UV and Visible Light Active Nanostructure Photocatalysts for Disinfection and Decomposition of Biohazards

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ABSTRACT

Rapid disinfection and effective removal of biohazards from water is important and necessary for safeguarding water, due to availing public health and environmental concerns. To achieve this aim, many techniques such as ultraviolet, chlorination, ultrasonic and ozone have been widely investigated and employed, though there are many drawbacks in these methods which are becoming more problematic in the developing world. In recent decades, two advanced oxidation techniques, photocatalysis (PC) and photoelectrocatalysis (PEC), have drawn extensive attentions, as they have displayed great potentials to be more sustainable, affordable, safer and robust for water purification technologies. There are still many issues however need to be solved, such as the identification of reaction intermediates, development of rate expressions and the photocatalytic efficiencies of the photocatalysts are still far from satisfaction. Therefore, it is necessary to develop high efficiency photocatalysts and study the fundamental mechanisms in the PC and PEC processes.

In this thesis, three types of UV and/or visible light active nanostructured TiO\(_2\) films with different structures and crystal phases have been developed, the fundamental aspects such as the electron transport properties in the photocatalyst films have been studied in detail, and the disinfection and decomposition performances of the obtained photocatalysts against *Escherichia coli* (*E. coli*) bacteria have been investigated. To achieve these objectives, systematic studies have been performed including the establishment of experimental methodology, characterisations of nanomaterials, performance evaluation and mechanistic aspects.

Firstly, vertically aligned nanorod-like rutile TiO\(_2\) single crystal nanowire bundles on FTO conducting substrates have been synthesised by hydrothermal method to study the photoelectrocatalytic properties. The inherent resistance (\(R_0\)) has been determined to quantitatively study the photoelectron transport properties of the photoanodes via a simple photovoltaic chemical method, the lower value of which explained the superior photoelectron transfer property of the nanorod-like rutile TiO\(_2\) film.

A pure rutile TiO\(_2\) photoanode with 100% exposed pyramid-shaped (111) surfaces has then been directly synthesised on FTO conducting substrate using a facile hydrothermal method, exhibiting excellent UV and visible light photoelectrocatalytic activity toward oxidation of water and organics. The photoelectron transfer properties
of the {111}-faceted pure rutile TiO\textsubscript{2} photoanodes under both UV and visible light have been further studied using the inherent resistances (R\textsubscript{0}) by a simple photoelectrochemical method. The similar R\textsubscript{0} values under UV and visible light irradiation imply a similar photoelectron transport resistance inside the rutile TiO\textsubscript{2} film under UV and visible light irradiation, confirming that the measured R\textsubscript{0} is an inherent property of the photocatalyst film. The excellent visible light activity of the pure rutile TiO\textsubscript{2} film photoanode can be attributed to the Ti\textsuperscript{3+} doping in the bulk and high reactivity of the {111} crystal facets. Visible light photocatalytic and photoelectrocatalytic bactericidal performance of the {111} faceted TiO\textsubscript{2} photoanode has been investigated for the first time, and the photocatalytic inactivation performance under sunlight was evaluated as well. Results confirm the superiority of the photoelectrocatalysis over the photocatalysis for bactericidal application and high stability in PC and PEC processes.

A highly ordered anatase TiO\textsubscript{2} nanotube (TNT) array film has also been synthesised by anodisation and the disinfection capability has been studied as well against \textit{E. coli} bacteria. For the first time, the TiO\textsubscript{2} nanotube array photoanode was combined with a home-designed photoelectrochemical flow reactor for bactericidal application, showing excellent disinfection efficiency compared with an anatase TiO\textsubscript{2} nanoparticle film electrode with a similar film thickness. The study demonstrates the possibility of using high efficiency TNT film photoelectrode combing with thin-layer photoelectrochemical flow reactor for effective removal of waterborne pathogens.
STATEMENT OF ORIGINALITY

The material in this thesis has not previously been submitted for a degree in any University, and to the best of my knowledge contains no material previously published or written by another person except where due acknowledgement is made in the thesis itself.

Xiaolu Liu
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Last but not least, I am deeply grateful and sorry to my parents. For eleven years I have not been around, studying alone thousands of miles away. I could not accompany with them when they were sick, or in other difficulties; I have even not seen them for two and a half years. But they are still there, standing behind me, supporting me all the time. I here dedicate the thesis to them.
PUBLICATIONS

This thesis includes 6 published papers as Chapters 2, 3, 4, 5, 6, and a part of Chapter 1, which are co-authored with other researchers. My contribution to each co-authored paper is outlined at the front of the relevant chapter.


ADDITIONAL RELEVANT PUBLICATIONS

In addition to the published works that formed the chapters of this thesis, I have several other co-authored publications that are relevant to my research topic, but they do not form chapters of the thesis. Details are as follows:

**Journal publications:**


7. X. Nie, G. Li, M. Gao, H. Sun, X. Liu, H. Zhao, P.K. Wong and T. An, Comparative Study on the Photoelectrocatalytic Inactivation of *Escherichia coli*


**Conference Posters:**


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CHAPTER 1 GENERAL INTRODUCTION
1.1 Introduction

The entire world is facing serious water problems. Many major rivers are running dry because of overdevelopment; water tables on every continent are falling due to the over-pumping of groundwater; freshwater aquifers are suffering saltwater intrusion along coastal regions; while the population of the world is increasing, demanding more fresh water to meet basic human needs.\textsuperscript{1,2} It has been a trend to utilize alternative water sources such as recycled wastewater and desalinated water to ensure drinking water supply. However, the introduction of alternative water sources inevitably gives a rise to potential water quality risks from possible contaminants, especially waterborne pathogens, in treated alternative water sources. Therefore, the effective removal of pathogenic biohazards is critically important for safeguarding the usage of alternative water sources and has been the biggest obstacle for public acceptance.\textsuperscript{3-6}

It is well known that biohazards (waterborne pathogens) have been major concerns for managers of water resources, as they can directly or indirectly cause diseases or major disorder and even death in humans or animals when they are ingested or got in touch with.\textsuperscript{7,8} For the sake of safeguarding the use of water, effective removal of biohazards from water supply system is one of the most important aspects and has been the biggest obstacle for water and public safety.\textsuperscript{9} To achieve an effective and rapid disinfection and decomposition of microorganisms in water system, many techniques have been developed such as ultraviolet, chlorination, ultrasonic, ozone and so on. However, there are still many drawbacks in these technologies which are becoming more problematic in the developing world. Researchers are seeking for some methods that are more sustainable, affordable, safer and robust to increase supplies and purify water to serve public throughout the world.

In recent decades, two advanced oxidation techniques, photocatalysis (PC) and photoelectrocatalysis (PEC), have drawn extensive attention. Although there are still many problems that need to be solved, such as the identification of reaction intermediates, development of rate expressions and the photocatalytic efficiencies of the photocatalysts are still far from satisfaction, they have been considered to be promising in water treatment for environmental remediation.

In this chapter, the literature on biohazards removal using PC and PEC techniques including the developed photocatalysts is reviewed.
1.2 Removal of Biohazards

Biohazards, as the name implies, refer to the infectious agents or hazardous biological materials that pose a threat to health of humans, animals or the environment. Disease-causing bacteria, viruses and protozoa, known as waterborne pathogens, are transmitted to people when they consume untreated or inadequately treated water which can lead to severe health problems and even death to human.

Figure 1.1 displays typical cell structures of a prokaryotic cell (bacterium), a eukaryotic cell (basic cell structure of fungi, protozoa, helminths and algae) and a virus. The structures of the microorganisms are more complicated than the inorganic or organic chemical waste, making it more challenging of the removal of biohazards. The main sources and the risks of those biohazards will be briefly introduced below.

Figure 1.1 Cell structures of (a) a prokaryotic cell, (b) a eukaryotic cell and (c) a virus.

1.2.1 Sources and Risks of Waterborne Pathogens

Disease caused by exposure to water contaminated with waterborne pathogens is a global burden of great magnitude. Millions of people die from diseases transmitted through unsafe water every year, and countless more are sickened from disease and contamination. The consumption of waterborne pathogens can lead to severe problems of the digestive system, which can be life-threatening to the very young, very old, or those with damaged immune systems. Increasingly, public health and environmental concerns drive more efforts to decontaminate waters previously considered clean, which could be contaminated by biohazards. The sources of biohazards contaminants have been studied, which may mainly include human and animal faeces, hospitals, food factories, water distribution pipes and so forth.
Sources

The most common sources of biohazards in water are human and animal faeces from infected individuals, human and animal carriers. From former study, the majority of large-scale waterborne disease outbreaks in the past have been attributed to human contamination or inadequacies at water treatment plants, and waterborne outbreaks, upon contact with contaminated recreational water bodies, are attributed to human faecal contamination or sewage. Bacterial pathogens can be widely and rapidly dispersed from contaminated water, and some species can colonise piped water supplies depending on the bacterial activities in these supplies. The World Health Organisation (WHO) Guidelines for drinking-water quality recognizes the gram-negative bacteria *E. coli* as the indicator of choice to assess the presence of faecal pathogens. It is noticeable that sewage effluent could be an important source of contamination of the water system, as the transmissive stages of intestinal parasites voided in the faeces of infected individuals, whether human or animal, could be a potentially pathogenic component of sewage. It could be of public health significance, particularly if sewage is discharged into water that is subsequently used for drinking, recreation, or agricultural purposes, even though they may be disinfected.

Wastewater from hospital and contaminated sites containing bacteria and viruses are also important sources of waterborne pathogens. An early study reported that the detection rate at which pathogenic species were found in hospital wastewater was relatively high, i.e. 14.6% for *Shigella* spp. and 33.3% for *Salmonella* spp., based on a study of 48 hospitals. Nosocomial infections caused by antibiotic bacterial strains like methicillin-resistant *Staphylococcus aureus*, mass food poisoning caused by contaminating pathogenic bacteria like enteropathogenic *E. coli O157*, and infections caused by the microscopic *parasites Giardia* and *Cryptosporidium* are examples of biohazards from hospital wastewater causing diseases.

Wastewater from food factories may contain bacteria and viruses, as the fruits or vegetables are presumably contaminated with post-harvest plant pathogens or microbe by improperly composted fertilizer, irrigation with infected water or through infected. Microorganisms will be transmitted into the wastewater when the foods were washed in the factory, reproduce excessively with the nutrients from the treatments of food, and then enter into water system along with the wastewater.

Water distribution pipe could also be a potential source of waterborne pathogenic species. Some of the microorganisms can easily adhere on the surfaces
of water distribution pipes, forming biofilms, particularly at the ends of distribution systems where flows can be low. Indeed, ageing and deterioration of drinking water distribution systems and the associated growing of biofilms within them has emerged as a key infrastructure rehabilitation challenge that significant resources are needed to maintain and upgrade distribution systems.

**Risks**

In developing countries, 1.2 billion people lack access to safe drinking water, while 2.6 billion have little or no sanitation. The situation has rather gotten worse rather than better and contaminated water is still the leading cause of disease and death in developing countries. Also in developed countries, the future of microbiological water safety is a highly relevant topic. 183 waterborne disease outbreaks were reported caused by chemical contaminants (16%), viruses (8%), bacteria (17%), protozoa (21%), and unidentified agents of acute gastrointestinal illness (38%) in U.S. from 1991 to 2002, where drinking water is among the safest in the world. During 2009-2010, 33 drinking water-associated outbreaks were reported, comprising 1,040 cases of illness, 85 hospitalisations and nine deaths. Areas with deteriorating water system infrastructure and inadequate disinfection are likely to face an increasing incidence of water-caused diseases. Table 1.1 displays some typical waterborne pathogens of concern to human health and their associated diseases.

**Table 1.1 Waterborne pathogens of concern to human health and their associated diseases**

<table>
<thead>
<tr>
<th>Bacteria</th>
<th>Main Sources</th>
<th>Disease</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Campylobacter</em></td>
<td>Domestic, wild animal faeces</td>
<td>Campylobacteriosis</td>
<td>Acute diarrhoea</td>
</tr>
<tr>
<td><em>Escherichia coli</em></td>
<td>Cattle faeces</td>
<td>Gastroenteritis</td>
<td>Vomiting, diarrhoea</td>
</tr>
<tr>
<td>(enterotoxigenic)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Legionella pneumophila</em></td>
<td>Aquatic environments</td>
<td>Legionellosis</td>
<td>Acute respiratory illness</td>
</tr>
<tr>
<td><em>Leptospira interrogans</em></td>
<td>Urine of dogs, livestock, rodents, wild animals</td>
<td>Leptospirosis</td>
<td>Jaundice, fever</td>
</tr>
<tr>
<td><em>Salmonella typhi</em></td>
<td>Domestic and wild animal faeces</td>
<td>Typhoid fever</td>
<td>High fever, diarrhoea, ulceration of small intestine</td>
</tr>
<tr>
<td><em>Salmonella (~1,700 serotypes)</em></td>
<td>Domestic and wild animal, human faeces</td>
<td>Salmonellosis</td>
<td>Diarrhoea</td>
</tr>
<tr>
<td><em>Shigella (4 spp.)</em></td>
<td>Infected humans</td>
<td>Shigellosis</td>
<td>Bacillary dysentery</td>
</tr>
<tr>
<td><strong>Vibrio cholerae</strong></td>
<td>Sediments, shellfish, asymptomatic human carriers</td>
<td>Cholera</td>
<td>Extremely heavy diarrhoea</td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------------------------------------------</td>
<td>---------</td>
<td>-------------------------</td>
</tr>
<tr>
<td><strong>Yersinia</strong></td>
<td>Animal faeces, pork, unpasteurized milk</td>
<td>Yersinosis</td>
<td>Diarrhoea</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Viruses</strong></th>
<th><strong>Main Sources</strong></th>
<th><strong>Disease</strong></th>
<th><strong>Effects</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Adenovirus</em> (48 serotypes; types 40 and 41 are of primary concern)</td>
<td>Infected humans</td>
<td>Respiratory disease, gastroenteritis</td>
<td>Acute respiratory disease, pneumonia, conjunctivitis, gastroenteritis</td>
</tr>
<tr>
<td><em>Astrovirus</em></td>
<td>Infected humans</td>
<td>Gastroenteritis</td>
<td>Vomiting, diarrhoea</td>
</tr>
<tr>
<td><em>Caliciviruse</em></td>
<td>Infected humans</td>
<td>Gastroenteritis</td>
<td>Vomiting, diarrhoea</td>
</tr>
<tr>
<td><em>Enterovirus</em></td>
<td>Infected humans</td>
<td>Gastroenteritis, heart anomalies, meningitis</td>
<td>Respiratory illness, common cold</td>
</tr>
<tr>
<td><em>Reovirus</em></td>
<td>Infected humans</td>
<td>Gastroenteritis</td>
<td>Vomiting, diarrhoea</td>
</tr>
<tr>
<td><em>Rotavirus</em></td>
<td>Infected humans</td>
<td>Gastroenteritis</td>
<td>Vomiting, diarrhoea</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Protozoa</strong></th>
<th><strong>Main Sources</strong></th>
<th><strong>Disease</strong></th>
<th><strong>Effects</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Cryptosporidium parvum</em></td>
<td>Human, animal and bird faeces</td>
<td>Cryptosporidiosis</td>
<td>Diarrhoea, death in susceptible populations</td>
</tr>
<tr>
<td><em>Cyclospora</em></td>
<td>Human faeces</td>
<td>Cyclosporiasis</td>
<td>Diarrhoea</td>
</tr>
<tr>
<td><em>Entamoeba histolytica</em></td>
<td>Human faeces</td>
<td>Amebiasis (amoebic dysentery)</td>
<td>Prolonged diarrhoea with bleeding abscesses of the liver and small intestine</td>
</tr>
<tr>
<td><em>Giardia lamblia</em></td>
<td>Human, animal and bird faeces</td>
<td>Giardiasis</td>
<td>Mild to severe diarrhoea, nausea, indigestion</td>
</tr>
<tr>
<td><em>Naegleria fowleri</em></td>
<td>Bird and aquatic mammal faeces</td>
<td>Primary Amoebae meningoencephalitis</td>
<td>Inflammation of brain and meninges</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Helminths</strong></th>
<th><strong>Main Sources</strong></th>
<th><strong>Disease</strong></th>
<th><strong>Effects</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Ascaris lumbricoides</em></td>
<td>Human, animal and bird faeces</td>
<td>Ascariasis</td>
<td>Bloody sputum, fever, abdominal discomfort</td>
</tr>
<tr>
<td><em>Tricharis trichiura</em> (whipworm)</td>
<td>Human, animal and bird faeces</td>
<td>Trichuriasis</td>
<td>Immunological disorders</td>
</tr>
<tr>
<td><em>Taenia solium</em></td>
<td>Pork</td>
<td>Taeniasis</td>
<td>Intestinal irritation, anaemia, indigestion</td>
</tr>
</tbody>
</table>

Exposure pathways of waterborne pathogens in drinking water include ingestion, dermal contact and inhalation. Diarrhea is the major symptom to people infected by polluted water, which is one of the five most common disease causes of death. According to the World Health Organisation (WHO 2007), diarrheal disease is responsible for the deaths of 1.8 million people annually, accounting for approximately 4.1% of the total disability adjusted of life years (DALYs) global
burden of disease. Diarrhea is responsible for 21% of deaths of children younger than five years of age, which is mostly concentrated in children in developing countries. Of the pathogens identified, *Giardia* and *Cryptosporidium* were identified to cause the largest number of drinking water-associated illness cases and outbreaks reported to the Centres for Disease Control (CDC).  

Exposure pathways of pathogens in recreational waters are dermal contact, ingestion, and inhalation resulting in skin, ear, eye, gastrointestinal and respiratory illnesses. Report showed that during 1971 - 2000, the most frequently identified agents responsible for outbreaks associated with US recreational waters are *Cryptosporidium* (15%), *Pseudomonas* (14%), *Shigella* (13%), *Naegleria* (11%), *Giardia* (6%), and toxigenic *E. coli* (6%). Diseases in heavily used recreational waters are mainly due to agents transmitted from people to people.  

### 1.2.2 Conventional Technologies for Disinfection of Biohazards

The overarching goal for providing safe water is to disinfect water from traditional and emerging pathogens, without creating more problems due to the disinfection process itself. Conventionally, water disinfection can be always achieved by physical methods such as ultraviolet (UV), filtration and microwave, or chemical methods such as chlorination and metals, most of which can effectively meet the discharge permit requirements for treated wastewater. Using these methods, disinfection commonly takes place because of cell wall corrosion in the cells of microorganisms, or changes in cell permeability, protoplasm or enzyme activity (because of a structural change in enzymes). These disturbances in cell activity disable the microorganisms from multiplying, and will cause the microorganisms to die out. Oxidizing disinfectants also demolish organic matter in the water, leading to a lack of nutrients.

A special class of oxidation techniques, named as advanced oxidation processes (AOPs), has been given special attention in recent decades. It refers to a set of chemical treatment procedures that rely on the generation of highly reactive hydroxyl radical (•OH) as the main oxidative species to remove organic pollutants in wastewater by oxidation, which usually operates at or near ambient temperature and pressure. Different AOP techniques have been developed such as ultrasonics, ozone (*O₃*) and hydrogen peroxide (*H₂O₂*) method, thus allowing making choices the most appropriate for the specific treatment problems. The advantages and disadvantages of some existing disinfection technologies are summarized in Table 1.2. However, when
selecting a disinfection method, the advantages and disadvantages of each method should all be taken into consideration and weighed before making decision. As there are many disadvantages in the conventional technologies, for example, they are often chemically, energetically and operationally intensive, focused on large systems, and thus require considerable infusion of capital, engineering expertise and infrastructure, researchers are still seeking for some methods which are new, sustainable, affordable, safe and robust to increase supplies and purify water to serve people throughout the world.

Table 1.2 Advantages and disadvantages of existing methods for disinfection of biohazards in water and wastewater

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultraviolet (UV)</td>
<td>Reliability; Low cost.</td>
<td>High energy consumption and cost; Chlorination still required.</td>
</tr>
<tr>
<td>Filtration</td>
<td>Minimal chemical use; No toxic residual; Minimal safety concerns.</td>
<td>Limited effectiveness; Energy and cost intensive; Chlorination still required.</td>
</tr>
<tr>
<td>Ultrasonication</td>
<td>Effective against many microbes; Increase settling rate of activated sludge and mixed liquor.</td>
<td>High cost; Low effectiveness with thick films.</td>
</tr>
<tr>
<td>Microwave</td>
<td>High efficiency; Waste volume reduced; Environmentally sound.</td>
<td>Potential operation and maintenance problems.</td>
</tr>
<tr>
<td>Metals (Cu(^{2+}), Ag(^{+}))</td>
<td>Independent on temperature; Non-corrosive; No transport and storage difficulties.</td>
<td>Dependent on pH value; Low deactivation rate; No persistent disinfection.</td>
</tr>
<tr>
<td>Chlorination</td>
<td>Proven technology; Low cost.</td>
<td>Safety issues; Toxic residual; Labour intensive.</td>
</tr>
<tr>
<td>Other Halogens (Br(_2), I(_2), etc.)</td>
<td>Effective; Function at low concentration.</td>
<td>Safety issues; High cost; Handling difficulties.</td>
</tr>
<tr>
<td>Ozone (O(_3))</td>
<td>No chlorination by-products; O(_2) concentration increase.</td>
<td>High energy and cost; DBPs Production; Chlorination required; No persistent disinfection.</td>
</tr>
<tr>
<td>Hydrogen peroxide (H(_2)O(_2))</td>
<td>Non-toxic; Safe by-products (O(_2) and H(_2)O); No aeration needed.</td>
<td>H(_2)O(_2) is too oxidative and can decompose slowly.</td>
</tr>
<tr>
<td>Photocatalysis</td>
<td>Effective; Low energy; Easy to operate.</td>
<td>Low efficiency owing to rapid recombination of electrons and holes; Recycling issue of powder-formed photocatalyst.</td>
</tr>
</tbody>
</table>
**Ultraviolet (UV)**

As one of the most widely used disinfection method around the world, ultraviolet (UV) disinfection is gaining more attention because of its several advantages, such as high disinfection efficiency with most viruses, bacteria and protozoa, no unidentified toxic disinfection byproducts (DBPs) and safe operation. Generated by an electrical discharge through mercury vapour, UV radiation can penetrate cell wall of microorganisms and then damage the genetic material and to retard their ability for reproduction. Exposure to UV results in damage to the nucleic acids of the microorganisms, which is the basis of UV disinfection. Unlike chemical disinfectants, low-pressure UV produces almost no byproducts, and does not affect the biological stability of the water. However, many microorganisms have the ability to repair UV-induced damage and display high resistance to UV treatment, which is disadvantageous for UV disinfection. Due to this, chemical disinfectants are still needed for secondary disinfection.

**Filtration**

Filtration is commonly used to mechanically or physically separate solids from fluids by interposing a medium through which only the fluid can pass. Nowadays, this method is increasingly used in advanced drinking water treatment, with the development of membrane technology. In filtration, a multilayer lattice retains those particles that are unable to follow the tortuous channels of the filter. However, the oversize particles may form a cake layer on top of the filter and may also block the filter lattice, preventing the fluid phase from crossing the filter, which is a primary cause of membrane fouling. Moreover, some of the microorganisms are reported to be able to pass through the membranes which were once considered sterilized. More importantly, retention objects by membrane filtration can only change from one physical form into another form, and the secondary treatment is necessary, which increases no doubt practical operation complexity and cost.

**Microwave**

Microwave radiation is widely used for bacterial killing particularly for sterilisation of hospital waste and industrial food processing because of its effectiveness, commercial availability and low cost. With this method, a material can be heated directly, rapidly and selectively, resulting in a reduction of power consumption. In addition, Microwave is effective not only for the surface sterilisation of a material but also the interior, as the microwaves are irradiated from all angles.
The actual mechanism of bacterial killing by microwave approach is still controversial: some researchers attribute the killing effect exerted by microwaves to the heat the waves generate, while others propose a nonthermal effect due to microwave energy itself.\textsuperscript{54-56} Although microwave approach has exhibited great potential for bactericidal application, the limited dimension of microwave reactor is a critically limiting factor for its practical application.

**Chlorination**

Chlorination is the most popular class of chemical disinfection methods. It is also one of the oldest disinfection methods which could be traced back to the mid-nineteenth century when Dr. John Snow first successfully used chlorine disinfection to restrain the spread of the 1854 Broad Street cholera outbreak in London.\textsuperscript{57} Chlorination has been considered to be a cost-effective bactericidal approach, as it provides a primary disinfection to inactivate waterborne pathogens as well as a secondary disinfection with the necessary residuals in the distribution system.\textsuperscript{58} Free chlorine, chloramines, and chlorine dioxide are common disinfectants, which are also oxidizers, helping to remove iron, hydrogen sulfide, and other minerals.\textsuperscript{59} However, in some circumstances, disinfection by chlorination can be problematic, as the residual chlorine reacts with naturally occurring organic compounds found in the water, producing new compounds known as disinfection byproducts (DBPs).\textsuperscript{60} Due to the potential carcinogenicity of these compounds, drinking water regulations across the world require regular monitoring of the concentration of DBPs in the distribution systems of municipal water systems.\textsuperscript{61} Although it has some disadvantages in disinfection applications, chlorine and its derivatives will still be used as disinfectants in the final disinfection for much longer because chlorine is the only agent with residual power, ensuring the arrival of disinfected water to points of consumption.\textsuperscript{62-64} Some studies demonstrated that many viruses, such as *norwalk*, *hepatitis A*, *coliphage MS2*, *poliovirus 1* and *feline calicivirus* are found to resistant to the chlorine treatment, which is also disadvantageous factor for bactericidal application.

**Ultrasonication**

The use of ultrasonic treatment for wastewater disinfection as a standalone method or combined with other physical or chemical methods has been studied in recent years.\textsuperscript{65, 66} The disinfection capacity of sonication in water is due to the phenomenon of acoustic cavitation, which is the formation and collapse of microbubbles occurring in milliseconds and producing extreme temperature and pressure
It was reported to be effective for disinfection of bacteria, viruses as well as some fungus, though the bactericidal mechanisms have not been fully disclosed yet. Some studies demonstrated that it is the elevated temperatures, elevated pressures, high velocity water “darts” and subsequent free radical action that are responsible for microbial inactivation.

**Ozone Disinfection**

Ozone (O₃) is an effective disinfectant for the reduction of waterborne pathogens which is commonly used in water treatment. As ozone is a very strong oxidizing agent, it treats organic and inorganic contaminants in much the same way as chlorine but even more effective against bacteria and other germs. In treated water, ozone can follow two pathways: direct oxidation of compounds by molecular ozone and indirect oxidation through hydroxyl free radicals (•OH) produced during the decomposition of ozone and from reactions between ozone and some organic and inorganic species in water. It is still not clear whether the molecular ozone or the intermediate radicals formed is primarily responsible for the inactivation of microorganisms. Some researchers believe that ozone disinfection is a result of direct ozone reaction, while some others believe it is the hydroxyl radical that plays the key role for disinfection of microorganisms. Considering the potentially carcinogenic activity of disinfection byproducts with chlorination, ozone is possible to gradually substitute chlorine in water treatment. However, ozone disinfection systems are uncommon in much of the world, because they are infrastructure intensive, and could be expensive to implement, and lower concentration of DBPs was also observed during ozonation disinfection process.

**Hydrogen Peroxide Disinfection**

Hydrogen peroxide (H₂O₂) is a strong oxidant which is widely used in industrial sterilisation or disinfection processes. The disinfection properties of H₂O₂ result from direct molecular action and, more importantly, from free radicals formed by catalytic reactions. However, spore DNA is protected against peroxide by small, acid-soluble, spore proteins (SASP) which bind to DNA and protect it from being damaged. As a result, DNA does not appear to be a main target in hydrogen peroxide sterilisation, at least not in spores with a full complement of SASP. What is more, commercial hydrogen peroxide solutions typically have poor stability, and the effective concentrations for high-level disinfection are corrosive to many medical instruments such as flexible endoscopes.
The antimicrobial action of H$_2$O$_2$ can be enhanced by surfactants and organic acids. In recent years, a newly developed, high-level disinfection technology which is known as Accelerated Hydrogen Peroxide (AHP) has been taken into use.\textsuperscript{91} The evidence available suggests that products based on AHP, apart from being good germicides, are safer for humans and benign to the environment.

\textbf{1.2.3 Photocatalysis (PC) and Photoelectrocatalysis (PEC) Disinfection Techniques}

In an attempt to overcome the shortfall of conventional disinfection techniques, varieties of advanced oxidation disinfection techniques have been developed, among which photocatalysis and photoelectrocatalysis have aroused extensive concern in the fields of science and technology, and are considered to be valid as alternatives to the existing methods.\textsuperscript{92-94} The two techniques make use of a semiconductor metal oxide as catalyst under UV and/or visible light excitation to achieve oxidation of microorganisms.\textsuperscript{95} The main attraction of these techniques is that the disinfection and decomposition of biohazards such as bacteria and viruses can be concurrently achieved in a single process without the need to use toxic chemicals or producing hazardous byproducts.\textsuperscript{96-98} Nevertheless, there are still many issues that should be solved for these methods, such as identification of reaction intermediates, development of rate expressions, identification of scale-up parameters and criteria for cost effectiveness and maximum destruction efficiency, and a more efficient exploitation of sunlight radiation which could ensure more economic solutions to the problem of water disinfection and decomposition of biohazards. Therefore, development of new functional semiconductor photocatalysts is still highly desired for future PC and PEC disinfection technologies.

\textbf{Photocatalysis}

In a typical photocatalysis process, the semiconductor particle can be excited by photons possessing energies of sufficient magnitude under irradiation, producing electrons on the conduction band (CB) and photoholes on the valence band (VB), which can induce reduction half-reaction and oxidation half-reaction on the same photocatalyst particle simultaneously, as demonstrated in Figure 1.2a.\textsuperscript{92, 99, 100} However, such approach generally results in a rapid recombination of photogenerated electrons and holes, thus greatly decreasing photocatalytic efficiency.
Figure 1.2 Principle of (a) photocatalysis and (b) photoelectrocatalysis using semiconductor photocatalysts.

Since Matsunaga reported for the first time the effective inactivation of E. coli, L. acidophilus and S. cerevisae using Pt-loaded TiO$_2$ photocatalyst, photocatalytic disinfection has been widely studied for disinfection and decomposition of various microorganisms.\textsuperscript{101-103} Some examples of the application of semiconductor photocatalysts for PC disinfection and decomposition of biohazards have been summarized in Table 1.3.

Table 1.3 Semiconductor photocatalysts for PC disinfection of biohazards

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Biohazard</th>
<th>Light Source</th>
<th>Performance</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ membrane</td>
<td>E. coli</td>
<td>mercury lamp</td>
<td>100% inactivation of $10^2$ CFU/mL, 30 min</td>
<td>104</td>
</tr>
<tr>
<td>TiO$_2$ powder</td>
<td>14 strains of mutans</td>
<td>Near-UV light</td>
<td>100% inactivation of $10^3$ CFU/mL, 3 min (1 mg/mL TiO$_2$)</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>streptococci</td>
<td>(peak 352 nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$/FeSO$_4$</td>
<td>MS2</td>
<td>UV lamp (365 nm)</td>
<td>99.997% inactivation of $6\times10^4$ CFU/mL, 65 min</td>
<td>106</td>
</tr>
<tr>
<td>TiO$_2$ P25</td>
<td>E. coli</td>
<td>UVA lamp (peak 365 nm)</td>
<td>&gt; 6 log10 reduction in 60 min</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>P. aeruginosa</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S. aureus</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>E. faecium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C. albicans</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$/Fe$_2$O$_3$</td>
<td>E. coli</td>
<td>mercury lamp (253.7 nm)</td>
<td>99% removal of $10^6$ CFU/mL in 60 s</td>
<td>108</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>E. coli</td>
<td>400W sodium lamp</td>
<td>100% inactivation in 120 min except A. niger (100% inactivation in 240 min)</td>
<td>109</td>
</tr>
<tr>
<td>ZnO</td>
<td>S. aureus</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>P. aeruginosa</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A. niger</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C. albicans</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S. cerevisae</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Similar as other AOPs, the highly reactive oxygen species (ROSs), such as •OH, \( \text{O}_2^* \), \( \text{HOO}^* \), and \( \text{H}_2\text{O}_2 \) produced by the photoexcitation of the photocatalyst, are commonly recognized as the main oxidants that are responsible for the inactivation of various microorganisms, including viruses, bacteria, spores and protozoa.\(^{123-125}\) A detailed photocatalytic disinfection mechanism was proposed based on the experimental data of TiO\(_2\) photocatalytic reaction.\(^{126}\) It was illustrated that the cell wall where the photocatalyst particles get contacted with is oxidatively damaged firstly, and then oxidative damages take place on the underlying plasma membrane as

<table>
<thead>
<tr>
<th>TiO(_2) P25</th>
<th>A. polyphaga Cysts</th>
<th>Simulated solar irradiation</th>
<th>33% - 66% inactivation in 8 h (2×10(^4) CFU/mL - 3.4×10(^5) CFU/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-doped TiO(_2)</td>
<td>M. lylae</td>
<td>visible light (( \lambda &gt; 420 \text{ nm} ))</td>
<td>100% inactivation of 3×10(^6) CFU/mL in 1 h</td>
</tr>
<tr>
<td>Ag/TiO(_2)</td>
<td>E. coli</td>
<td>UV lamp (365 nm)</td>
<td>100% inactivation of 10(^8) CFU/mL in 50 min (100 mL)</td>
</tr>
<tr>
<td>Ag/AgBr/TiO(_2)</td>
<td>E. coli</td>
<td>Xe arc lamp (( \lambda &gt; 420 \text{ nm} ))</td>
<td>complete inactivation of 2×10(^7) CFU/mL in 60 min</td>
</tr>
<tr>
<td>TiO(_2)/CuO</td>
<td>bacteriophage T4</td>
<td>UVA lamp (365 nm, 2.24×10(^{-3}) W cm(^{-2}))</td>
<td>&gt;9 log kill after 80 min</td>
</tr>
<tr>
<td>PdO/TiON</td>
<td>E. coli</td>
<td>halogen desk lamp</td>
<td>survival ratio&lt;10(^{-5}) in 30 min (10(^7) CFU/mL)</td>
</tr>
<tr>
<td>ZnO</td>
<td>S. aureus</td>
<td>LED array (415 nm, 100 mW/cm(^2))</td>
<td>80%-90% reduction in 5 min with 0.05 mg/mL ZnO (bacteria OD(_{660}) = 0.3)</td>
</tr>
<tr>
<td>AgI/Al(_2)O(_3)</td>
<td>S. dysenteriae</td>
<td>Xe arc lamp (( \lambda &gt; 420 \text{ nm} ))</td>
<td>100% removal of 2×10(^9) CFU/mL in 25 min</td>
</tr>
<tr>
<td>Ag-AgI/Al(_2)O(_3)</td>
<td>S. dysenteriae</td>
<td>Xe arc lamp (( \lambda &gt; 420 \text{ nm} ) and ( \lambda &gt; 450 \text{ nm} ))</td>
<td>100% removal of 2×10(^9) CFU/mL in 10 min when ( \lambda &gt; 420 \text{ nm} ) and in 15 min when ( \lambda &gt; 450 \text{ nm} )</td>
</tr>
<tr>
<td>Ag(_2)Si/Ag</td>
<td>E. coli</td>
<td>mercury lamp (peak 365 nm)</td>
<td>100% inactivation 10(^7) of CFU/mL in 50 min</td>
</tr>
<tr>
<td>BiOI</td>
<td>E. coli</td>
<td>Xe arc lamp (( \lambda &gt; 420 \text{ nm} ))</td>
<td>3 log inactivation in 30 min with BiOI and 5.4 log inactivation in 10 min with Ag/BiOI (5×10(^7) CFU/mL)</td>
</tr>
<tr>
<td>Ag/BiOI</td>
<td>E. coli</td>
<td>Xe arc lamp (( \lambda &gt; 420 \text{ nm} ))</td>
<td>7 log inactivation in 3 h with 100 mg/L of CdIn(_2)S(_4) (2×10(^7) CFU/mL)</td>
</tr>
<tr>
<td>Cdln(_2)S(_4)</td>
<td>E. coli</td>
<td>Xe lamp (( \lambda &gt; 400 \text{ nm} ), 193 mW/cm(^2))</td>
<td>70 log inactivation in 3 h with 100 mg/L of Cdln(_2)S(_4) (2×10(^7) CFU/mL)</td>
</tr>
<tr>
<td>graphitic-C(_3)N(_4)</td>
<td>E. coli</td>
<td>Xe lamp (( \lambda &gt; 400 \text{ nm} ))</td>
<td>100% removal of 2×10(^7) CFU/mL in 4 h</td>
</tr>
<tr>
<td>Bi(_2)WO(_6)</td>
<td>E. coli</td>
<td>Xe lamp (( \lambda &gt; 420 \text{ nm} ))</td>
<td>&gt;95% removal of 2×10(^7) CFU/mL after 2 h (20 mL with 0.5 mg/mL of Bi(_2)WO(_6))</td>
</tr>
</tbody>
</table>
the protection of the cell wall is eliminated. With these damages produced by the photocatalytic reaction, the intracellular contents flow out freely and the produced ROSs enter cells and directly attack on the intracellular components, which eventually lead to cell death.\textsuperscript{126} The appeal of this technology is that photocatalysis does not require additional consumable chemicals and does not produce hazardous waste products. UV light is commonly used to provide the energy for the photoexcitation of photocatalyst, however, with the development of semiconductor materials, visible light and sunlight have also shown great potential to be used for driving the disinfection process.\textsuperscript{127, 128} Although PC technique using photocatalyst suspension system has shown to be promising for bactericidal application, some drawbacks of PC technique have become the biggest limitation for its practical application, such as long bactericidal time (e.g., 1-6 h) owing to insufficient concentration of ROSs and low bactericidal efficiency owing to rapid recombination of photogenerated electrons and holes.

**Photoelectrocatalysis**

For conventional suspension photocatalysis system, it is well known that redox reactions including photooxidation and photoreduction happen on the same photocatalyst particle, which inevitably results in a fast recombination of photogenerated electrons and holes to release heat or light, thus vastly decreasing the photocatalytic disinfection efficiency.\textsuperscript{129} This shortcoming can be overcome by simply applying a small positive potential bias to the semiconductor photocatalyst electrode (immobilizing photocatalyst onto conductive substrate to fabricate photoelectrode), which is known as photoelectrocatalysis (PEC).\textsuperscript{130} For PEC technique, the role of additional potential bias is only to force the photoelectrons to external circuit, and then to auxiliary electrode, where photoreduction reaction will occur. Therefore, the oxidation half-reaction and the reduction half-reaction which take place on the same catalyst particle in conventional PC process can be physically separated by PEC technique, importantly suppressing the recombination of photogenerated electrons and holes and allowing the reaction of interest (e.g., the photocatalytic oxidation of water and organics) to be quantitatively studied in isolation (see Figure 1.2b).\textsuperscript{94, 131}

Owing to many distinct advantages, photoelectrocatalytic (PEC) techniques have been developed and employed for water disinfection, as listed in Table 1.4. Among these studies, Butterfield’s group first described the photoelectrochemical
disinfection of *E. coli* and *Clostridium perfringens*, and a significant improvement in the disinfection efficiency was observed upon the application of an electrical bias. The same group also investigated photoelectrocatalytic disinfection abilities by using various kinds of photocatalysts, and the photoelectrocatalysis results were compared with the photocatalysis results under the same conditions, confirming high disinfection performance of PEC approach. They also reviewed the potential advantages of photoelectrocatalytic treatment of water, and studied the general problems associated with the practical application of photoelectrocatalytic treatment of water such as UV penetration, mass transfer and electrode fouling etc. In addition, Baram et al. synthesised the immobilized TiO$_2$ nanotube electrodes with high surface areas, and a high photocurrent and an extremely rapid *E. coli* inactivation rate of $\sim 10^6$ CFU/mL (colony-forming unit/mL) bacteria within 10 min could be obtained by the electrodes, predicting its potency for water purification.

### Table 1.4 SEMiconductor photocatalysts for PEC disinfection of biohazards

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Biohazard</th>
<th>Light Source</th>
<th>PEC condition</th>
<th>Performance</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ film</td>
<td><em>E. coli</em></td>
<td>UVB lamp</td>
<td>AE: Ni mesh</td>
<td>100% removal of <em>E.coli</em> (3000 CFU/mL)</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td><em>C. perfringens</em></td>
<td></td>
<td>RE: Ag/AgCl</td>
<td>2 log of <em>C. perfringens</em> (6000 CFU/mL), 25 min</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$ film</td>
<td><em>E. coli</em></td>
<td>xenon lamp ($\lambda &gt; 300$ nm)</td>
<td>AE: Pt RE: SCE</td>
<td>99.996% inactivation of $6 \times 10^4$ CFU/mL after 120 min</td>
<td>95</td>
</tr>
<tr>
<td>TiO$_2$ film</td>
<td><em>E. coli</em></td>
<td>UVA lamp</td>
<td>AE: Ni gauze</td>
<td>95% killed at 3 V in 25 min, 15% at 1.3 V in 10 min (10$^7$ CFU/mL)</td>
<td>134</td>
</tr>
<tr>
<td>Fe-doped TiO$_2$</td>
<td><em>E. coli</em></td>
<td>black-light lamp (peak 370 nm)</td>
<td>AE: Ni mesh RE: Ag/AgCl</td>
<td>95% removal at 1.3 V and 99.5% at 3.0 V in 25 min (10$^7$ CFU/mL)</td>
<td>137</td>
</tr>
<tr>
<td>ZnIn$_2$S$_4$</td>
<td><em>E. coli</em></td>
<td>xenon lamp ($\lambda &gt; 400$ nm)</td>
<td>AE: Pt RE: SCE</td>
<td>almost 100% inactivation of $3 \times 10^8$ CFU/mL in 1 h</td>
<td>138</td>
</tr>
<tr>
<td>TiO$_2$/CdS</td>
<td><em>E. coli</em></td>
<td>Xenon lamp (150 mW/cm$^2$)</td>
<td>CE: Pt Potential: + 0.5 V</td>
<td>100% inactivation $10^7$ of CFU/mL in 3 min</td>
<td>139</td>
</tr>
<tr>
<td>Ti/TiO$_2$-Ag</td>
<td><em>M. avium</em></td>
<td>mercury lamp ($\lambda = 351 - 400$ nm, 9.23 W/cm$^2$)</td>
<td>AE: Pt gauze RE: Ag/AgCl</td>
<td>99.9% kill of <em>M. kansasii</em> and 99.8% inactivation of <em>M. avium</em> in 240 min (5x$10^5$ CFU/mL)</td>
<td>140</td>
</tr>
</tbody>
</table>

Recently, a PEC-X (X represents halogen, e.g., Br) bactericidal technique has been developed and reported by our group utilizing in situ photoelectrocatalytically
generated photoholes (h⁺), long-lived di-bromide radical anions (Br₂⁻) and AOSs as bactericides for instant inactivation and rapid decomposition of Gram-negative bacteria. The experimental results demonstrated that this PEC-Br approach can inactivate 99.90% of 10⁷ CFU/mL E. coli within 0.40 s, which is almost 350 and 2200 times faster than that of only PEC and PC treatment using same TiO₂ nanoparticle film photoanode, under identical experimental conditions (except in absence of Br⁻). Moreover, E. coli body occurs obviously damage with bactericidal time, after 600 s of PEC-Br treatment, over 90% decomposition of E. coli body mass can be obtained. Using TiO₂ nanoparticle film photoelectrode in the presence of halides (e.g., Br⁻ and Cl⁻), photoelectrocatalytically virucidal performance was also investigated by us. The results demonstrated that the photoelectrocatalytic treatment in the presence of 1.0 mM Br⁻ shows the highest virucidal efficiency, enabling complete inactivation of a ~1000 TCID₅₀ replication-deficient recombinant adenovirus (QDQADS) population within 31.7 s. The superior virucidal performance can be ascribed to the increased production of reactive oxygen species and additional viricides resulting from the photoelectrocatalytic halide oxidation, as well as prolonged lifetime of photoholes (h⁺) for direct inactivation.

Although PEC technique has displayed great potential for bactericidal applications including inactivation, decomposition and mechanism investigation, some drawbacks of photoelectrocatalytic technique make it not suitable for large-scale application, such as limited illumination area, low bactericidal capability and electrochemical instability of some photoelectrodes. The low bactericidal capability may result in the formation of some disinfection byproducts that are considerably complex and hard to be confirmed, especially the impact on public health. To balance these shortcomings, it is critically important to develop high efficiency photoelectrode (key component of PEC system) with high chemical/electrochemical/photo stability, especially for visible light bactericidal applications.

1.3 UV and Visible Light Active Photocatalysts for Disinfection Applications

Photocatalyst can promote reactions in the presence of light and are not consumed in the overall reaction. Semiconductor materials are used as photocatalysts due to their electronic structure which is characterised by a filled valence band and an empty conduction band. Considerable research has been carried on the development semiconductor photocatalysts, and more than 190 semiconductors
have so far been reported to be suitable for photocatalysis. Over the past 40 years, many photocatalysts have been reported with high photocatalytic activities in the UV light region. However, the UV irradiation only takes a small fraction (ca. 5%) of the incoming solar spectrum, whereas the visible light spectrum is far more abundant (ca. 46%). Therefore, it is essential and highly desirable to develop visible-light-driven photocatalysts with high stability and high efficiency for PC and PEC applications. Various semiconductor materials including coupled binary nano-structures, and even complex ternary composites have been developed and reported to be effective for environmental remediation, water disinfection, hydrogen production and dye-sensitized solar cells. As the structures of the semiconductor photocatalysts play key roles in the PC and PEC process, an increasing number of researches have been focusing on the development of semiconductor photocatalysts with unique structures and high reactive facets, aiming at improving PC and PEC efficiencies.

1.3.1 UV and Visible Light Active Photocatalyst for PC and PEC Disinfection

As demonstrated previously, when a photon with an energy that matches or exceeds the bandgap energy of the semiconductor, an electron is promoted into conduction band (CB), leaving a hole in valence band (VB). Being in the excited state, the semiconductors can induce reduction or oxidation reactions to achieve water splitting, degradation of organic pollutants or inactivation of biohazards. The reduction strength of electrons in the semiconductor is measured by the energy level of the conduction band edge, while the oxidation power of holes is measured by that of valence band edge. Figure 1.3 displays the bandgap energy of some semiconductor photocatalysts and their relationship with the redox potentials. For a photocatalyst with excellent photocatalytic reactivity, the bottom level of the conduction band has to be more negative than the redox potential of H⁺/H₂ (0 V vs. NHE), while the top level of the valence band be more positive than the redox potential of O₂/H₂O (1.23 eV). Among them, simple oxide and sulfide semiconductors such as TiO₂ (bandgap 3.0-3.2 eV), SrTiO₃ (bandgap 3.2 eV), ZnO (bandgap 3.2 eV),WO₃ (bandgap 2.8 eV) and ZnS (bandgap 3.6 eV) have been commonly reported as UV-light active photocatalysts in H₂ production, organic degradation and water disinfection, etc.
Figure 1.3 CB and VB energy levels of several semiconductors.

**UV Light Active Photocatalyst**

Generally, the UV-active photocatalysts can be classified as d⁰ metal (Ti⁴⁺, Zr⁴⁺, Nb⁵⁺, Ta⁵⁺, W⁶⁺ and Mo⁶⁺) oxides, d¹⁰ metal (In³⁺, Ga³⁺, Ge⁴⁺, Sn⁴⁺ and Sb⁵⁺) oxides, f⁰ metal (Ce⁴⁺) oxides and nonoxide photocatalysts based on their electronic configuration properties. Table 1.5 listed some examples of the UV-light-active semiconductor materials and their PC applications, while numerous more studies have been performing on the synthesis and applications of various photocatalysts. To enhance the PC efficiency, modification or combinations of photocatalysts have also been studied frequently, such as the Ag-doped TiO₂, SnO₂/TiO₂ and NiO₂/ZrO₂, showing great improvement in the photocatalytic activities.

**Table 1.5** UV-light-active semiconductor materials for photocatalytic applications

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Co-catalyst</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td></td>
<td>H₂ production, degradation, disinfection of bacteria</td>
<td>100, 105, 156-158</td>
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However, some of the photocatalysts listed, for instance, ZnO, CdS and α-Fe<sub>2</sub>O<sub>3</sub>, do not possess long-term stability in the PC or PEC process, on which photooxidation or photocorrosion are tent to happen in photocatalysis process. It is clear that the development of semiconductor photocatalysts with improved photocatalytic efficiencies will continue to be a hot topic and challenge of research in the near future.
1.3.2 Photocatalysis and Photoelectrocatalysis at TiO$_2$

As a good photocatalyst should be photoactive (able to utilize visible and/or near UV light), photostable (biologically and chemically inert), inexpensive and nontoxic, TiO$_2$ is almost exclusively used as photocatalyst due to its distinctive advantages in environmental remediation and energy conversion applications.\textsuperscript{229-231}

Under UV illumination, the strong oxidation power possessed by the photogenerated holes at TiO$_2$ valence band can readily decompose the environmentally hazardous species into harmless compounds such as CO$_2$ and H$_2$O. These fundamental processes for heterogeneous photocatalysis on TiO$_2$ can be depicted as follows.\textsuperscript{92}

Charge-carrier generation:

\[ TiO_2 + h\nu \longrightarrow h_{vb}^+ + e_{cb}^- \] \hspace{1cm} (1.1)

Charge-carrier trapping:

\[ h_{vb}^+ + >Ti^{IV}OH \longrightarrow \{ >Ti^{IV}OH\}^+ \] \hspace{1cm} (1.2)

\[ e_{cb}^- + > Ti^{IV}OH \longleftrightarrow \{ > Ti^{III}OH \} \] \hspace{1cm} (1.3)

\[ e_{cb}^- + > Ti^{IV} \longrightarrow > Ti^{III} \] \hspace{1cm} (1.4)

Charge-carrier recombination:

\[ e_{cb}^- + \{ > Ti^{IV}OH\}^+ \longrightarrow > Ti^{IV}OH \] \hspace{1cm} (1.5)

\[ h_{vb}^+ + \{ > Ti^{III}OH \} \longrightarrow Ti^{IV}OH \] \hspace{1cm} (1.6)

Interfacial charge transfer:

\[ \{ > Ti^{IV}OH\}^+ + \text{Red} \rightarrow > Ti^{IV}OH + \text{Red}^{*} \] \hspace{1cm} (1.7)

\[ e_{tr}^- + \text{Ox} \rightarrow > Ti^{IV}OH + \text{Ox}^{*} \] \hspace{1cm} (1.8)

In the above processes, $e_{cb}^-$, $h_{vb}^+$ and $e_{tr}^-$ represent a conduction-band (CB) electron, a valence-band (VB) hole and a trapped conduction-band electron, respectively. Red and Ox are Reduced and Oxidized forms of the reactants, while $> Ti^{IV}OH$, $\{ > Ti^{IV}OH\}^+$ and $\{ > Ti^{III}OH \}$ represent the primary hydrated surface functionality of TiO$_2$, the surface-trapped VB hole (i.e., surface-bound hydroxyl radical), and the surface-trapped CB electron. Known from the mechanism, the overall photocatalytic quantum efficiency is determined by two critical factors: one is the competition between the recombination and trapping of the charge carrier, and the other is the competition between the trapped charge carrier recombination and the interfacial charge transfer. Thus, either increasing the recombination lifetime of
charge carriers or increasing the interfacial electron-transfer rate constant can facilitate the photocatalytic process.

An increasing number of researches have been conducted on the disinfection and destruction of microorganisms using TiO$_2$ photocatalyst.\textsuperscript{105, 232-237} Variables that affect the photoactivity of the TiO$_2$ photocatalyst such as particle size, surface area, crystal structure and the preparation method of particles have been studied as well as extrinsic parameters such as temperature of reaction, incident light intensity and pH of solution.\textsuperscript{112, 238-244} It was reported that both anions and cations had negative effect on inactivation, while hydrogen peroxide could improve, and pH value did not affect the photocatalytic inactivation of \textit{E. coli}.\textsuperscript{112} Crystal structure and particle size of the photocatalyst are particularly important factors in determining photoactivity and inactivation efficiency.

Traditionally, pure TiO$_2$ with large band gap (3.2 eV for anatase and 3.0 eV for rutile) is not an ideal candidate for visible light applications. To improve the sunlight utilisation efficiency, a variety of approaches has been developed to obtain visible light active TiO$_2$ including doping, surface hydrogenation and combination with other semiconductors with narrow bandgaps.\textsuperscript{245-247} Since nitrogen-doped TiO$_2$ was reported in 2001, metal and non-metal doping has been intensively investigated in modifying the electronic structure of TiO$_2$ to improve its visible-light photocatalytic activity.\textsuperscript{111, 115, 137, 248-251} Sulfur-doped TiO$_2$ was synthesised and exhibited good performance in the inactivation of \textit{M. lylae} under visible light irradiation.\textsuperscript{111} Both neat TiO$_2$ and Ag-doped TiO$_2$ nanofilms on silicon wafers were fabricated, and the antimicrobial results indicated that the Ag/TiO$_2$ thin films showed enhanced bactericidal activities compared to the neat TiO$_2$ nanofilm both in the dark and under UV illumination against \textit{E. coli}.\textsuperscript{252}

Compared to single-phase semiconductor photocatalysts, hybrids of two or more semiconductor materials seem to be more efficient to make use of solar light by combining different electronic structures. Glass coated thin films of TiO$_2$, CuO and CuO/TiO$_2$ was successfully synthesised by Ditta et al., and their antimicrobial activities were investigated by inactivation of \textit{bacteriophage T4}.\textsuperscript{114} The results indicated that the TiO$_2$ photocatalytic inactivation rate was improved with the inclusion of copper in the catalyst, and the TiO$_2$/CuO coated surfaces might have applications in the food and healthcare industries.\textsuperscript{114} A ZnO-TiO$_2$ nanocomposite was obtained by modified ammonia-evaporation-induced synthetic method and was
experimented for inactivation of *E. coli*, showing a disinfection efficiency of 80% with an *E. coli* concentration of $8 \times 10^{14}$ CFU/mL in 30 min under natural sunlight. By combining two semiconductor materials with proper band edge positions, electrons and or holes can transfer from one component unit to another, which can greatly decrease the electron-hole recombination probability and increase the lifetime of charge carriers, thus promoting the photocatalytic efficiency.

1.3.3 Synthetic Methods

The performance of semiconductor photocatalysts is largely affected by the properties of the materials, which is in turn, determined by the synthetic method used. Ideally, the synthetic method employed should lead to samples of high purity with a narrow size distribution, which may be more effective in the photocatalysis application. Compared with the conventional bulk semiconductors, the extremely small-sized particles have aroused great attention due to their unique properties such as extremely large surface area and thermodynamically instability, and more importantly, the excellent electronic properties. Therefore, recent studies have mainly been focused on the synthesis and application of the nanostructured semiconductor photocatalysts. Over the past two decades, many methods for the preparation of nanostructured semiconductor photocatalysts have been reported including sol-gel method, template-assisted method, chemical vapour deposition, electrodeposition, and hydrothermal methods, by which various highly uniform semiconductor nanoparticles were yielded.

**Sol-gel Method**

Sol-gel method has been used to fabricate ceramic and glass materials since the mid-1800s, and has recently evolved into a general and powerful approach for preparing inorganic materials. In a typical sol-gel process, a solution of a precursor molecule hydrolyses to obtain a suspension of colloidal particles (the sol), and then the sol particles aggregate to compose a gel, and afterwards the gel is thermally treated to yield the desired material. By tailoring the chemical structure of primary precursor and controlling the processing variables, nanocrystalline semiconductor photocatalysts with high purity can be achieved.

An enormous range of colloidal powders with controlled size and morphologies synthesised by sol-gel method have been reported, including metal oxides (TiO$_2$, Fe$_3$O$_4$), hydroxides, carbonates sulfides (CdS, ZnS), metals, and various mixed phases or composites (Ni, Co, Sr ferrites) and coated particles. Burnside’s group
developed ordered TiO\textsubscript{2} thin films of only anatase phase from the base-catalyzed sol-gel synthetic scheme, and concluded that the ordering in the films was caused by balanced attractive and repulsive interactions of the tetramethylammonium-coated surfaces in an aqueous medium.\textsuperscript{258} Su et al. reported the sol-gel synthesis of TiO\textsubscript{2} powders using titanium (IV) n-butoxide as precursor, and studied the photocatalytic activity by the photodecomposition of salicylic acid.\textsuperscript{259} Our group also fabricated TiO\textsubscript{2} colloids via a sol-gel method, which displayed excellent photocatalytic and photoelectrocatalytic performance in degradation of organic model compounds as well as inactivation of bacteria.\textsuperscript{141, 260, 261}

As sol-gel process is a simple, cost-effective and low-temperature technique that allows for the fine control of the product’s chemical composition, it is considered to be one of the most successful techniques for preparing nanosized metallic oxide materials with high photocatalytic activities.\textsuperscript{262}

**Template-Assisted Method**

Template-assisted method is commonly used for preparing nanostructures, as it can supply a variety of porous structures with a wide range of diameters, well-defined morphologies on controllable length scales, and various chemical functionalities for different applications.\textsuperscript{263} Combined with other methods such as hydrothermal, electrospinning and electrochemical deposition, template-assisted method has been used to prepare various tubules and fibrils composed of electronically conductive polymers, metals, semiconductors, carbons and other materials.\textsuperscript{264-266} For example, Lakshmi et al. reported the combination of sol-gel and template methods to prepare a variety of inorganic semiconducting materials within the pores of an alumina template membrane including TiO\textsubscript{2}, ZnO and WO\textsubscript{3}, and predicted the applicability of the combined methods to a large number of materials.\textsuperscript{267} Mesoporous TiO\textsubscript{2} nanocrystals were prepared by surfactant-assisted template method under sol-gel process followed by calcination, the photocatalytic activity of which was tested to be promising by the formation of I\textsubscript{3}\textsuperscript{–} due to the oxidation of I\textsubscript{−} to I\textsubscript{2}.\textsuperscript{268}

As the template-based methods often involve the coating of nanocrystals on the template surface, calcination or etching processes are commonly used to remove the templates, which often compromise the structural integrity of the final product and therefore limit the application of the template-directed approach. Researchers have managed to fabricate various hollow or porous nanostructures in the absence of templates.
Chemical Vapour Deposition (CVD)

Chemical vapor deposition is an important technique in the semiconductor industry to produce thin films.\textsuperscript{269} It involves the dissociation and/or chemical reactions of gaseous reactants in an activated environment, followed by the formation of a stable solid product.\textsuperscript{270} The homogeneous gas phase reactions happen in the gas phase, while heterogeneous chemical reactions occur on the heated interface, leading to the formation of powders or films. Uniform films with good reproducibility and adhesion at reasonably high deposition rates can be produced by this method, and various films with different properties can be obtained adjusting deposition conditions.\textsuperscript{271-275} By CVD processes, Ding’s group coated of anatase TiO\textsubscript{2} onto three different particle supports, activated carbon, γ-alumina (Al\textsubscript{2}O\textsubscript{3}) and silica gel (SiO\textsubscript{2}) and investigated the effect of the CVD synthesis conditions on the loading rate of anatase TiO\textsubscript{2}.\textsuperscript{275} A TiO\textsubscript{2} thin film was fabricated by a radio frequency plasma enhanced chemical vapor deposition technique, which displayed good photocatalytic activity with degradation of benzene and aniline and disinfection of \textit{E. coli}.\textsuperscript{276} A carbon-containing nanostructured TiO\textsubscript{2} was synthesised by a metal-organic chemical vapor deposition process, and employed in the NO\textsubscript{x} mineralisation, exhibiting high photocatalytic activity of up to 48% removal for under visible-light illumination.\textsuperscript{277} However, there are still some drawbacks of the CVD technique, such as the safety hazards caused by the use of toxic, corrosive, flammable or explosive precursors, and the high cost of fabrication in the process.

Electrodeposition (ED)

Electrodeposition is also one of the commonly used methods to fabricate nanocomposite coatings. Because of its low cost, possibility of large-scale deposition, low temperature processing and direct control of film thickness, electrodeposition of chalcogenide semiconductors has recently emerged as a competitive technique for the fabrication of thin films.\textsuperscript{278-280} Ishikawa et al reported a direct electrodeposition of TiO\textsubscript{2} photocatalyst onto an Al/Al\textsubscript{2}O\textsubscript{3} substrate, and the photocatalytic activity as well as the deposition mechanism of the obtained photocatalyst was also studied.\textsuperscript{281} Zhang et al fabricated Ag nanoparticles loaded N-doped TiO\textsubscript{2} nanotube arrays (Ag/N-TNTs) via an electrodeposition process, which showed a promising photocatalytic material for organic pollutant degradation under visible light.\textsuperscript{282} Electrodeposition is recognized as a promising method for the fabrication of semiconductor films and
nanostructures, such as the chalcogenides, oxides and other ionic materials, and III - V compounds as well.

**Hydrothermal Method**

Hydrothermal methods refer to the processes of crystal synthesis that depend on the solubility of minerals in hot water under high pressure, which are most widely used methods to obtain large quantities of nanostructured semiconductor photocatalysts.\(^\text{283, 284}\) Typically, the process takes place in an apparatus consisting of a steel pressure vessel called autoclave, in which certain reagent is supplied along with water. Under high temperature and pressure, the solubility of aqueous solvent is increased, so that a difficultly soluble material can reach a point where it can be crystallized on a seed without appreciable self-nucleation.\(^\text{285}\) Using this technique, crystalline phases which are not stable at the melting point can be obtained by controlling the reaction parameters, and materials with a high vapour pressure can also be grown.

The method is particularly suitable for the growth of nanostructured semiconductors with good control of their microstructures which ultimately determine their optical and electrical properties.\(^\text{179, 286-289}\) For example, Yu et al reported the fabrication of ZnO hollow spheres with porous crystalline shells by hydrothermal treatment of glucose/ZnCl\(_2\) precursor, and elaborated that the average crystallite size, shell thickness, specific surface areas, pore structures, and photocatalytic activity of ZnO hollow spheres were controllable by varying the molar ratio of glucose to zinc ions.\(^\text{290}\) Our group also reported the formation of branched titanate nanotubes with a three-dimensional nanotubular network directly onto a titanium substrate using a hydrothermal process, and a continuous seed formation-oriented crystal growth mechanism was proposed for the unique branched titanate nanotubular network formation.\(^\text{291}\)

Most titanate nanotubes are obtained from the liquid phase hydrothermal processes, and are almost exclusively in the solution suspension or precipitation forms. Our group reported, for the first time, a facile vapour phase hydrothermal method to direct grow vertically aligned titanate nanotubes with larger and tunable diameter on titanium foil substrate which cannot be obtained by the conventional hydrothermal method, and demonstrated the subsequent crystal reformation processes via a distinctive nanosheet rolled-up mechanism.\(^\text{292}\) We also reported other novel nanostructured semiconductors with unique morphologies which can be used in
absorbance of hazard or radioactive chemicals, photocatalysis, hydrogen storage, supercapacitor and lithium ion batteries.293-295

In this thesis work, hydrothermal method as a main synthetic approach has been adopted to directly grow nanostructured TiO$_2$ films onto conductive substrates with different crystal structures and exposed crystal facets for investigation of photoelectron transfer properties and bactericidal application. To obtain a meaningful comparison, sol-gel method and anodisation technique were also used to fabricate TiO$_2$ nanoparticle film and highly ordered TiO$_2$ nanotube array film for bactericidal applications, respectively.

1.3.4 Effect of Crystal Structure of Anatase TiO$_2$ photocatalyst on PC and PEC Performance
STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

This part consists of a co-authored published review paper, including all authors, are:


This review paper summarised the progress of anatase TiO$_2$ nanocrystals with exposed high reactive \{001\} facets including their synthesis, morphologies, mechanistic aspects and their PC and PEC performance. By reviewing the relevant literatures reported, I learnt much knowledge about crystal structure effect of anatase TiO$_2$ on PC and PEC, and obtained significant guidance for my PhD project.

My contribution to the published paper involved:

- Search, collection and analysis of literatures.
- Preparation of the manuscript.

(Sign) _______________________ (Date) _______________________
Name of student: Xiaolu Liu

(Sign) _______________________ (Date) _______________________
Corresponding author of paper: Prof. Hujun Zhao

(Sign) _______________________ (Date) _______________________
Supervisors: Prof. Huijun Zhao, Dr. Haimin Zhang

In order to comply with copyright the article has been removed.
1.4 Scope of the Thesis

This work aims: (1) to develop a series of nanostructured TiO₂ photocatalysts with UV and/or visible light activity; (2) to study the fundamentals (e.g. the photoelectron transport properties in the photocatalyst film) of the TiO₂ photocatalysts with different structures; (3) to evaluate the disinfection and decomposition properties of the obtained nanostructured photocatalyst against biohazards by photocatalysis and photoelectrocatalysis techniques, and (4) to understand in-depth bactericidal mechanism and decomposition process of biohazards. To achieve these aims, systematic studies have been performed including the establishment of experimental methodology, characterisations of nanomaterials, performance evaluation and mechanistic investigations.

Chapter 1 provides comprehensive literature review for this project, including the importance of disinfection and decomposition of biohazards, the advantages and disadvantages of the existing disinfection technologies, the feasibility and challenges of PC and PEC techniques and the effect of crystal structures of photocatalysts on PC and PEC performance, which justify the significance of the present research. A part of the literature review in this chapter related to “Effect of Crystal Structure of Anatase TiO₂ photocatalyst on PC and PEC Performance” has been published as an invited review article in *Science China: Chemistry*, 2013, 56, 402-417.

Chapter 2 illustrates the control grown of the vertically aligned nanorod-like rutile TiO₂ single crystal nanowire bundles onto FTO conducting substrates via a facile, one-pot hydrothermal method. The excellent photoelectrocatalytic properties of the as-synthesised nanorod-like rutile TiO₂ photoanode towards water oxidation have been studied in detail, which can be due to the superior photoelectron transfer property of the nanorod-like rutile TiO₂ film providing the superior electron pathways. The results presented in this chapter have been published in *Journal of Materials Chemistry*, 2012, 22, 2465-2472.

To make better use of the solar energy, a pure rutile phase TiO₂ film on FTO substrate with 100% pyramid-shaped (111) surfaces was developed with both UV and visible light activities, as demonstrated in Chapter 3. As a photoanode, the rutile TiO₂ film exhibited excellent visible light photoelectrocatalytic activity toward oxidation of water and organics. The excellent visible light activity of the pure rutile TiO₂ film photoanode can be attributed to the Ti³⁺ doping in the bulk and high reactivity of the
exposed {111} crystal facets. The results shown in this chapter have been published in *Nano Research*, 2012, 5, 762-769.

Chapter 4 continues to study the photoelectrocatalytic performance and photoelectron transfer properties of the {111} faceted pure rutile TiO$_2$ photoanode under both UV and visible light irradiation. A simple photoelectrochemical method was used to manifest the photoelectron transport properties inside the rutile TiO$_2$ film and concurrently quantify the inherent resistances ($R_0$) of UV and visible light illuminated photoanodes. The similar $R_0$ values under UV and visible light irradiation imply a similar photoelectron transport capability inside the rutile TiO$_2$ film under UV and visible light irradiation, confirming that the measured $R_0$ is an inherent property of the photocatalyst film. This also implies that the rate of charge recombination is similar under UV and visible light irradiation. This part of research work has been published in *Journal of Material Chemistry A*, 2013, 1, 2646-2652.

In Chapter 5, visible light photocatalytic and photoelectrocatalytic bactericidal performance of the {111} faceted TiO$_2$ photoanode was investigated for the first time, the photocatalytic inactivation capability under sunlight was evaluated as well. The bactericidal performances of the photoanode with UV and visible light driven photocatalysis and photoelectrocatalysis processes were evaluated using *E. coli* as the probe bacteria. Results confirm the superiority of the photoelectrocatalysis over the photocatalysis for bactericidal application and high stability in photocatalysis and photoelectrocatalysis processes. The findings presented in this chapter have been published in *Catalysis Today*, 2014, 224, 77-82.

In Chapter 6, the synthesis of highly ordered anatase TiO$_2$ nanotube array photoelectrode was investigated as well as its disinfection capability against *E. coli*. The anatase TiO$_2$ nanotube array film electrode was for the first time combined with a home-designed photoelectrochemical flow reactor for bactericidal application, and the photoelectrocatalytic disinfection efficiency was compared with an anatase TiO$_2$ nanoparticle film electrode with a similar film thickness. This part of research has resulted in a research article being published in *RSC Advances*, 2013, 3, 20824-20828.

Chapter 7 provides a summary of the important results of this work and further research needed in the future.
1.5 References


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CHAPTER 2 VERTICALLY ALIGNED NANOROD-LIKE RUTILE TiO₂ SINGLE CRYSTAL NANOWIRE BUNDLES WITH SUPERIOR ELECTRON TRANSPORTS AND PHOTOELECTROCATALYTIC PROPERTIES
STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

This chapter is in the form of a co-authored published paper, assessing the electron transport and photoelectrocatalytic properties of the vertically aligned nanorod-like rutile TiO$_2$ single crystal nanowire bundle photoanode. There may be some repetitions due to the requirements of publication, but no material has been previously published or written by another person. The bibliographic details of the co-authored published paper, including all authors, are:


My contribution to the published paper involved:

- The concept development and experimental design;
- Performing photoelectrocatalytic experiments;
- Drafting the paper.

(Sign) ________________________  (Date) ________________________

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Vertically aligned nanorod-like rutile TiO$_2$ single crystal nanowire bundles with superior electron transport and photoelectrocatalytic properties†

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In this work, vertically aligned nanorod-like rutile TiO$_2$ single crystal nanowire bundles were directly grown onto FTO conducting substrates via a facile, one-pot hydrothermal method. The fabricated nanorod-like rutile TiO$_2$ single crystal nanowire bundles display a diameter range of 150–200 nm and a mean length of 6.9 μm. The nanorod-like bundles assemble by individual single crystal nanowires of 5–7 nm in diameter. The photoanode made of vertically aligned nanorod-like rutile TiO$_2$ single crystal nanowire bundles shows excellent photoelectrocatalytic activity towards water oxidation, which is almost 3 times higher than that of the photoanode made of vertically aligned anatase TiO$_2$ nanotube film of similar thickness. The high photoelectrocatalytic activity of the photoanode made of the nanorod-like rutile TiO$_2$ single crystal nanowire bundles is mainly due to the superior photodopentron transfer property, which has been manifested by the inherent resistance ($R_h$) of the rutile TiO$_2$ film via a simple photoelectrochemical method. Using this approach, the calculated $R_h$ values are 52.1 Ω and 71.0 Ω for the photoanodes made of vertically aligned nanorod-like rutile TiO$_2$ single crystal nanowire bundles and the vertically aligned anatase TiO$_2$ nanotubes, respectively. The lower $R_h$ of the rutile TiO$_2$ photoanode means a superior photodopentron transfer property. XPS valence-band spectra analysis indicates that the nanorod-like rutile TiO$_2$ film has almost identical valence band position (1.95 eV) when compared to the anatase TiO$_2$ nanotube film, meaning a similar oxidation capability, further confirming the superior photoelectrode transport property of the nanorod-like rutile TiO$_2$ single crystal nanowire bundles.

1. Introduction

Since Fujishima and Honda's pioneering work in 1972, enormous efforts have been devoted to the research on photoelectrocatalytic splitting of water for H$_2$ or O$_2$ production using TiO$_2$ based nanomaterials. Rutile TiO$_2$ has been widely used as a white pigment in paint, toothpaste, sunscreen, self-cleaning materials, and food additives. It possesses superior photoelectrocatalytic stability, higher refractive index, and cheaper production cost over anatase TiO$_2$. However, as a powdered form of photoelectrocatalyst, it has been widely accepted that anatase TiO$_2$ is more active for photoelectrocatalytic water splitting than rutile TiO$_2$.

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(at the working electrode) is physically separated from the reduction half-reaction (at the auxiliary electrode), which allows the reaction of interest (i.e., the photocatalytic oxidation of water) to be added in isolation. Another advantage is that an applied potential bias is employed to minimize photoelectron-photodetachment recombinations, and thus significantly improving the photocatalytic efficiency.15,16 These advantages of the photoelectrochemical method can significantly enhance the photocatalytic activity towards water oxidation using nanostructured TiO2 photocathodes.17

One-dimensional TiO2 nanostructures, such as nanotubes, nanorods and nanowires, have shown promising potential in photocatalytic splitting of water and dye-sensitized solar cells (DSSCs).18-20 These nanostructures can provide direct electrical pathways for photogenerated electrons and thus increase the electron transport rate, which in turn improves the performance of photocatalysts.21,22 In this regard, our group has developed a simple photoelectrochemical method to characterize the photoelectron transport process (e.g., determining the inherent resistance of the photocathode layer, R0) in semiconductor photocathode films,23,24 which is a simple and convenient approach when compared to the characterization methods for the charge transport process in semiconductor photocathode films, such as intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) techniques.25

Although rutile TiO2 nanorod/nanowire array films have aroused great research interest owing to their encouraging performance in DSSCs,26-28 most studies on photocatalytic water splitting under UV light irradiation so far are mainly focused on using highly ordered anatase TiO2 nanotube array films,29,30 while little attention has been paid to rutile TiO2 nanorod/nanowire based photocatalytic water splitting.31 Feng et al. fabricated vertically aligned rutile TiO2 single crystal nanowire array films on an FTO conducting substrate by a mild hydrothermal method.22 The obtained nanowire array films as photoanode for dye-sensitized solar cells (DSSCs) shows an overall conversion efficiency of 5.02%. Liu and Aydin used rutile TiO2 nanorod array film as the photoanode for DSSCs to obtain an overall conversion efficiency of 3.5%.22 Theoretical and experimental studies have indicated that rutile TiO2 (110) and (001) surfaces have high reactivity for spontaneous dissociative adsorption of water molecules,33,34 which could be favourable for photocatalytic oxidation of water.

In this work, vertically aligned nanorod-like rutile TiO2 single crystal nanowire bundles were directly grown on FTO conducting glass substrates by a facile, one-pot hydrothermal method. The structural, morphological, crystal phase and facets of the resultant nanorod-like rutile TiO2 single crystal nanowire bundles were systematically investigated. The growth process of the rutile TiO2 nanorods on an FTO substrate was experimentally examined and the possible formation mechanism was discussed in detail. The resultant nanorod-like rutile TiO2 single crystal nanowire bundles with exposed (110) and (001) surfaces were used to fabricate photoanodes and tested for photoelectrochemical oxidation of water. For comparison, vertically aligned anatase TiO2 nanotube array films on a titanium foil substrate fabricated by anodization was also used for photoelectrocatalytic oxidation of water.

2. Experimental section

Synthesis

Rutile TiO2 nanowire bundle array films on FTO substrates were fabricated by a facile, one-pot hydrothermal method. A typical synthesis, 0.5 mL of titanium (IV) isopropoxide ([Ti(OC3H7)4] 20% in 1-4% sulfamic acid, Aldrich) was first added to 20 mL of concentrated hydrochloric acid (HCl, 37% by weight, Sigma-Aldrich). After stirring for 2 min at ambient conditions, 20 mL of 0.65 M ammonium persulfate [(NH4)2S2O8, 98%, Sigma-Aldrich] was mixed with the above solution in a Teflon-lined stainless steel autoclave (80 mL of volume). The final concentration of ammonium persulfate in the reaction solution was 1 M. After stirring for another 2 min, a piece of pre-treated FTO conducting substrate with the conductive side facing up (30 mm × 15 mm × 2 mm) was immersed into the reaction solution. The subsequent hydrothermal reaction was kept at 160 °C for 24 h. After hydrothermal reaction, the autoclave was cooled to room temperature and the FTO substrate was taken out, rinsed adequately with deionized water and allowed to dry in ambient air. The obtained samples were then annealed at 300 °C (2 h in air, heating and cooling rates of 2 °C min−1) for characterization and photoelectrocatalytic application.

Anatase TiO2 nanotube films were fabricated using pretreated metal titanium foils (0.25 mm thick, 99.7% purity, Sigma-Aldrich) by anodization technique.35 After anodization, the obtained samples were calcined at 500 °C for 2 h in air with heating and cooling rates of 2 °C min−1 for subsequent photoelectrocatalytic application.

Characterization

SEM (JM-6300F), TEM (Philips F20), and XRD (Shimadzu XRD-6000 diffractometer, equipped with a graphite monochromator) were employed for characterizing the sample structures. Chemical compositions and valence-band spectra of the samples were analysed by X-ray photoelectron spectroscopy (Kraus Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer). All binding energies were carefully aligned with reference to the C 1s peak (284.6 eV) arising from surface hydrocarbons or possible adventitious hydrocarbons. UV–vis diffuse reflectance spectra of the films were recorded on a Varian Cary 5E UV-vis-NIR spectrophotometer.

Photoelectrochemical measurements

The photoelectrochemical measurements were performed at 23 °C in a photoelectrochemical cell with a quartz window for illumination.36 It consisted of a TiO2 nanostructured photoanode, a saturated Ag/AgCl reference electrode, and a platinum mesh counter electrode. A voltmeter (CV-27, BAS) was used for the application of potential bias. Potential and current signals were recorded using a Macintosh (AD Instruments). The illuminated area of the photoanode was 0.2826 cm². 0.10 M Na2SO4 solution was used as the electrolyte. Illumination was carried out using a 150 W xenon arc lamp light source with focusing lenses (JO-200W-5, Beijing Optical Instruments). To avoid the electrolyte being heated-up by the infrared light, a UV-band-pass filter (UG 5, Avontronics Pty. Ltd.) was used.
3. Results and discussion

Fig. 1A shows X-ray diffraction (XRD) patterns of the synthesized TiO₂ samples before (curve a) and after (curve b) annealing at 450 °C. As shown in Fig. 1A, the diffraction peaks for the samples before and after calcination can be indexed to a rutile phase of TiO₂ with lattice parameters of a = 4.517 Å and c = 2.938 Å (ICPDS, card no. 21-1276). Fig. 1B shows the scanning electron microscope (SEM) image of the synthesized rutile TiO₂ sample after calcination at 450 °C. It reveals an evenly distributed nanorod-like structures on the substrate. The cross-sectional SEM image (the inset in Fig. 1B) indicates that the vertically aligned rutile TiO₂ nanorods are directly grown on the FTO substrate, having diameters ranging from 150 to 200 nm with a mean length of 0.9 μm. To obtain more detailed structural information, the rutile TiO₂ nanorods were further examined by transmission electron microscope (TEM), as shown in Fig. 1C. It can be seen clearly that each nanorod is actually formed by a bundle of nanowires with 5-7 nm in diameter (Fig. 1D). A selected area electron diffraction (SAED) pattern (top inset in Fig. 1D) and HRTEM image (bottom inset in Fig. 1D) indicate that these bundled rutile TiO₂ nanowires are single crystals with the growth direction parallel to the c-axis. The fringe spacing parallel (or perpendicular) to the c-axis of the nanowire is 0.32 nm (or 0.29 nm) (bottom inset in Fig. 1D), which is consistent with the d value of (110) (or (001)) lattice spacing of the rutile TiO₂. Therefore, the circumferentially crystalline planes of the bundled rutile TiO₂ nanowires are (110) planes, growing along the preferred [001] direction. The above results demonstrate that the obtained rutile TiO₂ nanorod-like structures are actually the bundled single crystal nanowires with exposed (110) circumferential surfaces. This uniquely structured nanorod-like structure could be beneficial to the photocatalytically oxidation of water.

To better understand the formation process, the samples obtained from various reaction conditions, such as the concentrations of (NH₄)₂SO₄, TiCl₄, and HCl, and the reaction time, were examined by the SEM technique. Fig. 2A-C show SEM images of the samples fabricated in a reaction solution (40 mL) containing 0.012 M TiCl₄, 6 M HCl, and different concentrations of (NH₄)₂SO₄ at 160 °C for 24 h. When no (NH₄)₂SO₄ was added to the reaction solution, the rutile TiO₂ rod-like structures with 100-300 nm in diameter were obtained (Fig. 2A). The thickness of the obtained rod-like film is 2.3 μm (inset in Fig. 2A). TEM analysis further demonstrates that the

Fig. 1 (A) XRD patterns of the synthesized samples before (curve a) and after (curve b) annealing at 450 °C for 2 h; (B) surface SEM image of the synthesized sample after annealing at 450 °C (low magnification), the inset shows the cross-sectional SEM image; (C) TEM image of the synthesized sample after annealing; (D) high magnification TEM image of the sample, SAED pattern (top inset) and HRTEM image (bottom inset) taken from the area marked with a red circle.

Fig. 2 SEM images of the rutile TiO₂ samples fabricated under various reaction conditions. (A) (C): a reaction solution containing 0.012 M titanium (m) sulfate, 6 M HCl (37%), and different concentrations of ammonium persulfate; (A) 0 M; (B) 0.005 M; (C) 0.05 M. (D)-(F): A reaction solution containing 0.025 M ammonium persulfate, 6 M HCl (37%), and titanium (m) sulfate with various concentrations: (D) 0.005 M; (E) 0.023 M; (F) 0.03 M. (G) and (H) A reaction solution containing 0.012 M titanium (m) sulfate, 0.05 M ammonium persulfate, and HCl (37%) with 7.6 M and 4.6 M, respectively. The volume of the reaction solution was 40 mL and all reaction was kept at 160 °C for 24 h.
rutile rod-like structures are not formed by bundled single crystal nanowires (TEM image not given), indicating the significant role of (NH₄)₂S₂O₈ in formation of rutile TiO₂ single crystal nanowire bundles. The nanorod-like structure was obtained when 0.005 M of (NH₄)₂S₂O₈ was used (Fig. 2B). The obtained nanorods possess a diameter range of 150–250 nm and a mean length of 1.1 μm (inset in Fig. 2B). TEM characterization shows that the formed nanorods under such conditions were assembled by single crystal nanowires, confirming the decisive role of ammonium persulfate in formation of single crystal nanowire bundles (TEM image not given). With an increased (NH₄)₂S₂O₈ concentration to 0.025 M, uniformly distributed single crystal nanowire bundles with 150–200 nm in diameter and a mean length of 0.9 μm were obtained (Fig. 1B). The density of the single crystal nanowire bundles is higher than that obtained in 0.005 M (NH₄)₂S₂O₈ solution. When the concentration of (NH₄)₂S₂O₈ was further increased to 0.05 M, a compact rod-like structure was obtained (Fig. 2C). The cross-sectional SEM image (inset in Fig. 2C) reveals that the rod-like structures tend to grow together to form a compacted film with a mean thickness of 0.63 μm. Moreover, this rod-like structure is formed by nanoparticles, indicating that excessive amount of (NH₄)₂S₂O₈ is disadvantageous to the formation of single crystal nanowire bundles.

The above results indicate that the presence of ammonium persulfate in the reaction solution plays a key role in formation of uniformly distributed rutile TiO₂ nanorods that are configured by the bundled single crystal nanowires. In our approach, the persulfate anion (S₂O₈²⁻) with an oxidation potential of 2.01 V is used as an oxidant to oxidize the precursor (Ti³⁺) to Ti⁴⁺, as shown in eqn (1):

\[
2\text{Ti}^{3+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Ti}^{4+} + 2\text{SO}_4^{2-}
\]  

(1)

At the same time, (NH₄)₂S₂O₈ reacts with water to form NH₄HSO₄ and H₂O under the hydrothermal conditions (eqn (2)):

\[
(\text{NH}_4)_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{HSO}_4 + \text{H}_2\text{O}
\]  

(2)

The formed Ti⁴⁺ reacts with H₂O₂ assisted by the persulfate initiator, to form yellow peroxotitanium compounds, Ti₂O₂(OH)₆⁺⁻ (x = 1–6) (eqn (3)).

\[
\text{Ti}^{4+} + \frac{1}{2}\text{O}_2 \rightarrow \text{Ti}_2\text{O}_2\text{(OH)}_{x=2} (x = 1–6)
\]  

(3)

The formed Ti₂O₂(OH)₆⁺⁻ (x = 1–6) dehydrolyzes to produce TiO₂ nuclei that further grow into TiO₂ single crystal nanowires under the hydrothermal conditions (eqn (4)).

\[
\text{Ti}_2\text{O}_2\text{(OH)}_{x=2} (x = 1–6) \rightarrow \text{TiO}_2 + \text{H}_2\text{O}
\]  

(4)

In this study, it was found that the colour of the reaction solution changed from light yellow to dark yellow with increased ammonium persulfate concentration, indicating the increased concentration of yellow peroxotitanium compounds in the product. The formation of peroxotitanium compounds retards the hydrolysis of the titanium precursor (Ti₂(SO₄)₃), and thus provides sufficient time to allow the formation of rutile TiO₂ single crystal nanowires, and thus bundles. This means that in the absence of ammonium persulfate, the fast hydrolysis of the titanium precursor (Ti₂(SO₄)₃) leads to the formation of large size rod-like rutile TiO₂ structures without single crystal nanowire assembly (Fig. 2A). In presence of an appropriate concentration of ammonium persulfate, the formation of a suitable concentration of peroxotitanium compounds in the reaction solution is beneficial to the growth of the rutile TiO₂ nanorod-like structures with bundled single crystal nanowires (Fig. 2B and 2C). When the concentration of ammonium persulfate is increased (e.g., 0.05 M), the highly concentrated peroxotitanium compounds in the reaction solution result in the formation of a compacted rod-like film (Fig. 2C).

The effect of the concentration of titanium (iv) sulfate on the resultant morphology was also investigated. Fig. 2D-F show SEM images of the samples fabricated in the reaction solution (40 mL) containing 0.025 M ammonium persulfate, 6.1 M HCl and different concentrations of titanium (iv) sulfate at 160 °C for 24 h. Only nanoparticles were obtained when the concentration of titanium (iv) sulfate was below 0.0075 M, owing to the low hydrolysis of the formed peroxotitanium compounds (Fig. 2D and inset). Increasing the concentration to 0.012 M, rutile TiO₂ nanorods configured with single crystal nanowires were obtained, as shown in Fig. 2B. Further increasing the concentration to 0.023 M and 0.033 M, compacted films were observed, as shown in Fig. 2E and F, respectively. The above results demonstrate that lower concentrations of titanium (iv) sulfate in the reaction solution are disadvantageous for the growth of rutile TiO₂ nanorod-like structures with bundled single crystal nanowires assembly due to less growth seeds because of the significantly decreased hydrolysis rate of the titanium precursor (Ti₂(SO₄)₃) in ammonium persulfate and HCl solution (Fig. 2D). When the concentration of titanium (iv) sulfate is beyond a certain value, the production of large amount of TiO₂ growth seeds due to the increased concentration of peroxotitanium compounds in the reaction solution results in the formation of relatively compact and thick nanostructured films (Fig. 2E and F). Besides ammonium persulfate, hydrochloric acid also plays an important role in retarding the hydrolysis of titanium precursors including titanium (iv) sulfate and peroxotitanium compounds. When the HCl concentration is 7.6 M, the solution after hydrothermal reaction remains clear, and no TiO₂ nanostructures are observed on the FTO substrate (Fig. 2G). When the HCl concentration was decreased to 4.6 M, large size TiO₂ aggregates were clearly visible on the FTO substrate, as shown in Fig. 2H, indicating that the growth of rutile TiO₂ nanorods with bundled single crystal nanowires assembly requires a fairly strong acidic aqueous medium. Based on the above detailed investigation, a reaction solution containing 0.0212 M titanium (iv) sulfate, 0.025 M ammonium persulfate, and 6.1 M HCl is favored to fabricate vertically aligned nanorod-like rutile TiO₂ single crystal nanowire bundles on the FTO substrate.

In our synthetic method, the formation of a complicated titanium complex in the presence of ammonium persulfate is crucial to form the seeds for the growth of rutile TiO₂ single crystal nanowire bundles. Under optimal experimental conditions, a plausible mechanism for the formation of vertically aligned nanorod-like rutile TiO₂ single crystal nanowire bundles is depicted in Scheme 1. When the hydrothermal reaction time...
was set at 1 h, the slow hydrolysis of the formed peroxidotitanium compounds resulted in the formation of rutile nuclei (eqn (4)) that were aggregated into rutile TiO$_2$ nanoparticles, as shown in Scheme 1A. Subsequently, the rutile TiO$_2$ nanoparticle film served as the substrate for the anisotropic growth of single crystal nanowires that were assembled into nanorod-like bundles. The studies have demonstrated that the HCl in the reaction solution serves not only as a retardant for hydrolysis reaction but also facilitates the formation of single crystal rutile TiO$_2$ nanowires/nanorods. The selectively adsorbed Cl$^-$ at the (110) crystal plane of rutile TiO$_2$ nanowires/nanorods can effectively suppress further growth of the (110) crystal plane and make the [001] direction become the preferential growth direction. In this work, with further increase in the reaction time (e.g., 3 h and 6 h), the hydrolysis of the peroxidotitanium compounds on the preexisting TiO$_2$ film induced the preferential growth of rutile TiO$_2$ nanowires with 5–7 nm in diameter in the [001] direction which were aggregated into nanorod-like bundles, as shown in Scheme 1B and C. It is believed that the presence of Cl$^-$ and the formation of the complicated titanium complex significantly contribute to this unique nanorod structure.

The photocatalytic activity of the photoanode prepared by the direct growth of vertically aligned rutile TiO$_2$ single crystal nanowire bundles on the FTO substrate was investigated (Fig. 3A). In this study, water was chosen as a probe compound to evaluate the photocatalytic activity due to the global interest in the TiO$_2$ photocatalysis-based water splitting technique for hydrogen production. As a comparison, the photoelectrocatalytic oxidation at a photoanode made of vertically aligned anatase TiO$_2$ nanotube arrays on a titanium foil substrate by an anodization method was also investigated (Fig. 3B). Fig. SII (ESI) shows the XRD pattern and SEM image of the fabricated vertically aligned anatase TiO$_2$ nanotube array photoanode after annealing at 450 °C for 2 h. It can be seen that after calcination, the anatase is the primary crystal phase.
with the applied potential bias, ascribing to the limitation of free photoelectron transport within the TiO₂ photocatalyst films. The photocurrent at higher potentials due to the limitation of the interfacial processes at the photocatalyst/solution interface. For all cases with UV illumination, an increase in the light intensity results in an increase in the saturated photocurrents. Our previous studies have demonstrated that the magnitude of reflects the maximum rate of water oxidation under a given light intensity. The two photoanodes investigated, values under different light intensities were derived from voltammograms shown in Fig. 3A and B at 0.0 V, and plotted against the UV light intensities, ϕ (Fig. 3C). Linear relationships were obtained for both photoanodes with slope values of 0.683 mA m⁻¹ V⁻¹ (R² = 0.999) and 0.223 mA m⁻¹ V⁻¹ (R² = 0.998) for vertically aligned rutile TiO₂ single crystal nanowire bundle and vertically aligned anatase TiO₂ nanotube photoanodes, respectively. For a given set of experimental conditions, the slope of the curve quantitatively represents the photoelectrocatalytic activity of the photoanode. The slope obtained from the photoanode made of vertically aligned rutile TiO₂ single crystal nanowire bundle was almost 3 times higher than that of the vertically aligned anatase TiO₂ nanotube photoanode, which confirms a significantly improved photoelectrocatalytic activity towards water oxidation. Such a superior photoelectrocatalytic activity towards water oxidation could be due to many attributes, such as photoelectron transport and electronic band structure.

One-dimensional TiO₂ nanostructures, such as nanotubes, nanorods and nanowires, have aroused great attention due to their unique structures to provide superior photoelectron transport pathways. The electrical resistance of a photocatalyst is an intrinsic property of a semiconductor photocatalyst that can be used to express the charge transport process inside of the photocatalyst layer. The intrinsic resistance of the photocatalyst layer can be quantified using a simple photoelectrochemical method. In this study, the intrinsic resistance of photoanodes made of vertically aligned rutile TiO₂ single crystal nanowire bundles and the vertically aligned anatase TiO₂ nanotube arrays was measured to manifest the photoelectronic transport processes.

For a given light intensity, the voltammograms shown in Fig. 3A and B revealed a linear photocurrent increase with applied potential bias, before being levelled off. The linear part of the voltammogram exhibits a pure resistor-type behavior, indicating that the overall reaction was controlled by the photoelectron transport process inside the photocatalyst layer. Under such conditions, the photocurrent (the rate of the overall reaction) is determined by the rapidity of the photoelectron transport across the photocatalyst layer. The overall resistance (R) values of each voltammogram can be calculated in accordance with the Ohm law by dividing the total current change by the corresponding photocurrent within the linear part of the voltammogram. Plotting R against Iph gives the hyperbolic curve as shown in Fig. 4A and B for vertically aligned rutile TiO₂ single crystal nanowire bundle and the vertically aligned anatase TiO₂ nanotube array photoanodes, respectively. The quantitative relationship between R and Iph (see eqn (5)) can be obtained by the computer fitting of the data:

\[ R = kI_{\text{ph}} + R_0 = R_1 + R_0 \]  

where \( k \) is a proportionality constant; \( I_{\text{ph}} \) is the saturation photocurrent; \( R_0 \) and \( R_1 = kI_{\text{ph}} \) are the constant and the variant components of the resistance, respectively.

**Fig. 4** Relationships between the resistance and the saturation photocurrent measured at +1.0 V for the rutile TiO₂ nanowire bundle (A) and anatase TiO₂ nanotube (B) photoanodes. Relationships between the resistance and the inverted saturation photocurrent for the rutile TiO₂ nanowire bundle (C) and anatase TiO₂ nanotube (D) photoanodes. Data were derived from Fig. 3A and B.
Eqn (5) indicates that the total reaction resistance, $R_t$, is the sum of a variant ($R_1 = k_{\text{light}}$) and a constant ($R_0$) resistant component.\textsuperscript{11,13,22} For a given photoanode, $R_t$ depends on experimental conditions (i.e., light intensity and reactant concentration etc.), while $R_0$ collectively represents TiO$_2$ crystal boundary resistances and the resistances at TiO$_2$/conductive substrate interface, which is an intrinsic property of the semiconductor photoanode that is independent of experimental conditions.\textsuperscript{17,18,22} For the two photoanodes investigated, plotting $R$ against $I_{\text{light}}$ gives a straight line, indicating that the variant resistance component is inversely proportional to $I_{\text{light}}$, as shown in Fig. 4C and D. $R_0$ values for the two photoanodes can be obtained from the intercepts of the curves with a value of 52.1 $\Omega$ and 71.0 $\Omega$ for the vertically aligned rutile TiO$_2$ single crystal nanowire bundle and the vertically aligned anatase TiO$_2$ nanotube array photoanodes, respectively.

The obtained $k$ values are 592 $\Omega$ mA (mV) and 525 $\Omega$ mA (mV) for the vertically aligned rutile TiO$_2$ single crystal nanowire bundle and the vertically aligned anatase TiO$_2$ nanotube array photoanodes, respectively. The physical meaning of the slope, $k$, can be explained as the minimum applied potential bias required to remove 100% of the photogenerated electrons from the photocatalyst layer, as previously stated.\textsuperscript{18} The higher $k$ value (592 $\Omega$ mA) for the rutile TiO$_2$ over the anatase TiO$_2$ can be attributed to the more positive conduction band edge potential of the rutile TiO$_2$.\textsuperscript{13} Nearly 30% lower $R_0$ (52.1 $\Omega$) obtained from the vertically aligned rutile TiO$_2$ single crystal nanowire bundle photoanode compared to that of the single crystal nanowire bundles suggests a superior electron transport property when compared to the vertically aligned anatase TiO$_2$ nanotube array photoanode with an intrinsic $R_0 = 71.0 \Omega$. This is because the anatase TiO$_2$ nanotubes are composed of polycrystals (bottom left inset in Fig. S1B in the ESI), which enhance the electron scattering effect (as reflected by the higher $R_0$ value) at the crystalline boundaries. For the vertically aligned rutile TiO$_2$ single crystal nanowire bundle photoanode, the low intrinsic resistance could be a significant attribute for the significantly improved photoelectrocatalytic activity towards water oxidation.

It is well known that in a photocatalytic system using the particle form of suspended photocatalysts, anatase TiO$_2$ is more efficient than rutile TiO$_2$ due to the more negative conduction band edge potential of anatase TiO$_2$, which facilitates the reduction half reaction.\textsuperscript{19} However, this is not a disadvantage in photoelectrocatalysis.\textsuperscript{13,21} In photoelectrocatalysis, the applied potential bias provides a motive force to effectively remove the photogenerated electrons from the conduction band and then to the external circuit, so the rate of reduction half reaction no longer relies on the conduction band edge potential.\textsuperscript{13,21} Under the photoelectrocatalytic conditions, the capacity and efficiency of water oxidation is mainly determined by the valence band edge potential of the photocatalyst. For this, electronic band structures of the vertically aligned rutile TiO$_2$ single crystal nanowire bundle and the vertically aligned anatase TiO$_2$ nanotube array photoanodes were investigated. Fig. 5A shows a typical UV-vis diffuse reflection spectra of the two photoanodes. A noticeable red shift in the band gap absorption edge for the vertically aligned rutile TiO$_2$ single crystal nanowire bundle photoanode was observed.\textsuperscript{9} The calculated band gaps of the rutile TiO$_2$ nanowire bundle and anatase TiO$_2$ nanotube films are around 3.06 eV and 3.26 eV, respectively. For photoelectrocatalysis, the larger band gap (3.26 eV) for anatase TiO$_2$ nanotubes could be a beneficial factor under UV light irradiation.\textsuperscript{9} However, the situation could be very different under photoelectrocatalysis conditions. Fig. 5B shows X-ray photoelectron valence-band (VB) spectra of the rutile TiO$_2$ nanowire bundle and anatase TiO$_2$ nanotube films. The VB spectra reveals that the VB maximum of the two TiO$_2$ nanomaterials is at ca. 1.95 eV,\textsuperscript{22,23} meaning that their valence band edge positions are almost identical, and the conduction band (CB) minimum of the anatase TiO$_2$ nanotubes is 0.21 eV more negative than that of the rutile TiO$_2$ nanowire bundles. This is in agreement with the reported results.\textsuperscript{22,23} The electronic band structures of the two TiO$_2$ nanomaterials are illustrated in Fig. 5C. The almost identical valence band edge positions also mean a similar photocatalytic oxidation capacity for the two TiO$_2$ nanomaterials because only an oxidative process can occur at the nanomaterials. The XPS valence-band data also indicate that the nanorod-like rutile TiO$_2$ single crystal nanowire bundle photoanode has sufficient photocatalytic oxidation capacity towards water that is similar to the anatase TiO$_2$ nanotube photoanode (Fig. 5C). The XPS valence-band results further indicate that the low intrinsic resistance ($R_0$ representing superior photoelectron transport capability) of the rutile TiO$_2$ single crystal nanowire bundles contributes significantly to the high photoelectrocatalytic activity towards water oxidation.

4. Conclusion

In summary, vertically aligned anatase-like rutile TiO$_2$ single crystal nanowire bundles were successfully fabricated on FTO...
conducting substrates by a simple and one-pot hydrothermal method. The obtained rutile TiO₂ single crystal nanowire bundle films as photoanodes exhibited superior photocatalytic activity towards water oxidation. This improved photoelectrocatalytic activity using the rutile TiO₂ nanowire bundle photoanodes was mainly attributed to the sufficient oxidation capacity and superior photoelectron transport property. XPS valence-band spectra indicated that the rutile TiO₂ nanowire bundle film had almost identical valence band position with the anatase TiO₂ nanotube array film, meaning a similar oxidation capability. However, the lower intrinsic resistance (Rₑ) of the rutile TiO₂ nanowire bundle film contributed to almost 3 times higher photoelectrocatalytic activity towards water oxidation than the anatase TiO₂ nanotube array film, indicating the superior photoelectron transport property of the rutile TiO₂ nanowire bundles.

Acknowledgements

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Notes and references

CHAPTER 3  VISIBLE LIGHT ACTIVE PURE RUTILE
TiO$_2$ PHOTOANODES WITH 100% EXPOSED PYRAMID-SHAPED (111) SURFACE

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STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

Besides the vertically aligned nanorod-like rutile TiO$_2$ single crystal nanowire bundle photoanode, a UV and visible light active TiO$_2$ photoanode with 100% exposed pyramid-shaped (111) surfaces photoactivity have been developed. The synthesis and characterisation of the rutile {111} faceted TiO$_2$ photoanodes have been studied in this chapter, while the photoelectron transport properties and the disinfection and decomposition properties of the as-synthesised photoanode against biohazards will be studied in Chapter 4 and Chapter 5, respectively. There may be some repetitions due to the requirements of publication, but no material has been previously published or written by another person. The bibliographic details of the co-authored published paper, including all authors, are:


My contribution to the published paper involved:

- Concept development and experimental design;
- Vast majority of experimental work;
- Data collection and analysis;
- Manuscript preparation.

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CHAPTER 4  RUTILE TiO₂ FILM WITH 100% EXPOSED PYRAMID-SHAPED (111) SURFACE: PHOTOELECTRON TRANSPORT PROPERTIES UNDER UV AND VISIBLE LIGHT IRRADIATION

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STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

This chapter consists of a co-authored published paper, investigating the photoelectron transport properties of rutile TiO$_2$ films with 100% exposed pyramid-shaped (111) surface under UV and visible light irradiation. There may be some repetitions due to the requirements of publication, but no material has been previously published or written by another person. The bibliographic details of the co-authored published paper, including all authors, are:


My contribution to the published paper involved:

- The concept development and experimental design;
- Conducting majority parts of photoelectrocatalytic experimental work;
- Data Collection and analysis;
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CHAPTER 5 UV AND VISIBLE LIGHT PHOTOELECTROCATALYTIC BACTERICIDAL PERFORMANCE OF 100% \{111\} FACETED RUTILE TiO$_2$ PHOTOANODE

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CHAPTER 6 INSTANT INACTIVATION AND RAPID DECOMPOSITION OF *ESCHERICHIA COLI* USING A HIGH EFFICIENCY TiO$_2$ NANOTUBE ARRAY PHOTOELECTRODE
STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

This chapter is composed by a co-authored published paper, investigating the instant inactivation and rapid decomposition of *Escherichia coli* using a high efficiency TiO$_2$ nanotube array photoelectrode. There may be some repetitions due to the requirements of publication, but no material has been previously published or written by another person. The bibliographic details of the co-authored published paper, including all authors, are:


**My contribution to the published paper involved:**

- The concept development and experimental design;
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Instant inactivation and rapid decomposition of *Escherichia coli* using a high efficiency TiO₂ nanotube array photoelectrode

Xiaolu Liu, Yanhe Han, Guying Li, Haimin Zhang and Huijun Zhao

Highly ordered TiO₂ nanotube (TNT) array film fabricated by anodisation was used as a photoelectrode in a thin-layer photoelectrochemical flow reactor, exhibiting excellent capability of instant inactivation and rapid decomposition of *Escherichia coli* (E. coli). With photoelectrocatalytic (PEC) treatment, 100% inactivation of E. coli (10 × 10⁷ CFU ml⁻¹) can be achieved within 97 s using TNT, which was almost 2.2 times faster than using a TiO₂ nanoparticle (TNP) photoelectrode with a similar film thickness. The high efficiency TNT photoelectrode combining with the thin-layer photoelectrochemical flow reactor would be promising for scaling up application to effectively remove waterborne pathogens.

1 Introduction

Highly ordered TiO₂ nanotubes (TNTs) fabricated by anodisation have shown great potential in photocatalysis, photovoltaics, photoelectrocatalysis, biomedicine and sensing. It has been reported that in a TiO₂ nanotube film, the recombination rate of photogenerated electrons and holes is almost 10 times slower than that in a TiO₂ nanoparticle film. In this respect, our group has developed a photoelectrochemical approach to quantitatively characterise the photocatalytic resistance of a photocatalyst film. Using this method, the calculated photocatalytic resistances of TiO₂ nanotube and nanoparticle films are 42 Ω and 245 Ω, respectively. Obviously, the highly ordered TiO₂ nanotube array film possesses lower photocatalytic resistance and higher photocatalytic efficiency, which can be ascribed to the unique one-dimensional nanotubular structure providing superior electron transport pathway, thus effectively compressing the recombination of the photogenerated electron/hole pairs.

Due to the excellent photocatalytic activity, TiO₂ photocatalyst has been widely utilised not only to decompose organic pollutants but also to inactivate microorganisms. Although the killing mechanisms remain controversial to date, it has been generally agreed that the bactericidal effect of TiO₂ photocatalyst can be ascribed to the superior oxidative power of the active oxygen species (AOSs) such as \( \cdot \text{OH}, \text{H}_2\text{O}_2, \text{O}_2^-, \text{HO}^+ \) and \( \text{H}_2\text{O}_2 \) under irradiation. However, in a traditionally photocatalytic process (particle suspension system), high recombination of photogenerated electrons and holes, and short lifetime of the AOSs have been the biggest limitation of application. A solution can be achieved by using photoelectrocatalytic technique, by which the photooxidation and reduction half-reaction can be effectively separated, thus inhibiting the recombination of photogenerated electrons and holes, and improving the lifetime of photogenerated carriers and AOSs.

Home-designed thin-layer photoelectrocatalytic flow system has exhibited great potential in organic detection and bactericidal application. Although several works have indicated the potential of TiO₂ nanotube photoelectrodes in bactericidal application, to the best of our knowledge, this is the first report of the use of a highly ordered TiO₂ nanotube array photoelectrode combining with the thin-layer photoelectrocatalytic...
flow system for bactericidal application (Scheme 1). For this, highly ordered TiO₂ nanotube (TNT) film was successfully synthesised by a simple anodisation process. The fabricated TiO₂ nanotube array film was subsequently calcined at 450 °C for 2 h, and used as photoelectrode for photoelectrochemical inactivation and decomposition of E. coli. For comparison, TiO₂ nanoparticle (TNP) film with a similar thickness was also fabricated to evaluate its bactericidal performance.

2 Experimental section

Preparation of TNT and TNP films

Highly ordered TNT array film was prepared by anodisation technique, as reported by our previous work. Before anodisation, titanium foils (0.25 mm, 99.7%, Aldrich) were in turn washed with acetone (99.5%, Merck), isopropanol (A.R., Sigma) and deionised water (Millipore Corp., 18 MΩ cm). The anodisation experiment was performed using a two-electrode electrochemical system at a potential of 20 V in an electrolyte solution containing 0.44% hydrofluoric acid and 12.5% acetic acid (v/v), with titanium foil as anode and platinum mesh as cathode. The as-synthesised sample was rinsed with deionised water and dried by a N₂ stream, then annealed in air at 450 °C for 2 h.

TNP film was prepared by a dip-coating method, as described in our previous work. In brief, TiO₂ colloids containing ca. 60 g L⁻¹ of TiO₂ solid with particle sizes ranging from 8 to 10 nm were prepared by hydrolysis of titanium butoxide (97%, Aldrich), and a certain amount of carbowax (30% w/w based on the solid weight of the TiO₂ colloids) was added to the colloid before use. Pretreated indium tin oxide conducting glass slides (ITO, 8 Ω per square) were then dip-coated in the colloidal solution and dried at room temperature. After dip-coating, the obtained electrodes were then calcined in a muffle furnace at 500 °C for 2 h in air.

Characterisations

The morphology and crystallinity of TNT and TNP films were characterised by scanning electron microscope (JEOL JSM-6360F, Japan) and X-ray diffraction (XRD) (Shimadzu XRD-6000 diffractometer, Japan) techniques.

Measurements

The inactivation experiments were performed in a thin-layer photoelectrochemical flow system with an illumination area of 4.62 cm² and a LED array light source, as described in our previous report. The light intensity was controlled at 8.0 mW cm⁻². During bactericidal experiments, peristaltic pump was used to adjust the flowing speed of the bacteria solution and the time of inactivation and decomposition of bacteria (namely, resident time of bacteria at photoelectrode). E. coli cells incubated overnight at 37 °C were harvested, rinsed completely with sterilised distilled water and then diluted with 0.1 M NaNO₃ solution to 1.0 x 10⁷ CFU mL⁻¹. Reaction time was controlled using a peristaltic pump by adjusting the flow rate. Before and after reaction, 1 mL of E. coli suspension was withdrawn, serially diluted with sterilised saline and spread on nutrient agar plates for the viability count after incubation at 37 °C for 24 h. The viability of E. coli was also confirmed with the fluorescent microscopic method (Live/Dead Bac-light bacterial viability kit, Molecular Probes, Inc.). The decomposition of E. coli cells was assessed with TOC-VCPH/VOC/CPH Total Organic Carbon Analyser (Shimadzu Corporation, Japan), and the results were further confirmed by scanning electron microscope technique.

3 Results and discussion

Structural characteristics

After calcination at 450 °C for 2 h, the fabricated TNT film shows uniform nanotube structures with tube diameters ranging from 60 to 100 nm and a mean length of ca. 486 nm (Fig. 1A and inset). Moreover, anatase phase is dominant for the TNT film after calcination, demonstrating good crystalline nature of the calcined TNT film (Fig. 1B), which is advantageous for improving the photocatalytic activity of the resulting photoelectrode. The fabricated TiO₂ nanoparticle (TNP) film with particle sizes of 20-30 nm possesses a thickness of ca. 500 nm (Fig. 1C and inset). Similarly, the TNP film exhibits predominantly anatase phase after calcination at 500 °C (Fig. 1D).

Bactericidal performance

The bactericidal performance of the TNT film was investigated using E. coli K-12 as probe bacteria with an initial concentration of ca. 1.0 x 10⁷ CFU mL⁻¹ in a thin-layer photoelectrochemical flow reactor (Scheme 1). For comparison, inactivation experiments using a TNP film were also performed. Prior to bactericidal performance evaluation, photoelectrochemical experiments of TNT and TNP photoelectrodes were firstly conducted to choose a suitable applied potential for subsequently photocatalytic experiments. Fig. 2 shows the
voltagmograms of TNT and TNP photoelectrodes in 0.10 M NaNO₃ solution including 1.0 × 10⁸ CFU mL⁻¹ E. coli with or without UV light illumination. For the two photoelectrodes, only a negligible dark current can be observed. Under UV light illumination, the measured photocurrents for the two photoelectrodes initially increase linearly with the applied potential bias due to the limitation of free photogenerated electron transport within the TiO₂ photocatalyst film.⁸⁻¹⁰ The photocurrents reach a saturation state at higher potentials for the two photoelectrodes (ca. -0.05 V for TPN and ca. +0.7 V for TNT) due to the limitation of the interfacial processes at the photocatalyst/electrolyte interface.⁷⁻¹⁰ In this work, +0.7 V of applied potential bias was chosen for the resulting inactivation experiments owing to the photocurrent reaching a saturation state at this potential for both TNT and TNP photoelectrodes.⁸⁻¹⁰

Fig. 3A and B shows the inactivation results by photocatalysis (PC) and photoelectro catalytic (PEC) using TNT and TNP photoelectrodes under UV irradiation. It is clear that the number of viable cells in all PC and PEC experiments for the two photoelectrodes decrease significantly with prolonging treated time. For TNT, it takes nearly 1200 s to achieve 100% inactivation of E. coli by PC, while this performance can be reached within 97 s of PEC treatment (Fig. 3A). Similarly, it requires 1200 s to obtain 99.99% inactivation by PC using TNP, however, 100% inactivation of E. coli can be achieved within 311 s of PEC treatment (Fig. 3B). For PC inactivation, nearly same time (ca. 1200 s) is needed for obtaining 100% inactivation of E. coli for both TNT and TNP photoelectrodes, indicating a very close PC inactivation capability of the two photocatalysts. However, the PEC inactivation efficiency of TNT is almost 3.2 times faster than that of TNP. This can be attributed to the unique nanotubular structure of TNT providing direct photogenerated electron transport pathway, which effectively inhibits the recombinant of the photogenerated electron/hole pairs, dramatically increasing the PEC efficiency.⁷⁻¹⁰ In these cases, direct photoysis using UV light can only obtain 42.5% inactivation of E. coli within 1200 s, further indicating the advantages of photocatalysis and photoelectrocatalysis. For both TNT and TNP photoelectrodes, PEC process exhibits higher inactivation performance of E. coli than PC process, further indicating the advantage of PEC technique, namely, effectively separating the photodissociation and reduction half-reaction by applying a potential bias, thus inhibiting the recombination of photogenerated electrons and holes, and improving the photocatalytic efficiency. The PC and PEC inactivation performance of the two photoelectrodes were also confirmed using the BacLight™ kit fluorescent microscopic method.²⁸ As shown in Fig. 4A-E, before PC and PEC treatments, all bacteria are labeled green as live E. coli can only accumulate Rhodamine 123. After PC and PEC treatments,
E. coli samples become red because the dead E. coli bodies accumulate both Rhodamine 133 and propidium iodide under the given experimental conditions.21 The excellent bactericidal performance of TNT photoelectrode can be due to the highly photoelectrocatalytic capability of the nanotube structure to effectively generate active oxygen species (AOSs) such as OH\(^{-}\), H\(_2\)O\(_2\), O\(_2\)\(^{2-}\), HOO\(^{\cdot}\), and H\(_2\)O\(_2\)\(^{\cdot}\) for E. coli inactivation under UV irradiation.

To quantitatively study the mineralisation level of E. coli cells treated by PC and PEC, total organic carbon (TOC) and inorganic carbon (IC) analyses were performed for TNT and TNP. As shown in Fig. 5, a 16.4% decrease of TOC was obtained for 311 s of PC/TNP treatment, while a 20.7% decrease was achieved for 311 s of PC-TNT treatment. However, the TNT exhibits a 62.8% decrease of TOC after 311 s of PEC treatment, which is much higher than that using TNP (40.2%). The above results were further confirmed by IC analysis, as it can be observed that in all cases, IC amount increases slightly with the decrease of TOC, which is in consistence with the TOC data. It is noticeable that the increase of IC is not equal to the decrease amount of TOC, which can be attributed to the low solubility of CO\(_2\) evolved from the mineralisation of intracellular constituents and framework of E. coli, indicating that the biological carbon contents were mineralised to the ground.22 The above results further support the excellent PEC activity of TNT for bactericidal application compared to TNP.

Electron microscope technique was employed to further examine the decomposition level of E. coli cell attached onto TNT and TNP films after PC and PEC treatments. As shown, the untreated cells present well-preserved cell walls (TNT(I) and TNP(I)), suggesting that the bacteria are active and healthy. No matter TNT or TNP with PC treatment, E. coli cells display a slight change in shape after short treatment time (e.g., 600 s, TNT(II) and TNP(II)). With prolonging PC treatment time to 900 s, severe damages can be observed on the cell wall (TNT(III) and TNP(III)). The cell damage can be due to the AOSs’ role, such as OH\(^{-}\), HOO\(^{\cdot}\), and H\(_2\)O\(_2\)\(^{\cdot}\). With PEC treatment, the TNT exhibits significantly improved decomposition capability (TNT(V, V, VI)) in comparison with the TNP (TNP(V, V, VI)). With 300 s of PEC treatment, the E. coli cell is almost decomposed completely using TNT (TNT(VI)), which is apparently better than using TNP (TNP(VI)), further indicating the superior PEC decomposition capability of E. coli cell for TNT. The above results combining with TOC/IC data provide a direct evidence to confirm the PEC treatment ability to facilitate the decomposition of E. coli compared to the PC treatment for both electrodes. This can be attributed to the PEC approach effectively decreasing the recombination of photogenerated carriers and AOSs and the

Fig. 5: TOC and IC concentration of E. coli solution against PC and PEC treatment time using TNT and TNP photoelectrodes.

Fig. 6: SEM images of E. coli cells attached onto the TNT and TNP films with different treatment conditions. TNT(I) and TNP(I): without treatment; TNT(II) and TNP(II): 600 s of PC treatment; TNT(III) and TNP(III): 900 s of PC treatment; TNT(V) and TNP(V): 600 s of PEC treatment; TNT(VI) and TNP(VI): 150 s of PEC treatment; TNT(VII) and TNP(VII): 300 s of PEC treatment.

Fig. 7: Bactericidal stability of anatase TiO\(_2\) nanotube film by photoelectrocatalytic technique. The concentration of E. coli of 1 × 10\(^{7}\) CFU ml\(^{-1}\), light intensity of 8.0 mW cm\(^{-2}\), an applied potential bias of 0.7 V and the resident time of 60 s.
photocatalytic performance. Moreover, the TNT possesses much higher capability to rapidly decompose E. coli cells than the TNP, owing to its unique one-dimensional nanotubular structures with the superior electron transport characteristics. The stability of the TiO$_2$ nanotube film for photocatalytic inactivation of E. coli after reuse was evaluated by a 10 successive inactivation experiments. As shown in Fig. 7, no obvious bactericidal performance change was observed, demonstrating a superior stability of the TiO$_2$ nanotube photocathode.

4 Conclusions

In conclusion, highly ordered TNT film was prepared, and used as photocathode to evaluate the bactericidal performance in a thin-layer photoelectrochemical flow reactor. Compared to TNP, the TNT exhibited superior photocatalytic performance for instant inactivation and rapid decomposition of E. coli. This work demonstrates the possibility of using high efficiency TiO$_2$ nanotube photocathode combing with thin-layer photoelectrochemical flow reactor for effective removal of waterborne pathogens.

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Notes and references

CHAPTER 7  GENERAL CONCLUSIONS AND FUTURE WORK
7.1 General Conclusions

This thesis systematically investigates the photocatalytic and/or photoelectrocatalytic properties of a series of nanostructured TiO$_2$ photocatalysts under UV and/or visible light irradiation, especially their photocatalytic and/or photoelectrocatalytic disinfection and decomposition capabilities against biohazards.

The superior electron transport and photoelectrocatalytic properties of a vertically aligned nanorod-like rutile TiO$_2$ single crystal nanowire bundles photoanode have been studied in Chapter 2. The vertically aligned nanorod-like rutile TiO$_2$ nanowire bundles were directly grown onto FTO conducting substrates via a facile, one-pot hydrothermal method, with a diameter range of 150-200 nm and a mean length of 0.9 μm, which were assembled by nanowires with 5-7 nm in diameter. As a photoanode, the obtained rutile TiO$_2$ nanowire bundle film shows excellent photoelectrocatalytic activity towards water oxidation, which is almost 3 times higher than that of the highly ordered anatase TiO$_2$ nanotube film photoanode with similar thickness. The improved photoelectrocatalytic activity of the rutile TiO$_2$ nanowire bundles photoanode is mainly due to the sufficient oxidation capacity and superior photoelectron transfer property, which has been manifested by the inherent resistance ($R_0$) of the rutile TiO$_2$ film via a simple photoelectrochemical method. Using this approach, the calculated $R_0$ values are 52.1 Ω and 71.0 Ω for the photoanodes made of vertically aligned nanorod-like rutile TiO$_2$ single crystal nanowire bundles and the vertically aligned anatase TiO$_2$ nanotubes, respectively. The lower $R_0$ of the rutile TiO$_2$ photoanode means a superior photoelectron transfer property. XPS valence-band spectra analysis indicates that the nanorod-like rutile TiO$_2$ film has almost identical valence band position (1.95 eV) when compared to the anatase TiO$_2$ nanotube film, meaning a similar oxidation capability, further confirming the superior photoelectron transport property of the nanorod-like rutile TiO$_2$ single crystal nanowire bundles.

A pure rutile TiO$_2$ photoanode with 100% exposed pyramid-shaped (111) surfaces has been directly synthesised on FTO conducting substrate via a facile one-pot hydrothermal method, which was detailely demonstrated in Chapter 3. The resulting rutile TiO$_2$ film possessed a film thickness of ca. 5 μm and showed good mechanical stability. Calcined at 450°C for 2 h in argon (Ar), the fabricated rutile TiO$_2$ films with 100% exposed pyramid-shaped (111) surfaces were used as photoanodes, exhibiting excellent visible light photoelectrocatalytic activity toward photocatalytic water oxidation and glucose mineralisation. The investigation
confirmed that the superior stability and visible light activity of the pure rutile TiO$_2$ film photoanode can be attributed to the Ti$^{3+}$ doping in the bulk and high reactivity of the exposed $\{111\}$ crystal facets. The findings suggest that other than elemental doping and sensitisation, a visible light active pure TiO$_2$ can be synthesised by a self-doping approach.

In Chapter 4, the photoelectrocatalytic properties of the as-synthesised pure rutile TiO$_2$ film photoanode with 100% exposed pyramid-shaped (111) surfaces have been investigated under both UV (main wavelength of 365 nm) and visible light ($\lambda > 400$ nm) irradiations using water as the probe compound. The photoelectrocatalytic activity of the UV light illuminated photoanode was found to be 0.144 mA/mW, significantly higher than that obtained from the visible light illuminated photoanode (0.102 $\mu$A/mW). Despite this, the determined value of 0.102 $\mu$A/mW represents an excellent visible light photoelectrocatalytic activity of the photoanode. The origin of visible light activity could be attributed to the doped Ti$^{3+}$ in the bulk TiO$_2$, while the superior photoelectrocatalytic activity could be due to the high reactivity of the exposed high energy (111) surface and the superior photoelectron transport property. The photoelectrocatalytic method introduced in Chapter 2 was also used here to manifest the photoelectron transport properties inside the rutile TiO$_2$ film and concurrently quantify the inherent resistances ($R_0$) of UV and visible light illuminated photoanodes. The determined $R_0$ values were 93.5 and 91.3 $\Omega$ for UV and visible light illuminated photoanodes, respectively. The similar $R_0$ values imply a similar photoelectron transport resistance inside the rutile TiO$_2$ film under UV and visible light irradiations, confirming that the measured $R_0$ is an inherent property of the photocatalyst film. This also implies that the rate of charge recombination is similar under UV and visible light irradiation. To our knowledge, this is the first time the electron transport properties of a rutile TiO$_2$ photoanode have been concurrently investigated under UV and visible light irradiation.

The obtained UV and visible light active rutile TiO$_2$ photoanode with 100% exposed $\{111\}$ faceted was utilized for photocatalytic and photoelectrocatalytic bactericidal applications, which has been illustrated in Chapter 5. The bactericidal performances of the photoanode with UV and visible light driven photocatalysis and photoelectrocatalysis processes were evaluated using *Escherichia coli* as the test bacteria. Under the UV irradiation, 99.97% inactivation of 45 mL of $1.0 \times 10^7$ CFU/mL *E. coli* cells can be achieved within 10 min for photoelectrocatalysis.
treatment, while only 96.40% inactivation can be obtained within 30 min for photocatalysis treatment. Under the visible light irritation, 88.46% inactivation can be achieved with 180 min photocatalytic treatment, while 100% inactivation by photoelectrocatalytic treatment can be achieved over the same period. The bactericidal performance of the rutile TiO$_2$ film was also evaluated for sunlight driven photocatalysis treatment. 1.0 mL of $1.0 \times 10^7$ CFU/mL $E. \text{coli}$ cells can be completely inactivated within 2.0 min. The rutile TiO$_2$ film photocatalyst can be used for 20 consecutive bactericidal experiments without a noticeable decrease in bactericidal performance. The experimental results confirm the superiority of the photoelectrocatalysis over the photocatalysis for bactericidal application.

In Chapter 6, highly ordered TiO$_2$ nanotube (TNT) array film fabricated by anodisation was used as a photoelectrode in a thin-layer photoelectrochemical flow reactor, capable of instant inactivation and rapid decomposition of $E. \text{coli}$. By PEC treatment, 100% inactivation of $1.0 \times 10^7$ CFU/mL $E. \text{coli}$ can be achieved within 97 s using the TNT film photoanode, which was almost 2.2 times faster than using a TiO$_2$ nanoparticle (TNP) photoanode with similar film thickness. The study demonstrates the possibility of using high efficiency TiO$_2$ nanotube photoelectrode combing with thin-layer photoelectrochemical flow reactor for effective removal of waterborne pathogens.

### 7.2 Future Work

Although extensive investigations have been carried on the synthesis and fundamental studies of UV and visible light active nanostructured TiO$_2$ photocatalysts and their photocatalytic and photoelectrocatalytic bactericidal applications, this research has raised a number of areas that deserve further investigation in the future.

- Despite superior photocatalytic and photoelectrocatalytic properties of the photocatalysts have been achieved in this study, especially for the photoactivity of the rutile TiO$_2$ photoanode with 100% exposed pyramid-shaped (111) surfaces under visible light irradiation, the PC and PEC bactericidal efficiencies are still far from satisfaction for practical applications. More efforts are therefore needed to develop highly efficient and functional nanostructure photocatalysts for disinfection and decomposition of biohazards.

- The fundamentals of the nanostructure photoanodes, such as the photoelectron transport properties need to be further investigated.
More studies should be carried on inactivation and decomposition of different strains and types of microorganisms. In this thesis and some related studies, disinfection of bacterial such as *E. coli* of different strains, virus and decomposition of some proteins have been investigated. It is necessary to perform more experiments to gain further understanding of PC and PEC disinfection of biohazards.

Furthermore, the mechanisms for PC and PEC disinfection and degradation of microbial cells at the molecular level, especially for the photocatalytic disinfection of viruses, are still at the feasibility studying stage. The lack understanding of precise lethal killing mechanisms has presented as a major obstacle for further improving the bactericidal or virucidal. In this regards, systematically investigation should be carried out to make it clear not just the primary bacteria breakdown mechanisms but also the mineralisation mechanisms of primary degradation products, which is one of the most challenging task in the future.

Overall, this thesis has demonstrated synthesis and characterisation of UV and visible light active nanostructure photocatalysts with superior PC and PEC efficiencies in the application of biohazards inactivation. Fundamentals for photoelectron transport of the synthesised materials, disinfection and decomposition of the bacteria have also been studied. The photocatalytic and photoelectrocatalytic methods with highly efficient, non-toxic, stable, and cost-effective nanostructure photocatalysts are promising for scaling up biohazards removal applications.
Appendix 1

The following appendix is the published Supporting Information for the research article included as Chapter 2 of this thesis:

Supporting Information

Vertically aligned nanorod-like rutile TiO₂ single crystal nanowire bundles with superior electron transport and photoelectrocatalytic properties

Haimin Zhang,¹ Xiaolu Liu,¹ Yibing Li,¹ Qingfeng Sun,¹, b Yun Wang,¹ Barry J. Wood, c Porun Liu,¹ Dongjiang Yang c and Huijun Zhao*¹

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³ Centre for Microscopy & Microanalysis, The University of Queensland, Brisbane, QLD 4072, Australia.
Figure SI 1. (A) XRD pattern of the fabricated anatase TiO$_2$ nanotube arrays after calcination at 450 °C for 2 h. (B) Surface SEM image of the fabricated anatase TiO$_2$ nanotube arrays after calcination; the top right inset of cross-sectional SEM image; the bottom left inset of SAED pattern of individual anatase nanotube.
Appendix 2

The following appendix is the published Supporting Information for the research article included as Chapter 3 of this thesis:

Electronic Supplementary Material

Visible Light Active Pure Rutile TiO₂ Photoanodes with 100% Exposed Pyramid-Shaped (111) Surfaces

Xiaolu Liu, Haimin Zhang, Xiangdong Yao, Taicheng An, Porun Liu, Yun Wang, Feng Peng, Anthony R. Carroll, and Huijun Zhao

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Supporting information to DOI 10.1007/s12274-012-0259-5

Figure S-1  XPS survey spectra of the as-synthesized rutile TiO₂ film (as-synthesized TiO₂) and the calcined rutile TiO₂ film samples in air (TiO₂-air) and Ar (TiO₂-Ar)

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STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

This chapter consists of a co-authored published paper, systematically investigating the bactericidal performances of 100% \{111\} faceted rutile TiO$_2$ photoanode under UV and visible light irradiation. There may be some repetitions due to the requirements of publication, but no material has been previously published or written by another person. The bibliographic details of the co-authored published paper, including all authors, are:


My contribution to the published paper involved:

- The concept development and experimental design;
- Vast majority of experimental work;
- Data collection and analysis;
- Manuscript preparation.

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