin densities of S and pyridinic-N co-doped graphitic carbon structures with atomic doping ratios of a), b) C:N:S=112:8:2 (close to the doping level for SN/C-900); c), d) C:N:S=120:4:1 close to the doping level for SN/C-1000); e), f) C:N:S=91:23:3 (close to the doping level for SN/C-400). Dark brown, gray, yellow and pink spheres represent C, N, S and H atoms. The blue and yellow contours indicate the spin densities of the samples with the spin density value of ±2.0×10^{-8} electron Å^{-3}.

It is well known that comparing to Pt/C, heteroatom-doped graphitic carbon electrocatalysts possess high resistance to crossover effects by fuel molecules. Figure 4.16 show that SN/C-900 electrode can tolerate the presence of 3.0 M methanol
without noticeable crossover effects when adding the methanol at around 100s. The durability of the electrodes is critically important for practical use, too. As revealed in Figure 4.16, SN/C-900 electrode is capable of retaining 95% and 83% of its initial activity after 5 h and 2 days of usage, respectively, while the Pt/C electrode could only retain 72% catalytic activity after 5 h of usage under the same conditions. This means the SN/C-X sample is very stable even used for a period of longer time.

**Figure 4.16** (a) Chronoamperometric response for ORR at SN/C-900 and Pt/C electrodes on addition of 3 M methanol after about 100 s. Durability evaluation of (b) Pt/C and (c) SN/C-900 electrode for 2 days at -0.4 V and a rotation rate of 1000 rpm.
4.4 Conclusion

In summary, in this chapter, we have demonstrated a facile yet effective self-sponsored doping method, capable of precisely controlling the co-doping of S, N during a concurrent graphitic carbon growth process by simply controlling the pyrolysis temperature. The method is also capable of reproducibly controlling the pore structure and surface area. The results reveal that the doping effect is heavily dependent on the doping density and a maximal catalytic activity could only be achieved with the optimal doping level. Low doping levels can introduce large doping effect to individual doping sites but having a limited overall doping effect because of fewer active sites. High doping levels can introduce large numbers of ‘active’ sites but the doping effect to individual doping sites is dramatically reduced. The presence of macro-pores in the trimodal-porous network enhances the mass transport, enabling the full utilization of large surface areas created by the micro- and meso-pore structures. The findings of this work would be valuable for design and fabrication of high performance carbon-based electrocatalysts.

4.5 References

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CHAPTER 5 Pt-FREE ELECTROCATALYSTS AS COUNTER ELECTRODE MATERIALS FOR DYE SENSITIZED SOLAR CELLS
5.1 Introduction

DSSCs have attracted much attention due to its high efficiency, low-cost and simple assembly process.\textsuperscript{1-3} The main framework of DSSCs consist of a dye-adsorbed nanocrystalline photoanode (conventionally TiO\textsubscript{2}-based semiconductor), an electrolyte (e.g. I\textsuperscript{-}/I\textsubscript{3}\textsuperscript{-}), and a counter electrode (CE, usually, a platinum (Pt) layer is coated on the conductive substrate). Photoexcitation of the dye molecules under sunlight illumination leads to the injection of electrons from the dye to the conduction band of TiO\textsubscript{2} and then to the external circuit. Simultaneously, the oxidized dye is reduced by I\textsuperscript{-} in the electrolyte and returns to its ground state, in which I\textsuperscript{-} gets converted to triiodide (I\textsubscript{3}\textsuperscript{-}).

High electrocatalytic activity of CE is essential for high performance DSSCs, because CE material is a critically important component of DSSCs, which plays a key role for catalyzing the reduction reaction of I\textsubscript{3}\textsuperscript{-} to I\textsuperscript{-} to regenerate the sensitizer after electron injection.\textsuperscript{4,5} The electrons that flow through the external circuit arrive at the CE and reduce the I\textsubscript{3}\textsuperscript{-}, by Equation (1),\textsuperscript{6}

\[ I_3^- + 2e^- \leftrightarrow 3I^- \] (1)

Owing to its superior electrocatalytic activity toward I\textsubscript{3}\textsuperscript{-} reduction, Pt-based catalysts have been the most widely used CE materials for DSSCs.\textsuperscript{6-10} However, large-scale application of DSSCs using Pt-based catalysts is hindered owing to its high-cost, scarcity and low resistance to crossover effect of methanol molecule. Therefore, extensive effort has been paid to develop high efficiency and low-cost non-Pt electrocatalysts. Recently, two types of low-cost materials with superior electrocatalytic activity have attracted great attention in the fields of science and technology.\textsuperscript{11,12} One is carbonaceous materials, such as CNTs,\textsuperscript{13} mesoporous carbon arrays,\textsuperscript{14} electroconductive polymers,\textsuperscript{15-17} and graphene-based materials etc.\textsuperscript{18,19} The other type is inorganic-based materials and their composites including Fe\textsubscript{2}O\textsubscript{3},\textsuperscript{20} metal sulphides, nitrides and selenides etc. such as CoS\textsubscript{x},\textsuperscript{21} MoS\textsubscript{2},\textsuperscript{22} WS\textsubscript{2},\textsuperscript{23} SnS\textsubscript{x},\textsuperscript{24} NiS\textsubscript{25-29} NiSe\textsubscript{30}, TiN\textsubscript{31,32} and copper zinc tin sulfide (CZTS)\textsuperscript{33} etc. These materials have been promising candidates as CE materials to replace Pt-based materials because of their low-cost, corrosion resistant, good electrical conductivity and superior catalytic properties.\textsuperscript{34} Even so, the reported results have indicated that using these materials as electrocatalysts for DSSCs still encounters some difficulties.

For carbon-based materials, the electrical conductivities especially their electron catalytic activities still cannot match up to those of Pt-based CE materials.\textsuperscript{35} Therefore, in order to tailor the electronic properties and catalytic activities of these
carbonaceous materials, various strategies have been adopted via physical or chemical means in reported results. For instance, doping with heteroatom into sp²-hybridized carbon frameworks such as CNTs or graphene could introduce more catalytic active sites and therefore tailor their electronic property and chemical reactivity which have both widely theoretical and experimental studied and show striking electrocatalytic performance as a catalyst for ORR.\textsuperscript{36, 37} Although these carbon-based materials may represent a new family of electrode materials, in these reports, they were mainly explored as replacements for conventional Pt in DSSCs.\textsuperscript{38, 39} Until recently, N-doped carbon-based materials were studied as CE and show excellent electrocatalytic activity for triiodide reduction in DSSCs.\textsuperscript{38-41} However, in this studies, one source as carbon and the other one or more precursors including toxic gas or toxic material as dopant are used, which involves careful fabrication, too tedious, too complicated. More importantly, although many investigations involving DSSCs catalysts based on N-doped carbon materials have been reported, to our knowledge, heteroatoms co-doped especially S and N co-doped porous carbon materials have never been investigated as CE for DSSCs before.

In addition, nickel sulfide (NiS) has been particularly interested as counter electrode materials in DSSCs because of its superior electrocatalytic activity, earth abundance and low-cost. However, to date, the highest light conversion efficiency (LCE) of 7.41% has been reported by Huang et al\textsuperscript{26} using NiS nanorod CE. But this efficiency is still lower than that using Pt catalyst (7.55%). Recently, Kim et al. demonstrated that the LCE using NiS nanostructured CE could surpass Pt-based CE.\textsuperscript{27} However, the DSSCs efficiency in their study could only reach 6.8% using the NiS CE (5.8% for Pt-based DSSCs). Therefore, exploring new NiS nanostructures with high electrocatalytic activity still remains as a challenge.

In this chapter, we synthesized S and N co-doped porous carbon through a simple pyrolysis process of 1-allyl-2-thiourea and silica template at 900 °C (denoted as SN/C-900), the resultant SN/C-900 sample exhibited excellent catalytic activity towards I\textsubscript{3}⁻ reduction. When used as CE material in DSSCs, the light conversion efficiency as high as 7.86% was obtained which is 1.07 times higher than that of cell assembled with Pt CE under the same condition.

Additionally, we will also report a facile and one-step hydrothermal method to directly grow (0001) faceted single crystal NiS nanosheet film onto FTO conducting substrate. Without the need for further treatment, single crystal NiS nanosheet films
were used as CEs for DSSCs, displaying an overall LCE of 8.62%, 17.1% higher than that of the Pt-based DSSCs (7.36%). The improved solar cell performance can be ascribed to the superior electrocatalytic activity of (0001) faceted NiS nanosheets due to the existence of sulfur vacancies, which have been verified by theoretical calculations and experimental characterizations. To our knowledge, the obtained DSSCs efficiency in this work is the highest among all reported DSSCs assembled with NiS CEs until now.

5.2 Experimental Section

5.2.1 Chemicals and Materials

All of the reagents with analytical grade purity were purchased from Sigma Aldrich unless special stated and used without further purification.

5.2.2 Preparation and Characterization of Porous SN/C-900

Silica nanospheres were prepared by Stober’s method. In a typical synthesis, 200 mL of absolute ethanol was mixed with 20 mL of deionized water and 10 mL of 25 wt. % ammonia aqueous solution. The mixture was stirred vigorously for 0.5 h followed by quick addition of 15 mL of tetraethylorthosilicate (TEOS). The solution was stirred for another 4 h at room temperature; Silica nanospheres were separated by centrifugation at 10,000 rpm for 10 min, followed by washing with ethanol and deionized water and finally kept at 70 °C for dry. The preparation of S and N co-doped graphitic carbon catalyst was as follows: the fabricated ordered silica nanospheres were used as hard templates; 500 mg silica was mixed with 500 mg 1-allyl-2-thiourea (melting point ~70-72 °C) in 5 mL of deionized water at 80 °C under stirring in an open crucible. At this temperature, the 1-allyl-2-thiourea dissolved very well. After evaporation of deionized water, the obtained 1-allyl-2-thiourea/silica composite was dried overnight at 60 °C in an oven and lightly crashed and subsequently calcinated at 900 °C for 2 h with a ramp rate of 5 °C min⁻¹ under Ar atmosphere, respectively. After the removal of silica template by HF etching, S and N co-doped porous carbon was obtained for further use and characterization (denoted as SN/C-900).

TEM (Philips F20) and SEM (JSM-6300F) were employed for characterizing the morphology of the prepared samples. Chemical compositions of the samples were analysed by X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyser). The Brunauer-
Emmett-Teller (BET) method was utilized to calculate the specific surface areas (SBET) using nitrogen adsorption-desorption isotherms of the samples on a Quantachrome Autosorb equipment.

### 5.2.3 Preparation and Characterization of NiS Nanosheet

A typical synthetic process is as follows: 30.0 mg thioacetamide was dissolved in 5.0 mL of deionized water and then 1.5 mL of N\textsubscript{2}H\textsubscript{4}·H\textsubscript{2}O (35 wt% solutions in water) was added to the above solution under vigorously stirring. After 5.0 min, 47.5 mg NiCl\textsubscript{2}·6H\textsubscript{2}O was added to the above mixture with stirring for 10 min. The resulting solution was transferred into a Teflon-lined stainless steel autoclave with a volume of 20.0 mL. Subsequently, a piece of pre-treated FTO conducting glass (15 Ω square\textsuperscript{-1}, Nippon Sheet Glass, Japan) with conductive facing up was put into the above reaction solution with an angle of 45°. The hydrothermal reaction was performed at different temperatures (120, 150 and 180 °C) for 24 h to study the temperature effect on the resulting NiS structure and electrocatalytic activity (denoted as NiS-X-24h, where X is reaction temperature). For the time-dependent experiments, the hydrothermal reaction was performed at 180 °C for different reaction times (6 h, 12 h and 24 h, denoted as NiS-180-N, where N is reaction time). After hydrothermal reaction, the autoclave was cooled down to room temperature and then FTO substrate was taken out, rinsed adequately with deionized water and allowed to dry in an ambient atmosphere.

The resulting NiS nanostructured films were further characterized and tested in DSSCs. TEM (Philips F20), SEM (JSM-6300F) and XRD (Shimadzu XRD-6000 diffractometer) were employed for characterizing the prepared samples. Chemical compositions of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer). Photoluminescence spectra (Hitachi F-7000, excitation wavelength: 370 nm, scanning rate: 1200 nm min\textsuperscript{-1}, PMT voltage: 800 V) was tested by dispersing the obtained powder (scraped from FTO) into deionized water after 30 min sonication. Fourier transform infrared spectroscopy (FT-IR) analysis of the samples was performed (Perkin Elmer spectrum 1000) using FT-IR spectrophotometer with KBr as the reference sample. KBr was grinded and dried before use so as to remove the adsorbed water on it. Then a weight ratio of the tested sample and KBr around 1:100 was used for tableting by using the Perkin Elmer spectrum 1000 system.
5.2.4 Solar Cell Measurements

A series of DSSCs cells were fabricated with traditional sandwich type configuration by using a dye-anchored TiO\textsubscript{2} photoelectrode (Dyesol, Australia) which was pre-calcinated at 450 °C for 0.5 h before dye loading. The dye-anchored TiO\textsubscript{2} photoanode (0.25 cm\textsuperscript{2}, 0.5 cm×0.5 cm) and NiS nanostructured film counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of the ionomer Surlyn 1702 (Dyesol, Australia). A hole (0.8 mm) was drilled on the FTO used for the growth of NiS before reaction. In order to obtain a good electrical contact, the edge of the FTO was roughened slightly with sandpaper. Then, for easy DSSCs characterization, a solder was applied on each side of the FTO electrode and a wire was extended outward. The position of the solder was 1 mm away from the edge of the Surlyn gasket and 4 mm away from the photoactive TiO\textsubscript{2} layer. The CE electrode was treated using similar procedure. When the soldering procedure was done, the photoanode and CE with a 0.25 cm\textsuperscript{2} ionomer film mask were put on the assembling machine which was heated to 110 °C under 0.2 MP pressures and kept for 30 seconds before cooling it under ambient atmosphere. Once assembling, a drop of electrolyte was dipped on the hole at the back of the counter electrode and it was introduced into the cell via vacuum backfilling.\textsuperscript{43} The cell was firstly placed in a small vacuum chamber to remove inside air and then exposed it to ambient pressure so as to drive the electrolyte into the cell. Finally, the hole was sealed using an ionomer film at room temperature.\textsuperscript{43} For a meaningful comparison, a commercially available Pt counter electrode (Dyesol, Australia) was also tested for DSSCs using a similar assembly approach described above. CV was tested in an acetonitrile solution containing 1.0 mM I\textsubscript{2}, 10.0 mM LiI and 0.1 M LiClO\textsubscript{4} in a three-electrode system at a scan rate of 50 mV s\textsuperscript{-1} with a computer-controlled potentiostat instrument. For all the investigated samples, the CV curves exhibit two pairs of oxidation and reduction peaks in the range of -0.6 to 1.2 V (vs. Ag/AgCl). For the light conversion efficiency testing, a 500 W Xe lamp (Trusttech Co., Beijing) with an AM 1.5G filter (Sciencetech, Canada) was used as the light source. The light intensity was measured by a radiant power meter (Newport, 70260) coupled with a broadband probe (Newport, 70268). The photovoltaic measurements of DSSCs were recorded by a scanning potentiostat (Model 362, Princeton Applied Research, US). Impedance measurements were performed with a computer-controlled potentiostat (Princeton Applied Research, Parstat 2273) using symmetric cells fabricated with two identical
electrodes. The frequency range is 0.1 Hz to 1 MHz and the magnitude of the modulation signal is 10 mV. Tafel polarization curves were obtained using the symmetrical cells as well, at a scanning rate of 10 mV s\(^{-1}\), using CHI 760D work station with a two-electrode system. The photocurrent-voltage curves (I-V curve) of DSSCs were recorded by PAR potentiostat and the solar energy-to-electricity conversion efficiency (\(\eta\)) is defined by Equation (2):\(^{44}\)

\[
\eta = \frac{J_{sc} V_{oc} FF}{P_{in}} \times 100\%
\]  

(2)

where \(J_{sc}\) is the short-circuit photocurrent density under irradiation, \(V_{oc}\) is the open-circuit voltage, \(P_{in}\) is the light power per unit area and \(FF\) is the fill factor which is calculated by Equation (3):

\[
FF = \frac{P_{max}}{J_{sc} V_{oc}} = \frac{I_{max}}{J_{sc}} \frac{V_{max}}{V_{oc}}
\]  

(3)

where \(I_{max}\) and \(V_{max}\) are the current and potential at the maximum power point respectively in \(J-V\) curves of the solar cells.

5.2.5 Theoretical Calculations

All the spin-polarized calculations were performed with Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation using the Vienna ab-initio simulation package (VASP) code.\(^{45-47}\) The project-augmented wave (PAW) method was used to represent the core-valence electron interaction. The valence electronic states were expanded in plane wave basis sets with energy cut-off at 450 eV. The occupancy of the one-electron states was calculated using the Gaussian smearing (SIGMA=0.05 eV) for the NiS (0001) surface. The ionic degrees of freedom were relaxed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme until the Hellman-Feynman forces on each ion were less than 0.05 eV Å\(^{-1}\). The dipole correction was performed throughout the calculations to take the polarization effect into account. As for model construction, considering that iodine molecule bond is up to 2.68 Å. A large \(p\) \((4\times4)\) NiS (0001) slab was built to minimize the lateral interaction between adjacent I atoms. The vacuum between slabs is ~20 Å, and a corresponding \(1\times1\times1\) k-points mesh was used during optimizations. To check the polarization effect for the polar NiS (0001) surface, we tested different atomic layers and got similar I adsorption energies of -0.62 eV, -0.58 eV and -0.66 eV for five-, nine- and thirteen layer, respectively.
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The adsorption energy of I ($E_{ad}^1$) is defined as Equation (4):

$$E_{ad}^1 = E(I/\text{sur}) - E(\text{sur}) - 1/2E(I_2)$$  \hspace{1cm} (4)

where $E(\text{sur})$, $E(I_2)$ and $E(I/\text{sur})$ are the energies of the catalyst surface, $I_2$ in the gas phase and I adsorbed on the catalyst surface, respectively. The more negative $E_{ad}^1$ is, the more strongly the species I bind on surface.

5.3 Results and Discussion

5.3.1 SN/C-900 as Counter Electrode Material in DSSCs

Structure and Morphology

Figure 5.1 (a) SEM and (b) TEM image of the synthesized SN/C-900 sample.

In this section, S and N co-doped porous structured carbon used as CE is successfully synthesized by pyrolysis of 1-allyl-2-thiourea at 900 °C by using silica nanospheres as hard template which are subsequently removed in hydrofluoric acid (concentration: 24%). The morphology of the synthesized samples is characterized by SEM and TEM. As seen from the SEM image in Figure. 5.1a, the SN/C-900 sample exhibits highly ordered porous structures. Moreover, typical TEM in Figure 5.1b further confirms the highly ordered porous structure of SN/C-900, as evidenced by large domains with well-ordered porous channels.

XPS is used to provide insight into the chemical bonding configuration of S and N with carbon. Figure 5.2a displays XPS survey spectra of the SN/C-900 sample. In clearly shows the existence of S and N signals in the final product. The presence of oxygen peak in the SN/C-900 product is possibly due to the incorporation of physicochemically adsorbed oxygen. The appearance of these bonds indicated that S and N atoms are successfully doped into the porous structured carbon network. In
order to characterize the inner porous structure of the SN/C-900 sample, nitrogen adsorption-desorption is carried out. Figure 5.2b shows a type 1B N$_2$ adsorption-desorption isotherm for SN/C-900 sample. A high BET surface area of 572 m$^2$ g$^{-1}$ can be obtained for this porous structure. The curve shows a steeply increased adsorption at low relative pressures, indicating the presence of substantial micro-pore structures,$^{48,49}$ whilst the sharply increased adsorption at the high relative pressure region suggests the presence of large percentage of macropore structures.$^{50-52}$ The existence of micro- and macro-pores structures in this material provides several benefits. Firstly, the micropores contribute to the formation of high surface area of the material. Secondly, the mass transportation ability of the electrolyte will be improved due to the appearance of the highly ordered macropores.

**Figure 5.2** (a) and (b) XPS spectrum and BET curves of SN/C sample, respectively.

**Electrochemical Characterization**

In order to investigate the catalytic activity of the synthesized SN/C-900 catalyst, the electrocatalytic abilities of the porous SN/C-900 as CE is firstly studied by CV in an acetonitrile solution containing I$_2$, LiI, and LiClO$_4$ in a three-electrode system.$^{19,39,53}$ The SN/C-900 is used as working electrode, whilst Pt as CE and Ag/AgCl as reference electrode with a scan rate of 50 mV s$^{-1}$ in the potential range of -0.6 V to 1.2 V. For comparison, commercial Pt CE was also measured. The obtained CV curves of I/I$_3$ redox couple on the CE are shown in Figure 5.3. It can be seen in Figure 5.3 that all CV curves show two pairs of redox peaks in the range of -0.6 V to 1.2 V. The redox peaks at more negative potentials (left pair redox peak), corresponding to the reaction of I/I$_3$ redox,$^{18,54-56}$ is the focus of our study because this redox peak is responsible for catalyzing ability of the CE, while the redox peaks at more positive potentials (right pair redox peak), corresponding to the oxidation
and reduction of $I_3^-/I_2$ redox couple is not our focus in this study. The electrocatalytic ability of a CE for $I_3^-$ reduction in a DSSCs can be visualized in terms of its cathodic peak potential ($E_{pc}$), cathodic peak current ($I_{pc}$) and peak-to-peak voltage separation ($E_{pp}$). In other words, the higher the cathodic peak current density, more positive cathodic reduction peak potential and lower $E_{pp}$ values indicate better electrocatalytic ability of CE for the reduction of $I_3^-$ in the corresponding DSSCs.

![Cyclic voltammograms of SN/C-900 and Pt on a FTO glass substrate cycled in I/I₃ electrolyte (10 mM LiI+1 mM I₂+0.1 M LiClO₄+acetonitrile) at a scan rate of 50 mV s⁻¹ in a three-electrode system.]

**Figure 5.3** Cyclic voltammograms of SN/C-900 and Pt on a FTO glass substrate cycled in I/I₃ electrolyte (10 mM LiI+1 mM I₂+0.1 M LiClO₄+acetonitrile) at a scan rate of 50 mV s⁻¹ in a three-electrode system.

From Figure 5.3, it can be seen that the cathodic peak potential of SN/C-900 CE cell is more positive than that of commercial Pt CE cell. It indicates that the overpotential for reduction of $I_3^-$ to $\Gamma$ of the SN/C-900 CE is much smaller than that of commercial Pt CE and produces favourable conditions for regeneration of the sensitizer. On the other hand, it is more effective to investigate their catalytic activities by comparing their $E_{pp}$ values. The $E_{pp}$ of the porous SN/C-900 sample is around 506 mV, a value which is much lower than that of Pt CE (701 mV). Taken together, all of these behaviours indicate a faster rate for triiodide reduction reaction and suggest that the porous SN/C-900 could be used as an efficient CE in DSSCs as previously demonstrated for N-doped graphene or CNTs for ORR.¹⁹,⁵⁷,⁵⁸
DSSCs Performance

![Graph showing current-voltage characteristics of DSSCs with SN/C-900 (red curve) and commercial Pt CE (black curve).](image)

**Figure 5.4** Current-voltage characteristics of DSSCs with SN/C-900 (red curve) and commercial Pt CE (black curve).

The performance of the porous SN/C-900 CE solar cell, whose photoelectrode is constructed with a N719-sensitized TiO₂, is evaluated under a standard simulated AM 1.5G at 100 mW cm⁻² illumination in contrast to the commercial Pt-based solar cell. The active area of the photoanode is 0.25 cm². Figure 5.4 shows *I–V* characteristic curves of DSSCs with SN/C-900 and Pt CE. As a reference, the DSSCs with commercial Pt as CE exhibits a short-circuit current density (*Jₘ*) of 15.21 mA cm⁻², an open-circuit voltage (*Vₜ*) of 713 mV, a fill factor (*FF*) of 67.9%, and an overall LCE of 7.36%, whilst the DSSCs assembled using SN/C-900 shows a *Jₘ* of 17.74 mA cm⁻², *Vₜ* of 713 mV, *FF* of 62.1% and a total PCE of 7.86%, as shown in Table 5.1, which is 1.07 times of that obtained using the commercial Pt CE (7.36%). It should be noted that the DSSCs using porous SN/C-900 exhibits a smaller *FF* value than that of the DSSCs with commercial Pt CE. This result may be attributed to the lower conductivity of SN/C-900 compared to that of Pt which deserves a further investigation.

**Table 5.1** Photovoltaic parameters of DSSCs assembled with SN/C-900 and commercial Pt CE, respectively.

<table>
<thead>
<tr>
<th>CEs</th>
<th><em>Jₘ</em>/mA cm⁻²</th>
<th><em>Vₜ</em>/mV</th>
<th><em>FF</em>/%</th>
<th>LCE /%</th>
<th><em>Rₛ</em> /Ω</th>
<th><em>Rₛ</em>/Ω</th>
</tr>
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<tbody>
<tr>
<td>Pt</td>
<td>15.21</td>
<td>713</td>
<td>67.9</td>
<td>7.36</td>
<td>25.58</td>
<td>7.96</td>
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<td>713</td>
<td>62.1</td>
<td>7.86</td>
<td>32.57</td>
<td>6.53</td>
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</table>
Electrochemical Impedance

To further evaluate the electrocatalytic abilities of the porous SN/C-900 sample, electrochemical impedance spectroscopy (EIS) and Tafel kinetic characterization are applied. EIS measurements are performed on dummy cells with a symmetric sandwich-like structure between two identical electrodes, that is, with a structure of counter electrode/electrolyte/counter electrode under dark conditions (as shown in the schematic structure pictured in Figure 5.5).

![Figure 5.5 Schematic structure of dummy cells for EIS and Tafel measurements.](image)

As can be seen, the cell is assembled as the same procedure as the cell for DSSCs testing. However, when testing, the working port is connected with one piece of the CE and the other piece of CE is connected simultaneously with reference and counter electrode port.

The Nyquist plots are shown in Figure 5.6a. The Nyquist plots for symmetric cells with different CEs illustrate impedance characteristics, in which two semicircles are observed in the higher (left) and lower (right) frequency regions. The high-frequency (corresponding to low $Z'$) intercept on the real axis ($Z'$ axis) represents the series resistance $R_s$. The semicircle in the low-frequency range results from the charge-transfer resistance ($R_{ct}$) at the electrolyte/CE interface, it changes inversely with the catalytic activity of different CE on the reduction of triiodide, and the corresponding constant phase element (CPE). These parameters are determined by fitting the impedance spectra using Z-view software, and good agreement between the measured and the fitted data is achieved in all cases. Table 5.1 summarized the values of $R_s$ and $R_{ct}$ by fitting the spectra in Figure 5.6a with an EIS spectrum analyzer. As shown in Table 5.1, the resistance $R_s$ of SN/C-900 catalyst is bigger than that of Pt, which may be related with the bad adherence ability of the material with the FTO surface. However, the $R_{ct}$ value of SN/C-900 catalyst is smaller than that of Pt which means a higher catalytic activity towards triiodide ion reduction, indicating that SN/C-900 has a superior electrocatalytic activity and finally resulting in the comparable photovoltaic performance to commercial Pt CE.
Figure 5.6 (a) Nyquist plots (inset shows the equivalent circuit mode of that used to analyze the EIS spectra) and (b) Tafel polarization curves of symmetric dummy cells with SN/C-900 and Pt CE, respectively.

Tafel-polarization measurements are also carried out in a dummy cell similar to the one used in EIS measurements to further evaluate the electrochemical catalytic activities of the SN/C-900 electrode. The curves show logarithmic current density as a function of voltage. As seen from Figure 5.6b, the slope for the anodic or cathodic branches of SN/C-900 catalyst is higher than that of Pt. A larger slope in the anodic or cathodic branch indicates a higher exchange current density \( J_0 \) on the electrode. The curve of SN/C-900 sample exhibited a large exchange current density \( J_0 \), the intersection of the cathodic branch and the equilibrium potential line (vertical black solid line), which could be seen from Equation 5 in comparison with that of the Pt electrode. This further indicates that SN/C-900 has superior catalytic activity for I\(_3^-\) reduction and higher light conversion efficiency as seen in Figure 5.6b.

\[
J_0 = \frac{RT}{nF R_{ct}} \tag{5}
\]

where \( R_{ct} \) is the charge-transfer resistance obtained from EIS spectra (Figure 5.6), \( R \) is the gas constant, \( T \) is the absolute temperature, and \( F \) is Faraday’s constant. In addition, the Tafel polarization curves contain the information about limiting current density \( J_{lim} \), which can be expressed by Equation (6),

\[
J_{lim} = \frac{2ne_0 DcN_A}{l} \tag{6}
\]

where \( N_A \) is the Avogadro constant, \( l \) is the spacer thickness, \( e_0 \) is the elementary charge, \( c \) is the concentration of I\(_3^-\). \( D \) is the diffusion coefficients of triiodide.
Section Summarization

In summary, in this study, we developed S and N co-doped porous structured carbon as highly catalytic active catalyst for the reduction of I/\text{I}^3\. The catalytic ability of the porous SN/C-900 catalyst was characterized by cyclic voltammetry, electrochemical impedance spectroscopy and Tafel polarization analysis. The results show that DSSCs based on SN/C-900 CE showed higher PCE of 7.86\%, which is 1.07 times of that obtained using the commercial Pt CE (7.36\%). The high power conversion efficiency may due to the improved catalytic activity after S and N co-doped into the porous carbon. Our results also demonstrated that the porous structured SN/C-900 catalyst may serve as potential alternatives to the expensive and scarce Pt for low-cost DSSCs.

5.3.2 NiS as DSSCs Counter Electrode Material

Structure and Morphology

\textbf{Figure 5.7} (a) XRD patterns of the as-synthesised NiS samples at different temperatures for 24 h. (b) XPS survey spectra of NiS samples synthesised at different temperatures for 24 h. (c) and (d) High resolution XPS spectra of S2p and Ni2p.

NiS nanostructured films were directly grown on FTO conducting substrates via a
facile hydrothermal method. Before the hydrothermal treatment, the FTO should be cleaned with the mixture of acetone and absolute ethyl alcohol. More importantly, the surface should be washed with large quantity of deionized water sufficiently or else the NiS crystal will not prefer to grow on the surface. Furthermore, the surface of the FTO with conductivity must face up when chemical reaction occurs. The failure of this procedure will also lead to the bad crystal formation of the NiS nanostructures. Figure 5.7a shows the XRD patterns of the as-synthesized products with different hydrothermal temperatures for 24 h (120 °C, 150 °C and 180 °C, denoted as NiS-X-24h, X represents reaction temperature). As shown, some diffraction peaks concentrated at $2\theta=30$–$50^\circ$ can be well indexed to $\alpha$-NiS crystal structure (JCPDS No. 65-0395, space groups: P63/mmc (194)) for all samples.

![Figure 5.7a](image)

**Figure 5.7a** (a) SEM images of the as-synthesized NiS sample at 180 °C for 24 h. (c) Cross-sectional SEM image of the sample. (d) SAED pattern and TEM image (inset) of the sample. (e), (f) SEM images of the as-synthesized NiS samples (a) 120 °C for 24 h. (b) 150 °C for 24 h, respectively.

The survey XPS demonstrate that the as-synthesized samples with different growth
temperatures are composed of S, C, O and Ni, and the calculated atomic ratios of all investigated samples are around 1:1, meaning the stoichiometric formation of nickel sulfide as NiS (Figure 5.7b). The core level of S2p and Ni2p XPS curves were also given in Figure 5.7c and d. As seen from it, there are no significant differences between the samples synthesizes at different temperatures which means the NiS nanocrystal could formed at lower temperatures. Improving the hydrothermal temperature mainly play the role of modulating the morphology of the product and let the electrolyte access to the electrocatalyst in a convenient way which will be illustrated in the following paragraphs. The morphologies of the samples were characterized by SEM and TEM so as to further show the differences details of the sample fabricated at different reaction conditions. Figure 5.8a shows the SEM image of the NiS sample synthesised at 180 °C for 24 h (denoted as NiS-180-24h). As shown, a uniform nanosheet with 3D network structures can be observed, magnification of the sample shows that the nanosheets with a thickness of ca. 10 nm are vertically grown on the film surface (Figure 5.8b).

![Image of original sample and tape adhesive test](image)

**Figure 5.9** *Stability of the NiS film characterized by testing the electrocatalytic activity after 200 cycles of and the resultant film cannot be also removed by the sticky tape.*

The formed nanosheet film onto FTO substrate possesses high mechanical stability and strong adhesion to the substrate with a grey-black appearance (inset in Figure 5.8a). This was confirmed further by a simple sticky tape measurement. To be more specific, as seen from Figure 5.9, there is a nonobvious change in electrocatalytic activity which was observed after 200 cycles of test and the resultant film cannot be also removed by the sticky tape (Figure 5.9). These evidences indicate that the NiS film directly grown onto the FTO substrate does possess good mechanical strength and strong adhesion to the substrate. The cross-sectional SEM image of the NiS film
shows a film thickness of ca. 1.5 μm, composed of top nanosheet layer with a thickness of ca. 0.5 μm and bottom compact particulate layer (Figure 5.8c). As an electrocatalyst for DSSCs, the top nanosheet structure may be responsible for catalytic reduction reaction of I$_3^-$ to I, while the bottom compact particulate structure could be favourable for electron transfer. To identify the exposed crystal facet, HRTEM and SAED were introduced. Figure 5.8d shows the SAED pattern of an individual nanosheet. The SAED pattern indicates typical hexagonal diffraction spots of the [0001] zone (I) of the NiS crystal, suggesting good single crystal nature of the nanosheet and largely exposed (0001) crystal facet. The high crystallinity and largely exposed (0001) faceted surface of the nanosheet structure may be highly advantageous for providing more electrocatalytic active sites, favourable for improving the DSSCs performance. Also, weak diffraction spots with the projection along [1 1 0 1] zone (II) are visible in the diffraction patterns with the coincident $(11\bar{2}0)_{II}$ reflections, demonstrating crystal twinning is present in the sample. Our experiments show that only highly packed rod-like aggregates can be observed at 120 and 150 °C (Figure 5.8e and f), however, as mentioned before, high growth temperature is favourable for the formation of nanosheet structure.67

Figure 5.10 SEM images of the as-synthesised NiS samples with different reaction time at 180 °C. (a) 6 h. (b) 12 h.

Apart from the influence factor of reaction temperature, the time-dependent experiments also demonstrate that the nanosheet array layer cannot be formed when hydrothermal reaction time is less than 24 h (denoted as NiS-180-N, N represents reaction time) (Figure 5.10a and b), which means not only the reaction temperature but the reaction time both have an influence on the final morphology of the products. Regarding to the formation mechanism of the nanosheet, we suppose the direct formation of high quality nanosheets-nanoparticles NiS film could be largely
attributed to the catalyst role of hydrazine in accelerating the decomposition of thioacetamide to form \( S^2^- \), leading to the formation of NiS nanoparticles on FTO substrate that enables the formation of NiS nanosheets during the further growth process.

FT-IR of the as-synthesized samples was further used to illustrate the formation process of the 3D NiS nanosheet (Figure 5.11). As seen from Figure 5.11, the spectra of NiS catalysts mainly show two stretch vibrations at 1631 and 3460 cm\(^{-1}\) attributing to the N-H bending and stretching mode, respectively,\(^{68}\) indicating the formed compound between hydrazine and thioacetamide molecules on the surface of nickel sulfide nanoparticles. More specifically, the thioacetamide serves as the sulfur source for particle growth, and the formed compound serves as the capping ligand that controls growth similar to what was found by Korgel et al. for the solventless synthesis of NiS nanorods and triangular nanoprisms\(^{66}\).

![Figure 5.11 FT-IR spectra of the samples obtained at 180 °C for different reaction times.](image)

**Figure 5.11** *FT-IR spectra of the samples obtained at 180 °C for different reaction times.*

**Electrochemical Characterization**

As electrocatalyst for DSSCs, the catalytic activity of the material is critically important for improving the solar cell performance. In this work, the electrocatalytic activities of the NiS samples are firstly examined by CV technique (Figure 5.12). As can be seen from Figure 5.12, the relative positive pair is assigned to the redox reaction of \( I_2/I_3^- \) and the negative one to the reaction of \( I^-/I_3^- \). As we mentioned before, the electrocatalytic ability of an electrocatalyst toward \( I_3^- \) reduction for DSSCs can be visualised in terms of its cathodic peak potential (\( E_{cp} \)), cathodic peak current (\( I_{pc} \)) and
peak-to-peak potential separation ($E_{pp}$) in CV curve. That means a higher $I_{pc}$, a more positive $E_{cp}$ and a lower $E_{pp}$ value indicating a better electrocatalytic ability of the electrocatalyst toward the reduction of $I_3^-$ for DSSCs.\textsuperscript{8,19,63} As shown in Figure 5.12, the NiS-180-24h sample exhibits higher $I_{pc}$, more positive $E_{cp}$ and lower $E_{pp}$ values compared to other samples even including commercial Pt electrocatalyst, therefore, the highest electrocatalytic activity among all investigated counter electrodes towards $I_3^-$ reduction reaction could be expected.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{cv.png}
\caption{CVs of different NiS and Pt CEs in $I/I_3^-$ electrolyte in an acetonitrile solution containing 1.0 mM $I_2$, 10.0 mM LiI and 0.1 M LiClO$_4$ in a three-electrode system at a scan rate of 50 mV s$^{-1}$ with a computer-controlled potentiostat (Princeton Applied Research, Parstat 2273).}
\end{figure}

**DSSCs Performance**

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{dssc.png}
\caption{Current-voltage characteristics of DSSCs with NiS and commercial Pt material as counter electrodes.}
\end{figure}
Once we have a general view of the catalyst activity of the different NiS CEs materials, DSSCs full-cell characterization was carried out. The NiS nanostructured films with different morphologies and electrocatalytic activities were evaluated as CE materials for DSSCs. Figure 5.13 shows the photocurrent-photovoltage (I–V) curves of DSSCs assembled with different CEs. The NiS-180-24h exhibits a short-circuit current density of 18.71 mA cm\(^{-2}\), an open-circuit voltage of 735 mV, and a fill factor of 62.7%, leading to an overall LCE of 8.62%, which is obviously superior to those of the DSSCs made of the commercial Pt (7.36%) and other NiS CEs (Table 5.2). As we expect, the NiS-120-24h sample shows the worst LCE property (LCE of 5.52%), which means although NiS single crystal could well formed under lower temperature, the morphology of the catalysts actually plays a key role for the I\(_3^-\) reduction reaction. However, prolonging reaction time and improving reaction temperatures, as shown in Figure 5.13, can significantly improve the LCE of the NiS CE based solar cells. This reason for the improved DSSCs performance can be due to many attributes, such as superior electrocatalytic activity and electron transfer property, however, it deserves a further investigation.

**Electrochemical Impedance and Tafel Spectroscopy**

![Electrochemical Impedance Spectroscopy](image)

**Figure 5.14** Nyquist plots of symmetric dummy cells with Pt and NiS counter electrodes, inset show the equivalent circuit model deduced from the Nyquist curve.

Since the DSSCs performance varies significantly, therefore, more evaluation technology should be used to find the reasons. Figure 5.14 shows the electrochemical impedance spectra of the NiS samples fabricated under different conditions. The Nyquist plots of all investigated counter electrodes show two semicircles. As we mentioned before, the high frequency intercept on the real axis represents the Ohmic series resistance (R\(_s\)). Usually, a smaller R\(_s\) value demonstrates that the electrocatalyst
is more strongly attached to the FTO glass substrate and better conductivity activity.
The semicircle in the high-frequency region corresponds to the charge-transfer process \( (R_{ct}) \) of electrolyte/electrode interface, while the semicircle in low-frequency region to the finite layer Nernst diffusion impedance within the electrolyte \( (Z_w) \) which can be calculated from Equation (7).

\[
Z_w = \frac{KT}{n^2 e_0 c A \sqrt{i \omega D}} \tanh\left(\frac{i \omega \delta}{D}\right)
\]  

(7)

Where \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( n \) is the number of electrons involved in the electrochemical reduction of \( \text{I}_3^- \) at the electrode (here \( n=2 \)), \( e_0 \) is the elementary charge, \( c \) is the concentration of \( \text{I}_3^- \), \( A \) is the electrode area, \( \omega \) is the angular frequency, and \( \delta \) is the thickness of the diffusion layer.\(^5\) Judged from Equation 7, \( D \) increases with increasing electrocatalytic activity of the counter electrode.

Based on Equation 7 and Figure 5.14, the calculated \( R_s, R_{ct} \) and \( Z_w \) values are shown in Table 5.2 for all investigated CEs. Compared to other NiS CEs and Pt electrode, The NiS-180-24h electrode exhibits smaller \( R_s, R_{ct} \) and \( Z_w \) values (see Table 5.2), indicating strong adhesion to the substrate and superior electrocatalytic activity of the NiS nanosheet film, and improved diffusion of triiodide ions at NiS nanosheet film, which means the 3D nanosheet networks grown on the top-side of the FTO is favourable for the transfer of the electrolyte.\(^{24}\) Inset in Figure 5.14 shows the equivalent circuit model deduced from the Nyquist curve, CPE is the constant phase element parameter that depends on frequency and is engaged in the model circuit which is more meaningful for estimating the capacitance resulted from the accumulation of ions at the electrode-electrolyte interface.\(^{69}\)

![Figure 5.15 Tafel polarisation curves of symmetric dummy cells with Pt and NiS counter electrodes.](image)
Meanwhile, Tafel polarisation curves indicate that the NiS-180-24h electrode possesses the highest electrocatalytic activity among all investigated CEs, too (Figure 5.15). However, the origin of the high electrocatalytic activity of the single crystal NiS nanosheet film deserves to be further investigated, to prove this, DFT calculation was explored further.

**Theoretical Calculations**

![Diagram](image)

**Figure 5.16** (a) Optimised bulk structure of NiS and (b) surface configuration of stoichiometric NiS (0001) surface with rows of three-coordinated S ion exposed. (c) Direct dissociation of I₂ molecule upon adsorption at the S-vacancy dimer in the direction of [0001] at NiS (0001) surface. (d) Adsorption configuration of I atom sitting at the S vacancy position. Light blue, yellow and brown represent Ni, S and I atom, respectively.

To illustrate the origin of high catalytic activity of NiS nanosheet film, a brief molecular-level investigation into triiodide reduction reaction on NiS (0001) surface was conducted by virtue of DFT calculations. For triiodide reduction reaction, its activity is significantly influenced by I₂ activation and I atomic desorption from the electrocatalyst, in which the adsorption energy of I atom ($E_{ad}^{I}$) on the electrocatalyst surface plays an essential role. Too high adsorption energy of I limits the overall activity due to the difficulty for I removal, while weak adsorption hinders I₂ molecular dissociation. It is known that, $E_{ad}^{I}$ was successfully used as a descriptor to
screen electrode materials and $E_{\text{ad}}$ values ranged from 0.33 to 1.20 eV were predicted to be usually catalytically active.\textsuperscript{20} The adsorption of I and activation of I\textsubscript{2} molecule on NiS (0001) surface to illustrate the electrocatalytic activity of the NiS nanosheets. As illustrated in Figure 5.16a, the bulk structure of NiS consists of six-coordinated Ni\textsuperscript{2+} and S\textsuperscript{2-}, whole lattice parameters were optimised to be $a=b=3.451$ Å and $c=5.394$ Å, according well with the experimental values ($a=b=3.448$ Å and $c=5.385$ Å). Figure 5.16b presents the surface configuration of stable NiS (0001) terminated by rows of three-coordinated sulfur ions (S\textsubscript{3c}) along the [0001] direction, from which one can see that on stoichiometric NiS (0001) surface Ni\textsuperscript{2+} cations keep the six-coordinated configuration and thus hardly adsorb I or I\textsubscript{2} species. To activate and adsorb I\textsubscript{2} molecule, some defects such as S vacancies have to be introduced at the NiS (0001) surface, which is accompanied and determined by the catalyst preparation process.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{photoluminescence_spectrum.png}
\caption{Photoluminescence spectrum of the as-prepared NiS nanosheet sample measured at room temperature at an excitation wavelength of 370 nm (inset). The peak cantered at 418 nm is corresponding to the S vacancy.}
\end{figure}

In this work, the state of the S-vacancy has been confirmed by investigating the photoluminescence spectra (PL) of the NiS sample. As shown in Figure 5.17, with excitation at $\lambda_{\text{ex}}=370$ nm, a fluorescence emission peak located at 418 nm can be obviously observed, which is attributed to the presence of sulfur vacancies and interstitial sulfur lattice defects in NiS nanosheet structure.\textsuperscript{25} Owing to the presence of the S-vacancy in NiS nanosheet (Figure 5.16c), upon adsorption at the S-vacancy dimer in the direction of [0001], it is found that I\textsubscript{2} molecule can readily dissociate into two I\textsuperscript{*} atoms with the bond length evidently stretched to 3.664 Å from 2.681 Å.
in the free I₂ molecule, indicating enough activation ability of NiS (0001) toward I₂ molecule. The formed I* atom preferably sits at the S vacancy and forms three Ni-I bonds at the distance, \(d\) (Ni-I), of \(\sim 2.709\) Å (Figure 5.16d). The corresponding adsorption energy \(E_{\text{ad}}^I\) was calculated to be \(-0.62\) eV relative to half a gaseous I₂ molecule, being within the active range for potentially good electrode material. More importantly, it is much close to that on Pt electrode surface \((-0.52\) eV). Therefore, the outstanding electrocatalytic activity of NiS (0001) surface can be expected, which results in high solar cell performance.

**Table 5.2 Photovoltaic and EIS parameters of DSSCs assembled with different counter electrodes.**

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>(J_{sc}) [mA cm(^{-2})]</th>
<th>(V_{oc}) [mV]</th>
<th>(FF) [%]</th>
<th>(LCE) [%]</th>
<th>(R_{ct}) [Ω]</th>
<th>(R_s) [Ω]</th>
<th>(Z_w) [Ω]</th>
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<tr>
<td>Pt</td>
<td>15.21</td>
<td>713</td>
<td>67.9</td>
<td>7.36</td>
<td>7.96</td>
<td>25.58</td>
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</tr>
<tr>
<td>NiS-120-24h</td>
<td>15.53</td>
<td>691</td>
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<td>5.52</td>
<td>12.42</td>
<td>31.97</td>
<td>5.62</td>
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<tr>
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<td>695</td>
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<td>7.71</td>
<td>7.23</td>
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</tr>
<tr>
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<td>62.7</td>
<td>8.62</td>
<td>2.22</td>
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</tr>
</tbody>
</table>

**Section Summarization**

In this part, single crystal NiS nanosheet films with largely exposed (0001) surface have been successfully fabricated on FTO substrate by a facile hydrothermal method. The theoretical calculations reveal that the exposed (0001) surface is highly catalytically active owing to the existence of S vacancies in nanosheet. As CE for DSSCs, the (0001) faceted NiS nanosheet film exhibits an impressive light conversion efficiency of 8.62%, which is almost 1.17 times of the Pt-based DSSCs (7.36%).

**5.4 Conclusion**

We have synthesized porous S, N co-doped graphitic carbon and single NiS 3D nanosheet network films as counter electrode catalyst materials for the I₃⁻ reduction reaction. When used as an electrocatalyst, both of them show superior light conversion efficiency performance. In details, the DSSCs based on SN/C CE showed a higher LCE of 7.86%, 1.07 times of that obtained using the commercial Pt counter electrode (7.36%). The improved catalytic activity after S and N co-doped into the porous carbon manly contribute to the observed high light conversion efficiency.
However, for NiS nanosheet CE catalysts, the existence of S vacancies on the exposed (0001) surface is the reason for the significantly higher light conversion efficiency obtained in our work.

5.5 References

(42) Stöber, W.; Fink, A.; Bohn, E. J. Colloid Interface Sci. 1968, 26, 62.
CHAPTER 6 FABRICATION OF HIGH PERFORMANCE CARBON-BASED ELECTROCATALYSTS FROM CELLULOSE AND CHITIN FOR ENERGY CONVERSION
6.1 Introduction

Nowadays, hydrogels and aerogels obtained from biomass are receiving immense attentions owing to their many advantages such as high swelling capacity, high surface area, biocompatibility, and biological functions. Hydrogels are chemically or physically cross-linked structures composed of hydrophilic polymers in a 3D network and can adsorb and retain a large quantity of water and have potential applications in biomedicine and cosmetics etc. Aerogels obtained by using freeze-drying or supercritical drying techniques possess significant advantages due to their non-periodic porous nanostructures and exhibit unusual properties, such as high porosity and surface area, low density (up to 95% of their volume is air), and low heat conductivity. Different types of aerogels have been synthesized and studied until now. For example, SiO$_2$ aerogels, metal oxide aerogels (Al$_2$O$_3$, TiO$_2$, ZrO$_2$, Fe$_3$O$_3$ etc.), inorganic and organic hybrid aerogels etc. These aerogels typically display porosities up to 99%, bulk densities in the range 0.004-0.500 g cm$^{-3}$, and surface areas between 100 and 1000 m$^2$ g$^{-1}$. However, these inorganic aerogels usually lack mechanical strength and easily tend to collapse when subjected to tiny stresses. On the contrary, aerogels made of organic polymers can be mechanically strong, which are able to be thermally treated for further use as carbon precursor, e.g., resorcinol-formaldehyde.

Until more recently, cellulose and chitin aerogels have gained much interest due to their renewability and biodegradability. To obtain cellulose, many researchers are now tackling the isolation of nanosized cellulose whiskers and fibers from plant sources. The methods include mechanical treatments, cryocrushing, grinding, high-pressure homogenizing, chemical treatments, biological treatments, TEMPO-mediated oxidation, synthetic and electrospinning, etc. The fabricated nanofibrillar materials with different types highly depend on the cellulose raw material, its pre-treatment procedure and the disintegration process. On the other hand, obtaining cellulose is the first step. To make it an aerogel, it is another story. Due to the existence of polydisperse linear glucose polymer chains which form hydrogen-bonded supramolecular structures, cellulose is actually insoluble in water and most common organic liquids. Recently, Zhang et al. developed a simple route using safe and low-cost chemical reagents for producing regenerated cellulose materials without producing any hazardous by-products. It involves dissolution of cellulose in aqueous NaOH/urea solutions at low temperatures, and then freeze-
dried to get the aerogel. However, using this method, it is hard to get ultralong nanofibers. Therefore, Liu et al. used a sonification way to solve this problem. This is because sonification impact can break the relatively weak interfaces between the microfibrils bonds which are mainly connected by nonbonding interactions such as van der Waals forces.\textsuperscript{67} On the other hand, the strong covalent bonds along the longitudinal direction of the cellulose molecule chains remain intact.\textsuperscript{68} Chitin is one of the most abundant biopolymers naturally produced in the biosphere in addition to cellulose, occurring mainly in the exoskeletons of shellfish and insects and the cell walls of mushrooms.\textsuperscript{69} It is biosynthesized at a rate of 1010 to 1011 tons per year.\textsuperscript{69} However, most chitins are thrown away as industrial waste. Chitin and its derivative, chitosan, also have many excellent properties including biocompatibility, biodegradability, nontoxicity, adsorption properties etc. and thus can be widely used in a variety of areas such as biomedical applications, agriculture, water treatment, and cosmetics. Chitin nanofibers can be isolated from animal shells by a simple grinding treatment way after the removal of proteins and minerals using chemical treatment.\textsuperscript{70}

In this chapter, we extract cellulose from natural grass \textit{via} a step by step chemical treatment process under mild heat treatment environment. After removal of the matrix substances such as hemicellulose and lignin, the obtained cellulose is kept in deionized water after sonification treatment and freeze-dried. To make it a good candidate for ORR, the obtained aerogel is further calcinated at 900 °C in an Ar protection environment. Since it contains no N atoms in cellulose, for comparison, chitin aerogel which contains very rich N content, is extracted from prawn shells. The rich N content in chitin structure makes possible to directly transform it to N-doped carbon materials \textit{via} a self-supported pyrolysis process without the need for additional N dopant source. N-doped carbon material is obtained after calcination and its performance as electrocatalyst for ORR will be investigated in this chapter.

6.2 Experimental Section

6.2.1 Chemicals and Materials

The Monkey Grass was obtained from Gold Cost, Australia. It was washed with deionized water and sonicated for 0.5 h thoroughly to remove the impurities adsorbed on the surface and dried in the oven for overnight. All other reagents with
analytical grade purity were purchased from Sigma Aldrich unless special stated and used without further purification.

6.2.2 Preparation of Cellulose and Carbon Catalyst without N-Doping

The extraction process was as follows: Cellulose nanofibers hydrogels were prepared according to the literature. 71, 72. 10 g of wood fibers were dewaxed in a Soxhlet apparatus with a 2: 1 (v/v) mixture of benzene and ethanol for 6 h. Afterward, the lignin in the sample was removed using an acidified sodium chlorite solution at 80 °C for 1 h; the process was repeated three times, which can be identified from the color change from dark brown to light white. The sample was then treated for 24 h with 4 wt% KOH at room temperature to remove other residuals such as hemicelluloses, starch, and pectin. The sample was next treated with acetic acid acidified sodium chlorite solution at 80 °C for 1 h, and then treated with 5 wt% KOH at 100 °C for 2 h. Highly purified cellulose fibers were prepared by further treating the sample with a 1 wt% hydrochloric acid solution at 90 °C for 2 h and thoroughly washing them with deionized water under filtration systems. Finally, the obtained solution containing purified cellulose fiber was stored under ambient atmosphere. When used, the solution will be placed in a common ultrasonic generator equipped with a cylindrical titanium alloy probe tip 2.5 cm in diameter and with a frequency of two seconds on and one second off. The subsequent ultrasonication was conducted for 0.5 h, and freeze-dried to get the 3D cellulose aerogel. For catalyst generation, the aerogel was calcinated under the protection of Ar at 900 °C with a ramp rate of 5 °C min⁻¹ (named as Cellulose-900).

6.2.3 Preparation of Chitin and Nitrogen-doped Carbon Catalyst

Chitin nanofibers were prepared by a chemical treatment procedure described by Ifuku et al. 69, 70, 73 firstly, prawn shells were cleaned thoroughly, dried and milled into fine powders. Then the refined prawn shell powders were refluxed in 5 wt % of KOH for 6 h under vigorous stirring to remove most of the proteins. This suspension was cooled down to room temperature, then filtered and washed with large quantity of deionized water under filtration. Secondly, the powders were treated with 7% HCl solution for 48 h at room temperature to remove the mineral salts. After filtration and rinsing with deionized water, the treated samples were dispersed and heated to 100 °C in an oil bath in a 5% KOH solution for 48 h to completely remove any residual proteins. Thirdly, the pigment was removed from the samples using 1.7
wt % of sodium chlorite in 0.3 M sodium acetate buffer for 6 h at 90 °C, followed by filtration and washing with thoroughly quantity of deionized water. The purified wet chitin powders from dry prawn shell were dispersed in water at 1 wt %, and acetic acid was added to adjust the pH value to approximately 3 to facilitate fibrillation. The suspension was treated with a domestic blender. Finally, the purified chitin fibers were stored in deionized water and stored under ambient atmosphere. When used, the solution will be placed in a common ultrasonic generator equipped with a cylindrical titanium alloy probe tip 2.5 cm in diameter and with a frequency of two seconds on and one second off. The subsequent ultrasonication was conducted for 0.5 h, and freeze-dried to get the 3D chitin aerogel. For N-doped carbon catalyst generation, the aerogel was calcinated under the protection of Ar at 900 °C with a ramp rate of 5 °C min⁻¹ (named as Chitin-900).

6.2.4 Characterization

SEM and EDXS (JSM-6300F) were employed for characterizing the morphology and structure of the obtained samples. Chemical compositions of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer). All binding energies were carefully aligned by reference to the C1s peak (284.7 eV) arising from surface hydrocarbons or possible adventitious hydrocarbon. FT-IR analysis of the samples was performed using Perkin Elmer spectrum 1000 FT-IR spectrophotometer with KBr as the reference sample. The Brunauer-Emmet-Teller (BET) method was utilized to calculate the specific surface areas (S_BET) using nitrogen adsorption-desorption isotherms of the samples on a Quantachrome Autosorb-1 equipment. The thermal processes of the precursor was heated from 100 °C to 1000 °C with a ramp rate of 5 °C min⁻¹ in an inert (Ar) atmosphere with simultaneous TG/DSC and online evolved gas analysis (TG/DSC-MS, Netzsch STA 449F3 equipment).

6.2.5 Electrochemical Measurement

The pre-treatment was as follows: prior to use, the electrodes were polished mechanically with aluminate powder under an abrasive paper to obtain a mirror-like surface, washed with ethanol and deionized water by sonication for 5 min and allowed to dry in a desiccator. 2 mg of each grinded sample was dispersed in 1000 µL of solvent mixture of Nafion (5%), absolute ethanol, deionized water (V:V:V=1:1:8) by sonication, respectively. 12.0 µL suspension of each catalyst was
pipetted onto the glassy carbon electrode surface. And the electrode was allowed to dry at 60 °C for 10 min in a desiccator before measurement.

Electrochemical measurements were performed using a computer-controlled potentiostat (CHI 760D, CH Instrument, USA) with a typical three-electrode cell, incorporating a working glassy carbon (GC) rotating disk electrode (RDE, 5.0 mm in diameter) for the examination in the cyclic voltammograms and linear sweep voltammetry, an Ag/AgCl, KCl (3 M) electrode as reference electrode, and a Pt electrode as counter electrode. The cyclic voltammogram experiments were conducted in O₂-saturated 0.1 M KOH solution for oxygen reduction reaction with the scan rate of 100 mV s⁻¹ from -1.2 to +0.2 V at room temperature. Linear sweep voltammetry measurements were performed on RDE in the oxygen-saturated 0.1 M KOH solution at rotation rates varying from 600 to 2000 rpm and with the scan rate of 10 mV s⁻¹. The exact kinetic parameters including electron transfer number (n) was analyzed on the basis of Koutecky-Levich equations shown in Equations. (1)-(3).

\[
\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{3/2}} + \frac{1}{J_K} \quad (1)
\]

\[
B = 0.2nFC_0(D_0)^{2/3}v^{-1/6} \quad (2)
\]

\[
J_K = nFKC_0 \quad (3)
\]

in which \( J \) is the measured current density, \( J_K \) and \( J_L \) are the kinetic and diffusion limiting current densities, \( \omega \) is the angular velocity of the disk (\( \omega=2\pi N \), \( N \) is the linear rotation speed), \( n \) is the overall number of electrons transferred in oxygen reduction. According to Equations (1) and (2), the number of electrons transferred (\( n \)) and \( J_K \) can be obtained from the slope and intercept of the Koutecky–Levich plots, respectively. \( F \) is the Faraday constant (\( F=96485 \text{ C mol}^{-1} \)), \( C_0 \) is the bulk concentration of O₂ (\( C_0=1.2\times10^{-3} \text{ mol L}^{-1} \)), \( v \) is the kinematic viscosity of the electrolyte (\( v=0.1 \text{ m}^2 \text{ s}^{-1} \) in 0.1 M KOH), and \( k \) is the electron transfer rate constant. \( D_0 \) is the diffusion coefficient of O₂ in 0.1 M KOH (\( D_0=1.9\times10^{-5} \text{ cm s}^{-1} \)). The constant 0.2 is adopted when the rotating speed is expressed in rpm, and it should change to 0.62 when the rotating speed is expressed in rps.
6.3 Results and Discussion

6.3.1 Morphologies and Structures of Cellulose and Chitin

![Figure 6.1](image)

**Figure 6.1** (a) Optical image of cellulose dried directly in oven. (b)-(d) SEM images of the sample dried directly by oven heating process.

Figure 6.1 shows the optical and SEM images of the cellulose aerogel dried *via* a directly oven-drying process. As shown in Figure 6.1a, the sample shows highly packed shape with large fibril bundle aggregated together, which means the oven-drying method is hard to break the relatively weak van der Waals forces interacted between the microfibrils. This can be further confirmed from Figure 6.1b to d. The bundles of the cellulose fibers vary greatly, with thickness from several hundred nanometers (Figure 6.1b) even up to several micrometers (Figure 6.1c). Moreover, the connected single cellulose inside the sheet produces pores with the size in the range of several to hundreds of nanometers/micrometers. Due to the packed density in the center and edges of the material vary significantly, after sonification, the amount of water adsorbed on the highly packed and sparse packed sites also changed greatly. Under this condition, the thinner areas retain less water around their surface, which means at higher heating temperatures, water is easy to evaporate. In this case, it is like the process of freeze-drying method and single cellulose fiber will be
formed (Figure 6.1d bottom right-hand corner). Under ambient pressure drying condition, all of the celluloses are fibril bundled together and form highly packed and thick bundle-like structure (Figure 6.1b-d). Moreover, most of fibers are twined together, leaving porous sizes from several hundred nanometers to several micrometers.

![Figure 6.2](image)

**Figure 6.2** (a) Optical image of cellulose using freeze-drying method. (b)-(d) SEM images of cellulose dried using the freeze-drying method.

However, using the freeze-drying method, light-weighted and sponge-like aerogels are formed because the removable of water from hydrogels is via a directly solid to gas evaporation process. Furthermore, this method could also be used to fabricate aerogels with size and shape controllable by changing the hydrogel molds. The light-weighted aerogel is easily lifted up by electrostatic attraction force as shown in Figure 6.2a. Moreover, the freeze-drying process leads to the formation of dispersed fiber network structure with high porosity (Figure 6.2b-d). This indicates that different from oven-drying process, the freeze-drying method is favorable for the formation of uniform aerogel structure. Although there is no chemical bond occurred in the cellulose aerogel system, physical cross-linking of the carbon nanofibers (CNFs) plays an important role in the formation of the aerogel. Moreover, the
cellulose aerogels obtained are highly flexible which can be bent or compressed without cracking. Therefore, such 3D porous structures are expected to have potential utilization in environmental remediation such as adsorbent, and can also be a good candidate as catalyst for energy conversion applications. Moreover, this particular 3D structures not only convenience the accessible of the electrolyte but also possesses large surface area and active site to improve the catalytic properties of the material.

Figure 6.3 (a) and (b) SEM images of cellulose purchased from Sigma-Aldrich.

For comparison, we also purchased commercial cellulose powder from Sigma-Aldrich. However, SEM images of the commercial cellulose show fibril bundle aggregated together with a diameter around 20 µm (Figure 6.3). It is therefore better to extract cellulose fiber from biomass and make it an aerogel with distinguished 3D, light-weighted and porosity structure. Furthermore, the synthesized cellulose fiber dispersed in deionized water could also easily be assembled into 3D membrane-like structure. The 3D membrane is assembled by a vacuum filtration method. Before filtration, the extracted cellulose fibers are ultrasonicated for 0.5 h, therefore, during the filtration process, the accumulations of the fiber are not existed which is critical important for the formation of the layered structures. As seen from Figure 6.4, a well ordered 3D layer-by-layered structure is formed. It is known that the layer-by-layered structure is easy to form when electrostatic exists on the dispersed precursor’s surfaces similar like the way to obtain graphene papers, and many thin films of graphite oxide sheets have also been previously prepared using this technique. Similarly, in our case, the electrostatic repulsion that functionalized on the fiber surface during the extraction process using chemical treatment may be one of the reasons for the formation of the layered structured morphologies using vacuum filtration procedure.
On the other hand, the structure of the cellulose obtained could also be easily tuned by changing the extraction conditions. For example, in order to cut the long cellulose fibers into fine and short ones, sodium chlorite, which is used previously during the extraction process, is once again used combining with H$_2$O$_2$ to partially degrade the long formed fibers of cellulose. After treatment of the dispersed cellulose fibers at 75 °C for 1 h, the solution is cooled down and dialyzed for 24 h and finally dried using the freeze-drying technique. As shown in Figure 6.5, a well-defined, interconnected, three-dimensional porous structured network is formed. Moreover, SEM images also confirm the obtained cellulose aerogel is consisted by homogenous fine fibrillar and highly porous network structure. Although it is very difficult to quantify the pore size distribution from such images, the structure does have an opened 3D porous structure after chemical treatment, which is significantly different from the original one. Therefore, it is sure that NaClO$_2$ and H$_2$O$_2$ plays an important role in the formation of this interesting porous morphology. Moreover the obtained structure possesses ordered porous walls, suggesting the orderly aggregated cellulose fibers.

**Figure 6.4 (a) and (b) SEM images of cellulose dispersed in deionized water and the assembled 3D cellulose membrane using vacuum filtration method.**
Figure 6.5 (a) and (b) SEM images of the obtained cellulose aerogel which further partially degraded with NaClO$_2$ and H$_2$O$_2$ at 75 °C for 1 h.

Figure 6.6 (a) and (b) SEM images of the obtained chitin aerogel synthesized from shrimp shells using chemical treatment method.

Since chitin is well known for its intractability and insolubility in water or common organic solvents, consequently, production of chitin nanofibers remains very challenging. In our method, the matrix components, proteins and minerals are removed from prawn shells by aqueous KOH and HCl treatments, respectively. Then, the purified wet chitin extracted from dried prawn shell is dispersed in water and acetic acid (1 wt %) is used to adjust the pH value to facilitate fibrillation. Interestingly, after acidic condition treatment, the obtained chitin slurry is high viscosity, similar to the chitin nanofibers prepared by previously reported method.\textsuperscript{70} This result suggests that the successfully fibrillated chitin is homogenously dispersed in acidic water with a high surface-to-volume ratio. As seen from Figure 6.6, the obtained chitin slurry treated with acetic acid at pH=3 is successfully fibrillated. The chitin sample has a very fine nanofibers network and a uniform structure is observed. The diameters of the fibers are around 20-30 nm.
6.3.2 FT-IR Spectrums of Cellulose and Chitin

Figure 6.7 FT-IR taken for a film of cellulose fiber obtained from the evaporation of the whisker suspension using freeze-drying method.

Figure 6.7 shows the FT-IR spectrum of the cellulose extracted from Monkey Grass which is obtained from Gold Cost, Australia. As shown in Figure 6.7, there is no peak observed at 1508 cm$^{-1}$ in the spectrum, which is attributed to the C=C stretching vibration in the aromatic ring of lignin. This indicates that lignin is completely removed from the prepared aerogel by repeated NaClO$_2$ treatment. The absence of peak at 1737 cm$^{-1}$ in the spectrum which represents either acetyl and uronic ester groups or the ester linkage of carboxylic group of the ferulic and p-coumeric acids of hemicelluloses. The absence of this peak in the cellulose aerogel is attributed to the removal of most of the hemicelluloses during the KOH treatment process. Moreover, other alkali insoluble hemicelluloses and lignin remained are further removed by HCl treatment. These results are in good agreement with the cellulose reported by Chen et al. Moreover, in Figure 6.7, the peaks at 1640 and 897 cm$^{-1}$ are attributed to the H-O-H stretching vibration of absorbed water in carbohydrate and the C$_1$-H deformation vibrations of cellulose, respectively. These results indicate that almost of hemicelluloses and lignin are removed during the chemical treatment procedures and cellulose fibers are successfully extracted from grass.

FT-IR analysis is also a conventional method that used to assess the purity of the chitin nanoparticles and to observe the presence of any residual surface bound proteins. Figure 6.8 shows the FT-IR spectrum of the obtained chitin fiber. The
infrared spectrum is taken for a film of chitin whiskers obtained from the evaporation of the whisker suspension using freeze-drying method in order to display the absence of residual proteins on the chitin fragments. In the carbonyl region, the spectrum presents three strong peaks at 1658 and 1622 cm\(^{-1}\) corresponding to amide band I, and 1556 cm\(^{-1}\) to amide band II are also observed. These strong peaks in the carbonyl region are especially characteristic of anhydrous α-chitin.\(^{69,82}\) The absence of the peak at 1540 cm\(^{-1}\) corresponding to the proteins\(^{83}\) proves that the successive treatments are strong enough to eliminate all the proteins and to obtain pure chitin. Furthermore, the OH stretching band at 3482 cm\(^{-1}\), NH stretching band at 3270 cm\(^{-1}\) of the chitin nanofibers are observed.

![Figure 6.8 FT-IR taken for a film of chitin whiskers obtained from the evaporation of the whisker suspension using freeze-drying method.](image)

**Figure 6.8** FT-IR taken for a film of chitin whiskers obtained from the evaporation of the whisker suspension using freeze-drying method.

### 6.3.3 Calcination of Cellulose and Chitin for ORR Catalysts

As we know, nowadays, catalysts for oxygen reduction reaction (ORR) used in fuel cells are intensively studied. Normally, Pt and its alloys remain the most efficient catalysts for ORR,\(^ {84-90}\) but the use of high-cost and scarcity of Pt has hampered further development of fuel cell. More importantly, Pt electrocatalyst still suffers from multiple drawbacks, such as susceptibility to fuel crossover from the anode, deactivation by CO, and poor stability under electrochemical conditions.\(^ {91,92}\) To change this situation, recently, considerable efforts have been made to develop advanced electrocatalysts for reducing or replacing Pt-based electrodes in fuel cells and a broad range of alternative catalysts based on nonprecious metals (Fe, Co, etc.),
metal oxides (Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), Co\(_3\)O\(_4\), IrO\(_2\), etc.), heteroatoms-doped carbon nanomaterials (e.g., carbon nanotubes, graphene, porous structured carbon) etc. are demonstrated to act as effective and cost-effective ORR electrocatalysts free from poisoning and crossover effect and having better long-term operational stability than commercially available Pt and Pt-based electrodes. However, the synthesis procedures of these materials are either to tedious and complicated or use thermal treatment of pre-synthesized carbon structures (e.g., graphene or graphene oxide etc.) in presence of heteroatom dopant precursors or through a single thermolysis process to simultaneously achieve the doping and graphitic carbon structure growth. However, neither of them are easy to handle due to the large quantities of chemicals to use or the afterwards modification process. In this section, we use the already extracted cellulose and chitin as precursor, which can be obtained from nature with large quantities. However, these extracted raw materials are not useful as catalysts in ORR due to their poor conductivities, which will hinder free transfer of the electrons that used to reduce the oxygen in the electrolyte. To overcome this obstacle, the raw materials are undergone a high temperature pyrolysis at 900 °C so as to turn the non-conductive material into highly conductive one but keep the high surface area and porosity of the aerogels and finally improve their catalytic activity and durability abilities. On the other hand, it is highly challenging but desirable to develop efficient and functional catalysts from Mother Nature for ORR and oxygen evolution reaction (OER), particularly for unitized regenerative fuel cells, a promising energy storage system that works as a fuel cell and in reverse as a water electrolyzer producing H\(_2\) and O\(_2\) to feed the fuel cell. Recently, N-doped carbon materials have become a subject of particular interest to researchers due to their remarkable performance for applications in energy storage and conversion, removal of contaminants, the environmental protection industry, and catalyst. Cellulose, however, has no N in its body, which means it is not a good candidate for ORR. On the contrary, chitin contains large amount of N atoms, which means after calcination, self-supported doping could be possible. As it’s known that the enhanced catalytic activity of these N-doped carbon nanomaterials toward ORR could be attributed to the electron-accepting ability of N species, which creates net positive charges on adjacent carbon atoms to facilitate oxygen adsorption for ORR with low overpotential.
6.3.4 Morphologies of Celluloce-900 and Chitin-900

Figure 6.9 (a) and (b) Optical images of the chitin aerogel before and after high temperature carbonization. (c) and (d) SEM images of cellulose and chitin aerogel after calcination at 900 °C with a ramp of 5 °C min⁻¹ under Ar protection.

Figure 6.9a and b show the optical images of the chitin aerogel before and after calcination. As can be seen, the shape of the obtained carbon aerogel is well preserved even after high temperature treatment. The only difference is the color of the aerogel changes from white to black indicating the carbonization occurred during the thermolysis process. Moreover, as seen from Figure 6.9c and d, both the aerogels still show 3D fiber-like structures after calcination which is similar to the non-calcinated ones, and this means the carbonization process will not destroy the formed 3D aerogel skeleton under higher temperature. This is highly appreciable that we can not only utilize the high surface area and porous structure of the precursor aerogels, but can change the electron transfer ability of the material by carbonization. This carbonization is important for the material used as ORR catalyst which will be shown in the following sections.

6.3.5 TG/DSC Curves of Cellulose and Chitin

The thermolysis process of the carbonization is characterized by TG/DSC technique. As shown in Figure 6.10, the obtained TG/DSC data suggests that the decomposition of cellulose and chitin starts at around 200 °C. Then it undergoes several endothermic and exothermic reactions and completed the decomposition
process at around 780 °C. Based on this TG/DSC results, therefore, it is reasonable to choose the pyrolysis temperature of 900 °C to fully achieve the carbonization process of the biomass aerogels.

![TG/DSC curves of cellulose and chitin under Ar protection from 100 to 1000 °C](image)

**Figure 6.10** (a) and (b) TG/DSC curves of cellulose and chitin under Ar protection from 100 to 1000 °C, respectively.

### 6.3.6 FT-IR and XPS Curves of Cellulose-900 and Chitin-900

![FT-IR spectra of the aerogel after calcination of the cellulose and chitin under 900 °C](image)

**Figure 6.11** FT-IR spectra of the aerogel after calcination of the cellulose and chitin under 900 °C. The curves were tested by mixing the sample with KBr with a weight ratio of 1:100.
Figure 6.11 shows the typical FT-IR spectra of the synthesized samples. Some characteristic bonds are observed and assigned to the stretching of carbonyl aromatic C=O bonds (1624 cm⁻¹), which means the carbonization is successful under 900 °C, corresponding to the TG/DSC result. The band at around 1383 cm⁻¹ is attributed to the stretching mode of C/N heterocycles. The broad band at around 3400 cm⁻¹ in both curves can be attributed to the adsorbed H₂O molecules. It can be clearly seen that higher pyrolysis temperature of chitin creates a distinct C/N bond which cannot be observed from the one with cellulose. This indicates N is successfully doped into the carbon structures in chitin aerogel. The obviously differences of the FT-IR spectra will lead to a totally different ORR properties which will be demonstrated later.

**Figure 6.12** (a) XPS survey spectrum of Chitin-900. (b) Core-level N1s XPS of Chitin-900.

The XPS survey spectrum confirms the presence of N (Figure 6.12). The presence of an O1s peak in the Chitin-900 graphitic carbon sheets could be due to the physicochemically adsorbed oxygen, which can be an additional advantage for an ORR electrocatalyst. Core-level XPS results show that the N1s XPS spectra of the sample can be fitted into three peaks centered at 398.3, 400.2, and 401.2 eV, respectively. The peaks with lower binding energy located at about 398.3 and 400.2 eV, corresponding to pyridinic-N and pyrrolic-N, respectively, while the peak centered at 401.2 eV corresponds to graphitic-N, both of these types of N have been
shown to serve as catalytically active sites for oxygen reduction. The calculated percentages of the three types N are 39.6%, 38.8% and 21.5% being pyridinic-, pyrrolic- and graphitic-N, respectively. Furthermore, the appearance of the N peak indicates N is successfully doped into the carbon network under high temperature calcination and an N doping level of 5.9% is achieved.

Figure 6.13 XPS survey spectrum of Cellulose-900.

For comparison, the XPS spectrum of the calcinated cellulose which contains no N is also obtained. Figure 6.13 shows the XPS survey spectrum of Cellulose-900. As shown, the absence of N means the catalyst synthesized is undoped one. The presence of O1s peak in the Cellulose-900 carbon could be due to the physicochemically adsorbed oxygen. The apparent differences between calcination of cellulose and chitin may lead to the significant ORR properties which will be shown in the following sections.

6.3.7 Porous Structures of Cellulose-900 and Chitin-900

As we know, large surface area and porous structure are critically important for a high performance electrocatalyst. The utmost utilization of the high surface area and porous structure of the material is useful for a catalyst due to the easily access of the electrolyte that the reactant could readily reach it. Figure 6.14a and b show the N2 adsorption-desorption isotherm for Cellulose-900 and Chitin-900 samples, respectively. A high BET surface area of 639 and 526 m² g⁻¹ are obtained for Cellulose-900 and Chitin-900, respectively. The larger surface area of the Cellulose-900 is mainly due to the more micropores created in higher pyrolysis temperature. The curve shows a steeply increased adsorption at low relative pressure, indicating the presence of substantial micropore structures (<2 nm) in both samples. Moreover,
the formation of hysteresis loops at relative pressure higher than 0.4 in the Chitin-900 sample indicates the existence of mesopores. These results indicate that the formed catalyst possesses a bimodal-pore structure (pore size distribution centered at 1.14 and 5.32 nm corresponding to micro- and meso-pore, respectively), which is good for the accessible of the electrolyte during oxygen reduction process.

**Figure 6.14** (a) and (b) BET curves of Cellulose-900 and Chitin-900, respectively. (c) Pore size distribution of Chitin-900.
6.3.8 Electrochemical Performance

![Cyclic voltammograms](image)

**Figure 6.15** (a) Cyclic voltammograms of Chitin-900 electrode in N₂ or O₂ saturated KOH solution and (b) Cyclic voltammograms of Cellulose-900 and Chitin-900 samples obtained in O₂ with a scan rate of 100 mV s⁻¹ in the potential range from -1.2 to +0.2 V at room temperature.

The samples with and without N-doped aerogel catalysts are evaluated as electrocatalytic for ORR. The CV of Chitin-900 electrode in a N₂ saturated KOH solution shows a typical pseudo-capacitive behavior of heteroatom-doped graphitic carbon which can be found in Figure 6.15a. On the other hand, a well-defined cathodic current peak at around -0.20 V resulting from O₂ reduction (OR) is observed from the O₂ saturated solution, indicating a pronounced ORR electrocatalytic activity. It is known that a less cathodic onset-potential indicates a lower ORR overpotential. Compare the CVs curves of the two samples, a higher cathodic current responses and positive shifting of cathodic peak potentials can be
observed for the sample of Chitin-900, indicating an improved catalytic performance with N doping.

**Figure 6.16** Linear sweep voltammograms of (a) Cellulose-900 and (b) Chitin-900 respectively. (c) Linear sweep voltammograms of Cellulose-900, Chitin-900 and Pt/C RDE electrodes at 1600 rpm and 10 mV s\(^{-1}\). All the tests were conducted from 0.2 V to -1.2 V with a scan rate of 10 mV s\(^{-1}\) in an O\(_2\) saturated 0.1 M KOH aqueous electrolyte.

To demonstrate the oxygen reduction process of the catalysts, linear sweep voltammograms of the two catalysts coated rotating disk electrodes are further carried out. As shown in Figure 6.16, the OR currents increased with increasing
rotation rates for all cases investigated. However, the Cellulose-900 shows a two-step reduction process which is significantly different with the catalyst using Chitin-900.

![Figure 6.17 Koutecky-Levich plots of (a) Cellulose-900, (b) Chitin-900 respectively and (c) Comparison of the Koutecky-Levich plots at -0.6 V.](image)

It is known that a less cathodic onset-potential indicates a lower ORR overpotential. In this regard, Chitin-900 electrode possesses an onset-potential much positive than that of Cellulose-900 and even positive than that of Pt/C electrode. Noticeably, the OR current obtained from Chitin-900 electrode is also much highest than that of Cellulose-900. The excellent performance of the Chitin-900 electrode could be...
attributed to N doping, superior electron and mass transport properties of the porous structured graphitic carbon network. The corresponding Koutecky-Levich plots of Chitin-900 electrode exhibit high linearity between -0.40 to -1.0 V (Seen from Figure 6.17). The number of transferred electrons determined from the Koutecky-Levich plots increases with a more cathodic potential. The Chitin-900 electrode exhibits better performance than that of Cellulose-900 electrode, having 3.52 to 3.96 transferred electrons within the potential range of -0.4 to -1.0 V (Figure 6.18), signifying a four-electron OR process, and the slopes remained approximately constant over the potential range from -0.4 to -1.0 V, which suggests that the electron transfer numbers are similar for oxygen reduction at different electrode potentials. However, the catalyst synthesized without N-doping shows a typical two-electron OR process. Moreover, the poor slope correlations behaviour means the electron transfer numbers are different for oxygen reduction in the tested potential range.

Figure 6.18 Transferred electron numbers of Cellulose-900 and Chitin-900.

To further give more prove on the good performance of the N-doped Chitin-900 sample, Tafel polarization curve is measured. As we know, Tafel plot is a semi-empirical parameter that can be used to characterize the catalysts’ properties and
their activities. Figure 6.19 shows the Tafel plots for ORR on the two electrodes. As seen in Figure 6.19, the Tafel plots clearly show the activity differences for the two electrodes. At the whole scanning voltage range, the kinetic current density of ORR on the Chitin-900 N-doped aerogel is significantly higher than that of undoped Cellulose-900 catalyst.

![Tafel plots of Cellulose-900 and Chitin-900.](image)

**Figure 6.19** Tafel plots of Cellulose-900 and Chitin-900.

![Chronoamperometric responses for ORR at Chitin-900 and Pt/C catalysts on addition of 3 M methanol after about 100 s.](image)

**Figure 6.20** Chronoamperometric responses for ORR at Chitin-900 and Pt/C catalysts on addition of 3 M methanol after about 100 s.

It is well known that comparing to Pt/C, heteroatom-doped graphitic carbon electrocatalysts possess high resistance to crossover effects by fuel molecules. Figure 6.20 show that Chitin-900 electrode can tolerate the presence of 3.0 M methanol without noticeable crossover effects. All of these electrochemical performances results indicate the Chitin-900 catalyst is a good candidate for ORR. The superior durability of Chitin-900 electrode can be ascribed to the superior structural stability and N-doping into the 3D aerogel-like carbon network. On the other hand, the
durability of the electrode is also critically important for practical use. As revealed in Figure 6.21, Chitin-900 and Pt/C electrodes are capable of retaining 98% and 76% of its initial activity after 2500 s of usage, respectively, which means a high stable property of the synthesized catalysts.

![Figure 6.21 Durability evaluation of Pt/C and Chitin-900 electrode at -0.4 V and a rotation rate of 1000 rpm.](image)

**Figure 6.21** Durability evaluation of Pt/C and Chitin-900 electrode at -0.4 V and a rotation rate of 1000 rpm.

### 6.4 Conclusion

In summary, cellulose and chitin 3D aerogel fibers have been successfully extracted from grass and prawn shell, respectively. However, the disadvantage of the materials used as catalysts for ORR is their poor electronic transfer abilities. To overcome this disadvantage, pyrolysis of the already shaped aerogel is further treated at 900 °C under Ar protection. After calcination, the stubborn 3D aerogel shape is kept and high surface area aerogel is obtained. Since cellulose contained no N in its matrix which is quite different from the chitin. After calcination, self-supported N-doped and undoped carbon catalysts are fabricated. The electrochemical performances of the two catalysts show obvious differences when used as ORR catalyst. The Chitin-900 with N-doping shows a significant four-electron oxygen reduction process and positive shifted oxygen reduction potential. The findings of this catalyst from biomass would be valuable for design and fabrication of high performance carbon-based electrocatalysts.

### 6.5 References

CHAPTER 7 GENERAL CONCLUSIONS AND FUTURE WORK
7.1 General Conclusions

This study carries out the investigations on development of heteroatoms-doped and co-doped graphitic carbon materials for energy and environmental applications with particular focuses on three important issues: (i) developing an effective means to tune bandgap structure for enhancement of light utilization efficiency and photocatalytic activity; (ii) demonstrating the feasibility of utilizing plentiful renewable biomass materials to replace petroleum-based synthetic chemicals for synthesis of high performance graphitic carbon materials; (iii) developing facile synthetic method to realize controllable doping and co-doping heteroatoms into graphitic carbon structures to produce high performance electrocatalysts.

In Chapter 2, we have successfully demonstrated a facile and effective thermal treatment method tuning the bandgap structure to enhance the light utilization efficiency and photocatalytic activity. The results confirm that the CN/rGO-X nanocomposites can be formed by cross-linked C-O-C bonds during a facile thermal treatment process. We have demonstrated that the bandgap can be readily tuned between 2.50 and 1.55 eV by simply control the ratios of g-C₃N₄ and rGO in the nanocomposites. The data obtained from visible light photocatalytic degradation of RhB and 4-nitrophenol confirms a significantly enhanced photocatalytic activity, resulting from the improved visible light utilization efficiency, improved conductivity and reduced charge recombination.

The feasibility of utilizing plentiful renewable biomass materials to replace petroleum-based synthetic chemicals for synthesis of high performance graphitic carbon materials have been demonstrated in Chapter 3 and Chapter 6.

In Chapter 3, Monkey Grass has been used as sole precursor and directly transformed into high quality N-doped graphitic carbon nanodots (N-CNDs) and nanodot/nanosheet aggregates (N-CNAs) via a facile hydrothermal process. The synthesized N-CNDs have been innovatively employed as sensitizer in solar cells. It is known that N-CNDs possess strong fluorescent emission properties that promote charge recombination to significantly reduce the utilization efficiency of photo-excited electrons, resulting in decreased light conversion efficiency. A fluorescent quenching principle has therefore been developed to dramatically improve the utilization efficiency of photo-excited electrons. We have successfully demonstrated that iodide (I⁻) can play a dual-functional role as a redox mediator and fluorescent quencher (electron donor) to improve the photo-excited electron utilization efficiency
and the performance of N-CND-sensitized solar cells. Detailed theoretical calculation confirms that N-doping leads to a positively charged surface that enhances the interactions between carbon nanodots and I, favorable for quenching. Our experimental results have demonstrated that the N-CND-sensitized solar cells with aqueous I/I₃ electrolyte can achieve an overall light conversion efficiency of 0.529%, the highest among all published CND-sensitized solar cells. The synthesized N-CNAs have successfully used as effective ORR electrocatalysts. The performance evaluation results confirm that compared to the commercial Pt/C electrocatalyst, N-CNAs possess higher ORR electrocatalytic activity, stability and resistance to crossover effects by fuel molecules. DFT calculation reveals that compared to pyrrolic-N and graphitic-N, the carbon atoms around pyridinic-N possess higher positive charge densities, beneficial to improve O₂ adsorption at the catalyst, hence the ORR performance. DFT calculations also confirm that O₂ adsorption on pyridinic-N is stronger than that on pyrrolic-N and graphitic-N, indicating a better ORR catalytic activity of the pyridinic-N.

In Chapter 6, the extracted cellulose and chitin from grass and prawn shell have been successfully utilized as precursors to fabricate graphitic carbon-based aerogels via a facial pyrolysis process at 900 °C. The resultant Cellulose-900 and Chitin-900 aerogels possess high surface area of 639 and 526 m² g⁻¹, respectively. However, electrochemical studies indicate that the ORR electrocatalytic behaviours of Cellulose-900 and Chitin-900 aerogels are differed significantly. The Cellulose-900 aerogel exhibits a typical two-electron ORR process, while the Chitin-900 aerogel shows a four-electron ORR process, positively shifted oxygen reduction potential with a comparable catalytic activity, better stability and high to tolerate the presence of methanol than that of commercial Pt/C electrode. Investigation confirms that the resultant Cellulose-900 aerogel with poor ORR electrocatalytic performance is because it does not contain N-doped carbons due to the lack of N element in cellulose. The presence of N-doped carbons is the origin of ORR catalytic activity for Chitin-900 aerogel due to the rich N element in chitin.

In Chapter 4, a self-sponsored co-doping approach has been successfully developed to facile control the doping of S and N into graphitic carbon network structures. The required S, N and C sources can be supplied by a sole precursor, 1-allyl-2-thiourea, without the need for any catalyst. The results confirm that the doping level and the type of heteroatom-carbon bonds, surface area, porous
structures, could be readily controlled by simply control the pyrolysis temperature. The BET results reveal that the synthesized catalysts possess a trimodal-pore structure covering pore sizes ranging from micro- to meso- and macro-pore. The micro- and macro-pore structures are dominant in determining the surface area and pore volume, respectively. The doping level and the type of bonds formed between dopant and graphitic carbon atoms are important factors affecting the electrocatalytic activity. The combined electrochemical and DFT studies demonstrate that the heteroatoms co-doping level is important in determining the ORR electrocatalytic activities of the resultant materials. An electrocatalyst with high ORR catalytic activity can only be achieved with an appropriate doping level where the highest overall doping effect is achieved. Low doping levels may introduce large doping effect to individual doping sites but having a limited overall doping effect because of fewer active sites. High doping levels can introduce large numbers of ‘active’ sites but the doping effect to individual doping sites is dramatically reduced. In this work, the SN/C-900 electrode with N/C and S/C atomic ratios of 7.2% and 1.6%, respectively, possesses the best ORR electrocatalytic activity. Comparing to Pt/C electrode, the SN/C-900 electrode shows superior ORR electrocatalytic activity, significantly enhanced stability and high tolerance to crossover effects by methanol. Such superior ORR performance of SN/C-900 electrode can be ascribed to the enhanced electrocatalytic activity by the maximized doping effects, the ability to fully utilize large surface area created by the micro-pore structures, the improved mass transport by the presence of meso- and macro-pore structures, and the improved stability because of superior structural stability of the graphitic carbon network.

Dye-sensitized solar cells (DSSCs) have been widely recognized as a promising alternative to Si-based solar cells. Owning to its superior electrocatalytic activity for I$_3^-$ reduction, Pt-based electrocatalysts have been the most widely used counter electrode (CE) materials for DSSCs. However, large-scale application of Pt-based electrocatalysts has been hindered by its high-cost and scarcity. In this regard, development of high performance and low-cost non-Pt electrocatalysts is of important for large-scale applications of DSSCs. In Chapter 5, two Pt-free electrocatalysts are investigated as CE for DSSCs. The S and N co-doped graphitic carbon networks (SN/C-900) is firstly investigated. The electrochemical characterization results confirm that the overpotential for reduction of I$_3^-$ to I at the SN/C-900 CE is much smaller than that of commercial Pt CE, favourable for the
regeneration of the sensitizer. On the other hand, the peak-to-peak voltage separation ($E_{pp}$) of SN/C-900 CE is 506 mV, much smaller than that of Pt (701 mV), indicating significantly improved reversibility. All obtained data indicate a faster kinetic process at SN/C-900 CE for triiodide reduction reaction, suggesting that the SN/C-900 should be an efficient CE for DSSCs. The DSSCs assembled with SN/C-900 CE can achieve light conversion efficiency as high as 7.86%, higher than that of cells assembled with Pt CE (7.36%) under the same condition. In this Chapter, single crystal NiS nanosheet films with largely exposed (0001) surface is directly fabricated on FTO substrate by a facile hydrothermal method and successfully used as CE for DSSCs. The resultant electrocatalyst (NiS-180-24h) is evaluated as CE for DSSCs. The electrochemical characterization resultants indicate a higher cathodic peak current, more positive cathodic peak potential and smaller $E_{pp}$ values compared to commercial Pt CE. The DSSCs assembled with NiS-180-24h CE exhibits a short-circuit current density of 18.71 mA cm$^{-2}$, an open-circuit voltage of 735 mV, and a fill factor of 62.7%, leading to an overall LCE of 8.62%, which is much higher than that of DSSCs assembled with commercial Pt CE (7.36%). Theoretical calculations reveal that the exposed (0001) surface possesses high catalytic activity due to the existence of S vacancies.

### 7.2 Future Work

Although this study has achieved its intended purpose, there are a number of issues related to this study require further investigation. The details are given as follows:

- g-C$_3$N$_4$ has a low surface area and poor conductivity which hinder its application for environmental remediation. Therefore, further research is needed to synthesize g-C$_3$N$_4$ with high surface area, large-scale production and good conductivity.

- Synthesize carbon nanodots with higher fluorescent quantum yield to enhance the photo-excited electron utilization efficiency for photovoltaic application and explore other electron donors to improve the quench fluorescent emission abilities should be investigated.

- Synthesize carbon nanodots with tunable bandgaps by controlling the size, shape, and surface functional groups deserves a further investigation to improve the visible light absorption range and increase the efficiency of the solar.
➢ Fabricate heteroatom-doped graphitic carbon materials with different pore size, surface area using silica as template in a large scale and used as electrocatalyst in oxygen reduction reaction and oxygen evolution reaction will be carried out.

➢ The use of different biomasses as precursors to fabricate high quality graphitic carbon materials for energy conversion and storage applications should be further investigated.

In summary, this study has successfully demonstrated a number of fabrication methods to obtain high quality carbon-based nanomaterials for energy and environmental applications. The findings of this work contribute to the knowledge of development and applications of graphitic carbon materials. Some methodologies developed in this study could be used as a general way to synthesize other carbon-based materials.