Chapter 1

Introduction

“Be a photocatalyst for change.”
—He Ya
Chapter 1

1.1 Introduction

Nanotechnology is an emerging field of research which involves the study, manipulation, creation, and use of materials, devices, and systems typically with dimensions smaller than 100 nm [1]. Nanotechnology offers the facility to engineer the properties of materials by controlling their size. The potential and spirit of nanotechnology is based on the demonstrated fact related to the different properties (i.e., chemical, electrical, magnetic, mechanical, optical, etc.) of nanomaterials to that of their bulk form. The major factors responsible for enhanced properties are the high surface area to volume ratio, quantum confinement as well as high aspect ratio of nanomaterials. Nanoparticles are intermediate structures between bulk materials and atomic structures [2].

Recently, nanotechnology is effectively utilized in a wide range of applications from air and water purifications to surface disinfection incorporating antibacterial effects using nanoparticles. Furthermore, nanotechnology has a variety of applications in the environmental and energy fields, including pollutant degradation, hydrogen evolution, photoelectrochemical conversion, sterilization, biomedicine, and biotechnology [3–5].

One of the most studied aspects of nanotechnology nowadays is their potential to offer the opportunity to fight against microbial infections by nanoparticles. Antibacterial agents are paramount to fight infectious diseases. However, with their extensive use and exploitation, the emergence of bacterial resistance to antibacterial material has become a common phenomenon, which is a major problem [6]. Thus, due to the resistance developed in bacteria against many common antibacterial agents, infectious diseases remain to be one of the supreme health challenges worldwide. Traditional chemical–based
disinfectants which have been applied for centuries in environmental cleaning include chlorine, phenols, iodine, alcohols, and aldehydes [7, 8]. Although these disinfectants are effective against pathogenic microorganisms; they have disadvantages. Many of these disinfectants are volatile, and their byproducts can be toxic and carcinogenic to humans [8]. In addition, drawbacks for conventional antimicrobial agents are the development of multiple drug resistance and adverse side effects, not effective in the longer term, cannot be standardized, and staff-intensive [9].

This has prompted the development of alternative strategies to treat bacterial diseases. Among them, nanomaterials have emerged as novel antimicrobial agents. Particularly, several kinds of antimicrobial nanoparticles and nanosized carriers for antibiotics delivery have proven their effectiveness for treating infectious diseases, including antibiotic-resistant ones, in vitro as well as in animal models [10]. The mechanism by which conventional antibacterial prevents bacterial growth is different from the mechanism by which nanomaterials inhibit bacterial growth. Therefore, nanomaterials have the potential to serve as an alternative antibacterial and to control microbial infections. In the review paper reported by Hajipour and colleagues [6], various application of nanoparticles as antibacterial agents are well documented. These include the utilization of silver, copper, gold nanoparticles, the use of carbon nanotubes, and metal oxides such as Al₂O₃, ZnO, NiO, CuO, and TiO₂ for antibacterial therapy. Bacterial infections can be reduced and healing can be accelerated by using a nanotechnological approach with photoactive antimicrobial materials.
1.2 Nanomaterials based antibacterial activity

Antibacterial activity is related to compounds that locally kill bacteria or slow down their growth, without being in general toxic to surrounding tissue. Bacteriostatic agents inhibit the growth and multiplication of bacteria but cells once again multiply when bacteriostatic agent is removed. Bactericidal agents are used to inhibit the growth of cells and they also trigger pathways within the cell that lead to cell death. These agents may interfere with cell wall synthesis, inhibit protein synthesis, interfere with nucleic acid synthesis or inhibit a metabolic pathway.

Several natural and engineered nanomaterials including chitosan, silver, copper, gold, fullerenes, carbon nanotubes, zinc oxide, and titanium dioxide have demonstrated strong antibacterial activity through diverse mechanisms including photocatalytic production of reactive oxygen species that damage cell components, compromising the bacterial cell envelope, interruption of energy transduction and inhibition of enzyme activity and DNA synthesis [7].

The large number of antibiotic–resistant bacterial strains has prompted a renewed interest in the use of nanoparticles as an antibacterial agent. In addition, currently used chemical agents including hydrogen peroxide, chlorine dioxide and liquid bleach are very corrosive and damaging to the surfaces they come in contact with. The problem associated with its clean up after use is also considerable. Liquid disinfectants are also prone to aging, which further increases the difficulty of their use. However, by using nanosized materials, such drawbacks could be minimized as the nanoparticles are much smaller and have much better penetration ability than micron–sized solid disinfectants. Further, the nanoparticles could be bactericidal by themselves, or they could carry an active disinfectant. Different types of nanomaterials are safe enough to be used on sensitive equipment and could be applied in closed spaces as well as
in open atmospheres. Nanomaterials are increasingly incorporated into bulk materials owing to their potential antimicrobial properties and some of the more recent biotechnological advances in this area have included the application of nanoparticles in textiles, wound repair and as preservatives in cosmetics [11].

The antimicrobial potential of nanomaterials has gone unrecognised throughout history due to the distinct lack of understanding of the mode of toxicity towards certain organisms, although the first reports of anti–microbial materials based on metals date back to Cyrus the Great, King of Persia, who established a board of health and medical dispensary for his citizens [12].

Antibacterial nanoparticles consist of metals and metal oxides, naturally occurring antibacterial substances, and surfactant–based nanoemulsions [7]. Unique physicochemical properties and high surface area to volume ratio are believed to contribute to effective antibacterial activity. Antibacterial nanomaterials offer a distinct benefit for materials that cannot withstand high temperature required for sterilization, under which conventional antibacterial are inactivated.

Photocatalytic bactericidal activity is an increasingly attractive method for both atmospheric and aquatic disinfections [8, 13]. Among all antibacterial materials, TiO$_2$ is probably the most widely used because of its ability of killing a wide range of gram–negative and gram–positive bacteria, filamentous and unicellular fungi, algae, protozoa, mammalian viruses, bacteriophage and cancer cells [13, 14]. Systematic research has been initiated to evaluate the antibacterial efficacy of nanostructured TiO$_2$ as an alternative treatment. The photocatalytic performance of anatase TiO$_2$ is desired to increase, an attempt to use it in a weak intensity visible light. The anatase type is expected to be suitable for such applications because of high photoactivity. Therefore, in the modification of the anatase TiO$_2$ by transition metal ion doping was
concentrated in this study our attention in improve its photocatalytic efficiency. The aims of this study are to tune the band gap of TiO$_2$ in the visible region of light and examine the effect of metal ion dopants on photocatalytic antibacterial activity under visible light illumination.

1.3 Titanium dioxide–as an antibacterial nanomaterial

Among the various semiconductor oxides, TiO$_2$ is an attractive versatile material due to its photo–stability, chemical structure, physical, optical, and electrical properties. One of the unique characteristic of TiO$_2$ is its antibacterial/disinfective activity upon activation by incident light. Its photocatalytic properties have been utilized in various environmental applications to remove contaminants from both water and air [15]. Titania–based photocatalytic systems are used for a variety of applications such as decomposition of unwanted and toxic organic compounds, destruction of pollutants from contaminated water/air and killing of harmful bacteria and cancer cells [16].

TiO$_2$ is an inert material and does not promote chemical reactions without light irradiations. Interfacial electron transfer reactions on the surface of TiO$_2$ have focused attention in strategic applications for solving several problems such as purification of air and water, solar energy conversion, etc. In order to attain a photoactivity application of the TiO$_2$, it is usually required to be in a crystalline phase with an adequate particle size, morphology, and opto–electronic properties [17]. TiO$_2$ is a wide band gap semiconductor material that presents photoactivity upon UV light irradiation, absorbing photons and transforming them into chemical redox species. Thus, its activity is limited to UV region of electromagnetic spectrum, which is less than 5% of solar spectrum. The catalytic properties of semiconductor photocatalyst are very
closely related to the electronic processes occurring inside and on the surface of them. Introduction of impurities into the semiconductor photocatalyst greatly influence it activity. Thus, one of the goals for improvement of the performance of TiO$_2$ photocatalyst is to increase their optical activity by shifting the onset of the response from the UV to the visible region for the efficient utilization of solar energy.

### 1.4 TiO$_2$ structure and properties

Titanium dioxide exists in three crystalline phases, anatase, rutile and brookite [15]. The most common are anatase and rutile, since brookite is quite unstable. The brookite type is not preferred cannot be used in industries because of its instability at room temperature. Rutile exists in a thermodynamically stable phase. Also brookite will be converted into rutile after calcination at higher temperature; while anatase phase is photochemically active as compared to others. The phase transformation also sequences very closely balanced energetics as a function of particle size [18]. Anatase and rutile phases are the main polymorphs and their key properties are summarized in Table 1.1 [19, 20].

Figure 1.1 shows crystal structures of anatase, rutile and brookite type of TiO$_2$. In crystal structure of these phases, each Ti$^{4+}$ ion is surrounded by an octahedron of six oxygen (O$^{2-}$) ions, while each oxygen atom by three titanium atoms. The octahedron in rutile is irregular, showing a slight orthorhombic distortion. The octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. The structures of anatase and rutile crystals have been demonstrated frequently in terms of chains of TiO$_6$ octahedra having common edges. In the rutile structure, each octahedron is in contact with 10 neighbor octahedrons (two sharing edge oxygen pairs and eight
sharing corner oxygen atoms); while in the anatase structure, each octahedron is in contact with eight neighbors (four sharing an edge and four sharing a corner) and in brookite both edges and corners are shared to give an orthorhombic structure [15].

Table 1.1
Physical and structural properties on anatase and rutile TiO₂

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Anatase</th>
<th>Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g mol⁻¹)</td>
<td>79.88</td>
<td>79.88</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1825</td>
<td>1825</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>2500–3000</td>
<td>2500–3000</td>
</tr>
<tr>
<td>Light absorption (nm)</td>
<td>&lt;390</td>
<td>&lt;415</td>
</tr>
<tr>
<td>Optical band gap (eV)</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Mohr’s Hardness</td>
<td>5.5</td>
<td>6.5–7.0</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>183</td>
<td>206</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.54~2.49</td>
<td>2.79~2.903</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>31</td>
<td>114</td>
</tr>
<tr>
<td>Solubility in HF</td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Solubility in H₂O</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>I41/amd</td>
<td>P42/mnm</td>
</tr>
<tr>
<td>Atoms per unit cell</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>a=3.78, b=9.52</td>
<td>a=4.59, b=2.96</td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>3.79</td>
<td>4.13</td>
</tr>
<tr>
<td>Ti─O bond length (Å)</td>
<td>1.94 (4)</td>
<td>1.95 (4)</td>
</tr>
<tr>
<td></td>
<td>1.97 (2)</td>
<td>1.98 (2)</td>
</tr>
</tbody>
</table>
Figure 1.1 Crystal structure of TiO\textsubscript{2} (a) anatase, (b) rutile and (c) brookite [21].
Of the three major polymorphs of TiO$_2$, the rutile TiO$_2$ is the most widely explored in fundamental studies, and anatase is the most widely investigated phase in the applied studies, which plays a central role in many industrial applications [22]. Anatase with a tetragonal crystal structure and a band gap of 3.2 eV has been used in photocatalytic and photoelectrolysis processes. Anatase type TiO$_2$ found to be the most photoactive and the most applied semiconductor for environmental applications such as water purification, wastewater treatment, hazardous waste control, air purification, and water disinfection [19]. The predominant commercial phase of titanium dioxide is anatase which has been widely investigated because of its high activity in photocatalytic applications. This is because in anatase, the bottom of the conduction band is located towards more negative than that of rutile, which results in the production of photogenerated electrons with higher reduction potential [23]. While, in the nanoscale TiO$_2$, there is increase in the optical band gap with slightly shifting of the conduction band levels towards higher reduction potentials with formation of more active, longer-life time radicals for photocatalytic applications.

Among the unique properties of nanomaterials, the movement of electrons and holes in semiconductor is primarily governed by quantum confinement. Nanomaterials transport properties related to phonons and photons are largely affected by their nanoscale and geometry. The specific surface area and surface–to–volume ratio increase dramatically as the size of a material decreases. The high surface area brought about by small particle size is beneficial to many TiO$_2$–based devices. It facilitates the reaction/interaction between the device and the interacting media, which mainly occurs on the surface or at the interface. Thus, the performance of TiO$_2$–based devices is largely influenced by the nanoscale of TiO$_2$ building units [24, 25].
1.5 TiO$_2$ vs. other semiconductor photocatalysts

The prime criteria for an efficient semiconductor photocatalyst is that of photogenerated electrons and holes depend on the position of the energy levels in the semiconductor, i.e., $e^-/h^+$, lies within the band gap domain of the photocatalyst. The energy level at the bottom of conduction band determines the reducing ability of photoelectrons while the energy level at the top of valence band determines the oxidizing ability of photogenerated holes. More specifically, the potential level of a donor species adsorbed on the surface of the photocatalyst needs to be more negative (higher in energy) than the valence band position of the semiconductor in order to swap the electron vacancies. Also, acceptor species must have a potential level more positive (lower in energy) than the conduction band [15]. In addition to possessing a suitable band gap energy, an ideal semiconductor should also be easy to produce and use, economic, photostable, safe for humans and the environment, efficiently activated by visible light and able to catalyze the reaction effectively [26, 27].

In this regard, the band positions of different semiconductors are shown in Figure 1.4. The positions are derived from the flat band potentials in a contact solution of aqueous electrolyte at pH = 0 [28]. One of the key advantages of TiO$_2$ among other semiconductors is that its electronic structure is such that it allows both the reduction of protons ($E_{\text{NHE}}(H^+/H_2)=0.0 \text{ eV}$) and the oxidation of water $E_{\text{NHE}}(O_2/H_2O) = 1.2 \text{ eV}$), which are the key processes for photocatalytic applications [28, 29]. Thus, TiO$_2$ is capable to activate both oxidation as well as reduction reactions simultaneously. However, other semiconductors are effective only for either reduction reaction like Si, or for oxidation reaction like SnO$_2$. The hydroxyl groups on the surface of TiO$_2$ groups can act as donor species, reacting with a valence band holes to produce hydroxyl radicals. These species have a very high oxidation potential.
(E_{\text{NHE}}(\cdot \text{OH}/\text{H}_2\text{O}) = 2.27 \text{ eV}) and are considered to be the key intermediate in the photooxidation reactions [15, 19, 29].

Figure 1.4 The relationship between the band gaps (eV) and redox potentials, using the normal hydrogen electrode (NHE) as a reference, for several semiconductors (Based on the data in ref. [19, 28, 29]).

1.6 Limitations and modifications

Though TiO$_2$ is a very good photocatalyst, it has some restrictions. Owing to its wide band gap energy, it is only active under UV light and has higher rate of recombination for photogenerated electrons and holes. The
photoactivity of TiO$_2$ is critically dependent on the presence of defects in the surface region of the crystal substrate. These defects, known to be oxygen vacancies located in the bridging oxygen rows, causes change in the electronic structure of the material and are also responsible for the electron–hole recombination process; which depends on charge transfer process [30]. Most of the photogenerated charge carriers recombine, releasing the absorbed energy as light or, more frequently, as heat. However, a small fraction of these carriers migrate to the surface where they can be captured by adsorbed species to start the catalytic process [29]. The rate of recombination of photogenerated charges directly affect the rate of photocatalytic process that occurs on the surface of photocatalyst. The rate of recombination is affected by several other factors including the incident light intensity, charge trapping, adsorption of target species, etc. Often, a sacrificial electron or hole scavenging agents are used to decrease the recombination rate which leads to increase the lifetime of the other charge carriers. For hole scavenging, ethanol [31], methanol [32], propanol [33], glycerol [34] and surface hydroxyl groups [35] are generally used. Additionally, that adsorbed molecular oxygen is, most frequently, referred as electron scavenger is used to extend the lifetime of photogenerated holes [36].

Many applications of TiO$_2$ are greatly associated with its optical properties. However, the potential applications of TiO$_2$ based materials are prevented by its wide band gap. The band gap of the anatase TiO$_2$ (3.2 eV) and rutile TiO$_2$ (3.0 eV) lies in the UV region, which absorbs only a small fraction of the sun’s energy (< 5–10%). Due to the inherent relatively large band gap characteristic of TiO$_2$, a great deal of research has been focused on lowering the band gap energy for excitation in order to utilize a large fraction of visible light for conversion of photochemical energy.

To overcome the serious drawbacks of low efficiency and narrow light–response range, many strategies have been developed in the past decades to
modify TiO$_2$ for the utilization of visible light, including non–metal and/or metal doping, dye sensitization, and coupling semiconductors [20]. Thus, one of the goals for enhancement of the photocatalytic performance of TiO$_2$ is to increase their optical absorption by shifting the onset of the response from the UV to the visible region of electromagnetic spectrum.

1.7 Heterogeneous photocatalysis of undoped/doped TiO$_2$

Heterogeneous photocatalysis is one of the most efficient, switchable and inexpensive technology. Scientists estimate that this system can be relevant method in the near future for removal of microorganisms, air and water purification. This method has attracted the attention of industry devoted to developing technology for removing pollutants and microbes from water and the indoor air of houses, hospitals, etc.

In heterogeneous catalysis, solid catalyst and reacting components are physically distinct phases. The cycle of interaction of photocatalyst with reacting species induces photochemical transformation by absorbing light. For better photocatalytic activity, at least one reactant remains in contact with the surface of photocatalyst. The extent of interactions of solid catalyst and reactant molecule depends on chemisorption and physical adsorption. The physical adsorption is the condensation of a vapor to form liquid or the liquefaction of gas on solid surface due to molecular interaction by Van der Waals forces. Chemisorption is due to the electronic rearrangement of both phases of the reacting components. The extent of adsorption and adsorption–desorption equilibrium depends on the temperature, pressure and specific surface area of the catalyst [37].

Photocatalytic activity is initiated through the presence of adsorbed radicals on the TiO$_2$ surface. These radicals are highly oxidative species having
free electrons and could be formed via an adsorbed water or oxygen molecule reacting with the photogenerated electrons and holes. Photogenerated carriers are generated upon irradiation of light having an energy greater than the optical band gap energy (3.2 eV) corresponding to UV wavelengths of 290~380 nm. The electrons are exited from the valence band to the conduction band leaving behind photogenerated holes in the conduction band. Then the excited electrons and holes migrate to the surface and they react with absorbed electron acceptors (typically dissolved oxygen) and electron donors, respectively. Therefore, all photo-induce phenomena of titania nanostructures involve surface bound redox reactions [20]. The resulting reactions give a model of the most commonly used mechanisms to describe the photogeneration of reactive radicals and their activity, in solution or in gaseous surroundings:

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{e}^- + \text{h}^+ \quad (1.1)
\]

\[
\text{H}_2\text{O} + \text{h}^+ \rightarrow \text{H}^+ + \cdot\text{OH} \quad (1.2)
\]

\[
\text{OH}^- + \text{h}^+ \rightarrow \cdot\text{OH} \quad (1.3)
\]

\[
\text{e}^- + \text{O}_2 \rightarrow \text{O}_2^{\cdot\cdot} \quad (1.4)
\]

The photogenerated charge carriers by UV/Visible light irradiation is in competition with the recombination tendency. TiO$_2$ has a relatively slow rate of charge carrier recombination in comparison with other semiconductors due to better diffusion of photogenerated holes. Photogenerated electron–hole pair needs a lifetime of at least 0.1 ns to affect the chemical reactions [19]. The
presence of localized states within band gap of TiO$_2$ can trap the photogenerated charge carriers and leads to the enhanced separation of carriers.

The visible light induced photocatalytic activity of metal–doped TiO$_2$ can be demonstrated by band gap narrowing as a result of new energy levels formed in the band gap of TiO$_2$ as shown in Figure 1.5. The latter levels could be created by doping with metals in the TiO$_2$ host lattice where electrons can be excited from the defect state to the TiO$_2$ conduction band by photons with energy equal or greater than $h\nu_1$. Another benefit of transition metal doping is the improved state of the art trapping of electrons to inhibit electron–hole recombination during irradiation. The decrease of the recombination of charge carriers results in enhanced photocatalytic activity of titania. Also, doping with nonmetals can lead to the formation of isolated impurity energy levels above the valence band which extends photoactivity in the visible regime.

Figure 1.5 Schematic diagram of the TiO$_2$ photocatalytic reaction.
1.8 Statement of problem

Literature survey reveals that there are very few reports available on antibacterial studies of metal–doped TiO$_2$ (M–TiO$_2$) nanoparticles. Antibacterial activity of traditional TiO$_2$ photocatalyst is effective only upon irradiation by ultraviolet light. This greatly restricts the potential applications of TiO$_2$ for use in our living environments. The advantage of visible light responsive photocatalyst might be complementary to existing disinfectants and provide the potential for developing a variety of alternative antibacterial applications. It is necessary to develop safe and cost effective antibacterial materials.

The current area of interest in this field of photocatalytic antibacterial by metal–doped TiO$_2$ is the modification of TiO$_2$ sensitive to visible light. The present work aims to prepare visible light responsive metal ion doped TiO$_2$ by sol–gel method. The prepared photocatalysts were planned to characterize by various sophisticated techniques. The photocatalytic antibacterial activities of the synthesized photocatalysts were planned to study by gram positive and gram negative bacterium.

The objectives of the present study involve:

i) To develop safe and effective antibacterial materials using undoped/metal–doped TiO$_2$ nanoparticles with dopants such as, iron, copper and nickel.

ii) To characterize structural and morphological properties of undoped/metal–doped TiO$_2$ nanoparticles.

iii) To study antibacterial effect of undoped/metal–doped TiO$_2$ nanoparticles in the ultraviolet and/or visible light.

iv) To understand interactions between undoped/metal–doped TiO$_2$ nanoparticles with gram–negative bacteria.
References


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