Chapter II Introductory Survey of Nanostructures for Photoelectrochemical Hydrogen Generation

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CHAPTER I

Introductory Survey of Nanostructures for Photoelectrochemical Hydrogen Generation

1.1 Research Background

Energy crisis today, triggered by depletion and pollution of fossil fuels, particularly of petroleum, is one of the perennial problems. A large amount of harmful gases is produced when fossil fuels are burnt, causing great damage to the environment. Therefore, there is a constant search for clean and renewable energy, which can be effectively substituted for petroleum.

Years of research and development efforts have shown that hydrogen is one of the best substitutes for fossil fuels. Hydrogen is a pure, clean and renewable green energy source. Also hydrogen atom makes up 94% of all the atoms in the universe, and is the most abundant of the chemical elements, constituting roughly 75% of the universe's elemental mass. The physical properties of hydrogen are shown in Table 1.1. Hydrogen can be produced through various routes, including steam reformation, oxidation, photoelectrochemical, photocatalysis, biological method etc. Particularly most attractive routes are photoelectrochemical and photocatalysis decomposition of water [1-8]. In 1972, Fujishima and Honda [1] published the results of photo-assisted water electrolysis using a photoelectrochemical cell (PEC) composed of TiO$_2$ single crystal as photoanode and Pt as cathode involving a chemical bias imposed by pH difference between the two electrodes.
Among a variety of hydrogen generation processes, the photoelectrochemical reaction to obtain hydrogen (H\(_2\)) and oxygen (O\(_2\)) from water-splitting is pollution free.

**Table 1.1 Physical properties of hydrogen**

<table>
<thead>
<tr>
<th>Phase</th>
<th>gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (273 K, 1 atm.)</td>
<td>0.08988 g/L</td>
</tr>
<tr>
<td>Atomic mass average</td>
<td>1.00794</td>
</tr>
<tr>
<td>Melting point</td>
<td>14.01 K</td>
</tr>
<tr>
<td>Boiling point</td>
<td>20.28 K</td>
</tr>
<tr>
<td>Triple point (7.042 kPa)</td>
<td>13.8033 K</td>
</tr>
<tr>
<td>Critical point (1.293 MPa)</td>
<td>32.97 K</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>0.117 kJ/mol</td>
</tr>
<tr>
<td>Heat of vaporization</td>
<td>0.904 kJ/mol</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.1815 W/m-K</td>
</tr>
<tr>
<td>Heat capacity (25°C)</td>
<td>28.836 J/mol-K</td>
</tr>
</tbody>
</table>


green process with advantages of saving energy. If the H₂ –O₂ fuel cell is further integrated, the whole system will form an energy cycle which will be beneficial to the earth protection [5, 9].

1.2 Photocatalysis, Hydrogen Generation and Challenges.

A semiconductor turns to the excited state by irradiating it with light. If the light energy received are high enough, electrons located in the valence band jump to the conduction band. The energy that makes electrons jump up is provided by the light with a desired wavelength. For a semiconductor photocatalyst to be efficient, the different interfacial electron processes involving e⁻ and h⁺ must compete effectively with the major deactivation processes involving e⁻ - h⁺ recombination, which may occur in bulk and at the surface. Fig. 1.1 shows the main processes occurring on a semiconductor particle.

Electron-hole (e⁻ - h⁺) recombination can occur at the surface or in the bulk of the semiconductor. At the surface of the particle, photogenerated electrons can reduce an electron acceptor A and photogenerated holes can oxidize an electron donor D [10]. Many kinds of n-type semiconductor materials have been investigated as photocatalyst, such as TiO₂, ZnO, CdSe, WO₃, ZnS, Fe₂O₃ and SnO₂. The band gap diagram of the different semiconductor materials is shown in Fig. 1.2 for comparison.

Various semiconductors exhibit photocatalytic activities that decompose organic compounds under the UV light. There are some semiconductors whose band gap is smaller than that of TiO₂. But most of these semiconductors are chemically or photochemically corrosive which is harmful to the environment. For example, CdSe has been found to be photocatalysis active and its band gap is 1.4 eV. However, due to its
Fig. 1.1 Illustration of the major processes occurring on a semiconductor particle following electronic excitation.
Fig. 1.2 Energy structures of various photo-semiconductors.
strong tendency to decompose and dissolve during illumination in aqueous solution, its application is limited. For the past three decades, the metal oxide systems have been studied extensively and are gaining popularity in a number of applications for their availability and ease of fabrication. The most frequently studied semiconducting photoanode materials are TiO$_2$ [11], SrTiO$_3$ [12], WO$_3$ [13], SnO$_2$ [14] and Fe$_2$O$_3$ [15]. The photocorrosion stability of the photoanode and/or photocathode, its wavelength response, and current-voltage behaviour are the key factors underlying the ability to achieve a useful device. An ideal semiconductor photocatalyst should be (1) chemically and biologically inert, (2) stable photocatalysis, (3) easy to produce and easy to use, (4) efficiently activated by solar light, (5) able to efficiently catalyze reactions, (6) cheap, and (7) harmless to the environment and human life. Titanium dioxide is close to being an ideal photocatalyst, displaying almost all the above attributes. One exception is that it does not absorb visible light.

Hydrogen is obtained from fossil fuel such as petroleum, coal, natural gas etc., water, biomass (bacteria) and various kinds of hydrogen containing sources. About 95% of the hydrogen is mainly produced by stream reforming of hydrocarbons (from fossil fuel, coal and natural gas). Most of the rest is produced by water electrolysis using electricity, which is mainly generated by fossil fuels. However, this technology results in the emission of CO$_2$ and CO, and so the hydrogen obtained from the combustion of fossil fuels can’t be considered to be environmentally benign.

A sustainable hydrogen economy requires hydrogen to be produced using a renewable method. Figure 1.3 shows a number of possible pathways to generate
H₂ utilizing solar energy. The heat energy contained in the solar irradiation can be utilized to

Fig. 1.3 Pathways of generating hydrogen.
directly decompose water to hydrogen and oxygen without electrolysis. This process, called thermolysis of water, takes place at elevated temperatures [16]. However, even at pressures as low as 0.05 bar and temperatures as high as 2500K only about 25% of the water dissociates [17]. The rapid back reaction of \( \text{H}_2 \) and \( \text{O}_2 \) to form water at these temperatures prevents this pathway from being a viable approach.

For the above reasons, therefore, many studies focus on developing advanced technologies to produce hydrogen from renewable energy resources, such as solar, wind, hydroelectric, or hydrothermal energy. Development of hydrogen produced from renewable energy resource is important and in more than one way including thermolysis where heat is from solar power; catalysis of biomass, electrolysis of water, photoelectrochemical hydrogen production and pyrolysis where sunlight is used as energy. In this study the main stress falls on photoelectrochemical hydrogen production.

In photoelectrochemical solar cells, light energy may be converted into electrical and/or chemical energy, see Fig. 1.4. The performance and effectiveness of a solar cell device mainly depend upon its design and the properties of the photovoltaic materials include especially the light absorbers and their connections to the external circuit. The choice of the charge mediator involved may also be crucial.

Light can be pictured as a stream of photons, energy packages of definite size, or quantum of electromagnetic wave energy, whose energy depends upon the frequency or colour. Whenever light is absorbed by matter, photons transfer their energy and electrons are excited to higher energy states, usually followed by relaxation to their ground states. In
a photovoltaic device, the relaxation may be avoided as the energy stored in the excited electrons is here quickly transferred to an external circuit, in order to do electrical work.

Fig.1.4 Illustration of the operating principle of a photoelectrochemical cell.
When an n-type semiconductor is immersed in solution, an electric field is formed spontaneously at the semiconductor-electrolyte interface; e- - h+ pairs get generated in the region of the electric field, i.e. the space-charge region, is separated efficiently, rather than undergoing recombination. The reaction is expressed as

\[ \text{TiO}_2 + 2\text{h}^+ \rightarrow 2\text{h}^+ + 2\text{e}^- \quad (1.1) \]

The photo-generated electrons and holes can recombine in bulk or on the surface of the semiconductor within a very short time, releasing energy in the form of heat or photons. For hydrogen production, the conduction band (CB) level should be more negative than the hydrogen production level \( (E_{\text{H}_2/\text{H}_2O}) \) while the valence band (VB) should be more positive than the water oxidation level \( (E_{\text{O}_2/\text{H}_2O}) \) for efficient oxygen production from water by photoanode. The overall reaction for hydrogen generation via photoelectrochemical splitting of water is given below.

\[ 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2 \quad (1.2) \]

\[ 2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+ \quad (1.3) \]

\[ 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 E_{\text{rev}} = 1.229 \text{ V} \quad (1.4) \]

The process results in oxygen and hydrogen evolution at the photoanode and cathode, respectively. The related charge transport involves the migration of hydrogen ions in the electrolyte and the transport of electrons in the external circuit.

### 1.3 Titania Nanotube Arrays in Photoelectrolysis

\( \text{TiO}_2 \) exhibits excellent charge transfer properties and photochemical stability; furthermore its bandgap includes the redox potential for the \( \text{H}_2\text{O} \) reaction allowing photogeneration of oxygen through watersplitting \([6, 18]\). However, the bandgap of...
TiO$_2$ limits its activation only to UV radiation which accounts for $\approx 5\%$ of solar spectrum energy. Highly-ordered vertically oriented TiO$_2$ nanotube-arrays fabricated by anodization of titanium at constant voltage constitute a material architecture that offers a large internal surface area without a concomitant decrease in geometric and structural order. The precisely oriented nature of the crystalline (after annealing) nanotube arrays makes them excellent electron percolation pathways for vectorial charge transfer between interfaces[19]. The use of vertically oriented titania nanotube arrays has been studied as an extraordinary enhancement of the extant TiO$_2$ properties, such as hydrogen sensing [19], photocatalytic property [20] and superior charge collection efficiency [21, 22]. While TiO$_2$ nanotube arrays demonstrate a photoconversion efficiency of 16.5% under UV illumination (320 nm – 400 nm) its efficiency under visible light is limited to only 0.6 % because of its bandgap [23-25].

**Properties and Structure of TiO$_2$**

TiO$_2$ occurs in three crystalline forms: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) structures. Brookite has an unstable structure, so it is not widely studied. Anatase and rutile are the common and stable structures. Rutile structure is stable at high temperature. Anatase can undergo transformation to rutile phase at high temperature. The anatase and rutile structures of TiO$_2$ can be described in terms of chains of TiO$_6$ octahedral in which each Ti$^{4+}$ ion is surrounded by an octahedron of six O$^{2-}$ ions as shown in Fig. 1.5.

The octahedron in anatase is far more distorted than that in rutile; hence the symmetry of anatase is lower than orthorhombic. The Ti-Ti bond distances in anatase (3.79 and 3.04 Å) are greater than that of rutile (3.57 and 2.96 Å) whereas the Ti-O bond
Fig. 1.5 Bulk structures of rutile and anatase.
distances are shorter than in that of rutile (1.934 and 1.980 Å in anatase versus 1.949 and 1.980 Å in rutile). Each octahedron in the anatase structure is connected with eight neighbour octahedrons; in rutile structure, ten neighbour octahedrons. The properties of anatase and rutile TiO$_2$ are shown in Table 1.2.

Crystal system of anatase and rutile TiO$_2$ belong to the tetragonal type. The space group of anatase is I4$_1$/amd and the space group of rutile is P4$_2$/mnm. Lattice constants of anatase TiO$_2$ are as follow: a = b = 3.78 Å, c = 9.49 Å and c/a ratio =2.51. Lattice constants of rutile TiO$_2$ are as follows: a = b = 4.58 Å, c = 2.95 Å and c/a ratio =0.64. Rutile exhibits higher value of specific gravity, refractive index, hardness and permittivity than anatase. Band gap energy of anatase and rutile TiO$_2$ are 3.2 eV and 3.0 eV, respectively. The above differences cause different specific gravities and electronic band structures between the two types of TiO$_2$. Both anatase and rutile phases are commonly used as photocatalyst under the UV light irradiation. It has been reported that anatase TiO$_2$ exhibits a greater photocatalytic activity than rutile.

**Need for ordered nanostructures**

Nanostructures have demonstrated unique properties and superior performance when compared to the bulk counterparts. The use of porous nanocrystalline semiconductor films has led to substantial progress in the field of low cost photoelectrochemical energy conversion [6, 26]. The most efficient photoelectrochemical energy conversion devices have consisted of porous crystalline nanoparticulate titania films of several microns thick, obtained by casting a colloidal sol, with a three dimensional network of interconnected 15-20 nm sized nanoparticles. The enormous internal surface area of the porous film enables efficient light harvesting and maximization
## Table 1.2 Properties of anatase and rutile TiO$_2$

<table>
<thead>
<tr>
<th>Properties</th>
<th>Anatase</th>
<th>Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Molecular weight (g/m)</td>
<td>79.866</td>
<td>79.866</td>
</tr>
<tr>
<td>Space group</td>
<td>I$_4$ /amd</td>
<td>P$_4$$_2$/mn</td>
</tr>
<tr>
<td>a</td>
<td>3.784.58</td>
<td></td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>b 3.78</td>
<td>4.58</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3.94.2</td>
<td></td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.52</td>
<td>2.71</td>
</tr>
<tr>
<td>Hardness</td>
<td>5.5-6.0</td>
<td>6.0-7.0</td>
</tr>
<tr>
<td>Permittivity</td>
<td>31</td>
<td>114</td>
</tr>
<tr>
<td>Band gap energy (eV)</td>
<td>3.23.0</td>
<td></td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>Converts to rutile 1858</td>
<td></td>
</tr>
<tr>
<td>Photo-activity</td>
<td>High Low</td>
<td></td>
</tr>
</tbody>
</table>
of the photogenerated charge in nanocrystalline electrodes. However, the structural disorder at the contact between two crystalline particles leads to an enhanced scattering of free electrons, thus reducing the electron mobility [27]. This results in charge transport being limited by the diffusion of holes into the electrolyte and by the hopping of electrons along a poorly formed network electrode [28]. Ordered and strongly interconnected nanoscale architecture would eliminate randomization of the particle network, increase contact points for good electrical connection and decrease small necking points that have been shown to develop between adjacent-bound particles in the current nanoparticulate titania system. Therefore, ordered nanostructures such as arrays of nanowires, nanorods and nanotubes are the focus of exploratory research for the potential enhancement of electron percolation pathways and light conversion as well as improved ion diffusion at the semiconductor-electrolyte interface.

1.4 Literature Review of Titania

Among the methods known for the synthesis of nanostructured titania, from nanotubes to nanowires and nanopores, the most important are anodization, sol-gel, hydrothermal, and vapour deposition methods [29,30]. Anodization has attracted attention as it is a relatively low cost process and represents an ideal solution for growing nanostructured TiO$_2$ for use in the variety of fields. During anodization of titanium metal, the oxide that is forming is a barrier type (pore free) film. Its anodizing ratio, defined as the maximum oxide thickness obtainable per volt, is in the range 1-3nm/V [31]. As the oxide film grows thicker and its resistance increases, it acts as a barrier to the flow of ions and electrons and the oxidation process slows and eventually ceases. The presence of a pore free barrier layer limits the final thickness of the oxide to within a few hundred
nanometres. Some of the electrolytes capable of forming barrier type TiO₂ films are based on aqueous solutions of sulfuric, phosphoric or acetic acid [32], as listed in Table 1.3. Nanoporous and tubular titania layers form on the passage of an anodization current while using fluoride containing electrolytes. The titania layers develop perpendicular to the metal substrate and, under controlled conditions, are self-organized [31]. Recently, bundles of TiO₂ nanotubes (not self-organised) have been prepared by rapid breakdown anodization (high voltage) in chloride (fluoride free) containing electrolytes [34, 35]. Titanium and titanium dioxide are readily dissolved in fluoride-based electrolytes, particularly those containing hydrofluoric acid. Forty ions react with both the metal and the oxide to form a titanium hexafluoride complex [TiF₆²⁻], which is stable in water. As shown in Table 1.3, the structure of a nanoporous or nanotubular oxide has a thin barrier inner layer at the metal/oxide interface (M/MO) and a porous outer layer at the oxide/electrolyte (MO/Electrolyte) interface [35].

The ability to grow porous oxide anodic structures, particularly nanoporous alumina, has been known for more than 60 years. In 1953 Keller and co-workers [36] described the anodic alumina array as a hexagonally close-packed duplex structure consisting of a porous and a barrier (pore free) layer. The degree of self-order in porous alumina was optimised in 1995 by Masuda and Fukuda [37] using a two-step anodizing approach. While the growth mechanism of nanoporous alumina is well understood, the generation of nanoporous and nanotubular titania is a relatively new research area. The recent developments in this area will now be described.

In 1999, Zwilling and co-workers commented on the formation of nanoporous anodized titania [38], while the first report on anodized titania nanotubes grown using a
Table 1.3 Different morphologies of titanium dioxide grown by anodization

<table>
<thead>
<tr>
<th>Barrier type oxide</th>
<th>Nanoporous and Nanotubular type oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td></td>
</tr>
<tr>
<td>Thin (few hundreds of nm) and compact</td>
<td>a. Inner layer at the M/MO interface: thin (≤ 50 nm), barrier type</td>
</tr>
<tr>
<td>b. Outer layer at the MO/Electrolyte interface: porous/tubular form (up to or &gt;1000 µm)</td>
<td></td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td></td>
</tr>
<tr>
<td>Solutions of a. Aqueous and organic solutions sulfuric, phosphoric, containing fluoride ions [31]</td>
<td></td>
</tr>
<tr>
<td>acetic acid [32] b. Chlorine based solutions [33, 34]</td>
<td></td>
</tr>
</tbody>
</table>

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dilute solution of hydrofluoric acid (HF) as an electrolyte, is dated 2001 [35]. The thickness of the anodic layer was limited to approximately 0.5µm, since the relatively aggressive HF etched and dissolved most of the growing oxide, preventing the formation of long nanotubes.

The rapid rate of titania dissolution was reduced by replacing the HF acid with less aggressive solutions containing fluoride salts, raising the maximum thickness up to 2-3µm [39-42]. It is interesting to note that tubes prepared in water based media exhibit irregularities (ripples) along the walls of the nanotubes. The dissolution rate of titania and titanium in fluoride ions is maximised at lower pH and Macak and colleagues [40] explained the increase in thickness in terms of a higher dissolution at the pore bottom (localised acidification due to titanium hydrolysis and oxide dissolution). While the pore bottom is at a low pH, the pore mouth (top of the pores/tubes) remains under a protective environment (higher pH) by using chemical buffer species \([\text{NH}_4\text{F}/(\text{NH}_4\text{)}_2\text{SO}_4]\). The same authors [40] speculate that a voltage ramp applied at the beginning of the anodizing process would help set up a pH gradient between the bottom and the top of the tubes extending the oxidation process to longer time.

The nanotubes refer to smooth tubes (i.e. no ripples along the wall), prepared in organic electrolytes (some almost water-free), where the dissolution rate of the forming oxide is minimised. It can be observed that the tube obtained using water are more rough and irregular (i.e. ripples along the wall) than the smooth tubes grown in organic media. At first, the idea was to use a viscous electrolyte [43], where ion diffusion was slower than in water, in order to increase the pH gradient between the bottom and the top of the tubes. This led to the formation of titania nanotubes up to 7µm thick. They also attributed the
smoothness and the regular morphology of the tube walls to the lower diffusion coefficient of the electrolyte which suppresses the pH bursts at the pore bottom which occur when working in aqueous media.

Over the last few years, tubes upto 320 µm long have been grown by Grimes’s research group using polar organic electrolytes to enhance the extraction of Ti$^{4+}$ from the metal and inhibiting the growth of the barrier layer at the metal/oxide interface, by using larger cations in the salts as a source of fluoride ions [44-47]. Nanotubes up to 1000µm have also been grown using ethylene glycol based electrolytes [48]. Schmuki and co-workers have obtained similar results [49], also enhancing the ordering to that of a hexagonally close packed array using a multi-step approach [50], opening the way for longer and thinner nanotubes.

Synthesis of TiO$_2$ nanotube arrays using fluoride free electrolytes includes HCl, H$_2$O$_2$, and their mixtures, perchloric acid solutions, and mixtures of oxalic acid, formic acid, and sulfuric acid with NH$_4$Cl [51-54]. In one of the first reports of ordered TiO$_2$ nanotube array fabrication using nonfluoride based electrolytes, Allam and Grimes synthesized nanotube arrays of ~300 nm length, 15 nm pore diameter, and 10 nm wall thickness using an aqueous solution containing 3M HCl, [51] in the potential range of 10–13 V. Longer nanotubes of up to ~600 nm length could be obtained by anodizing at 20 V but the resulting nanotube array was highly disordered. It is possible to further increase the nanotube length by adding hydrogen peroxide (H$_2$O$_2$) to the HCl-containing electrolyte. H$_2$O$_2$ acts as a strong oxidizing agent that offers a thicker oxide layer available for electrochemical etching [52].
Theoretically, all types of semiconductors that satisfy the above-mentioned requirements can be used as photoanode for hydrogen production. However, most of the semiconductors, such as CdS and SiC, that cause photocorrosion, are not suitable for water-splitting. Having strong catalytic activity, high chemical stability and long lifetime of electron-hole pairs, TiO$_2$ is the most widely used for photoanode. Recently, most studies have focused on the TiO$_2$ nanotube photoanode for water splitting reaction. Table 1.4[55-72] summarizes the previous results for photoelectrochemical cell’s efficiencies with different structures from literatures.

Khan et al. (2002)[62] synthesized a chemically modified (CM) n-type TiO$_2$ by flame pyrolysis of Ti metal. This material, which carbon substitutes for some of the lattice oxygen atoms, absorbs the ultraviolet and most of the visible light of the solar spectrum. The obtained efficiency of maximum photoconversion efficiency was 8.35%. Recently, the fabrication of functional titania nanotubes have been intensively studied due to its unique physico-chemical properties for water-splitting applications. Mor and co-workers[56] have made films of tapered, conical-shaped titania nanotubes using anodic oxidation with time-dependent linearity. They achieved highly ordered TiO$_2$ nanotube arrays up to 220 µm in length, with aspect ratios up to 1400[67], by anodizing of Ti foil, as well as enhancing the photocleavage of water. However, the maximum photoconversion efficiency was 16.25%. The energy conversion efficiency from solar to hydrogen by TiO$_2$ photoanode water-splitting is still low, mainly due to the following reasons:
(1) **Recombination of photogenerated electron-hole pairs:** CB electrons can recombine with VB holes very quickly and release energy in the form of unproductive heat or photons;

**Table 1.4. Experimental data on efficiency of photoelectrochemical cell of titania.**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Cell structure</th>
<th>Light source</th>
<th>Efficiency</th>
<th>Hydrogen generation rate</th>
</tr>
</thead>
</table>
| Fujishima et al. [55] | a: TiO₂  
c: Pt-black  
e: 1M NaOH (a) / 0.5M H₂SO₄ (c) | Sun light           | η = 0.4 % | 0.028 mL/h cm²           |
| Mor et al. [56]  | a: TiO₂ nanotubes /Ti  
c: Pt-black  
e: 1M KOH | UV light 320-400 100 mW/cm² | η = 6.8 % | 2.4 mL/h cm²             |
| Nozik [57]       | a: TiO₂  
c: Pt  
e: 1M Phosphate buffer | UV light 300 – 400 26 mW/cm² | η = 2.4 %  
(V<sub>Bias</sub>=0.8 V) | 0.379 mL/h cm² |
| Nozik [57]       | a: TiO₂  
c: Pt  
e: 0.1M KOH | UV light 300 – 400 26 mW/cm² | η = 3.4 %  
(V<sub>Bias</sub>=1.0 V) | 0.755 mL/h cm² |
| Nozik [57]       | a: TiO₂  
c: Pt  
e: 0.2M H₂SO₄ | UV light 300 – 400 26 mW/cm² | η = 6.8 %  
(V<sub>Bias</sub>=0.8 V) | 0.65 mL/h cm² |
| Nozik [57]       | a: TiO₂  
c: Pt  
e: 0.1M KOH (a)/0.2M H₂SO₄ (c) | UV light 300 – 400 26 mW/cm² | η = 10.1 %  
(V<sub>Bias</sub>=0.4 V) | 1.016 mL/h cm² |
| Quanet al. [58]  | a: TiO₂ nanotubes/Ti  
c: stainless steel  
e: 0.1M Na₂SO₄ | Hg lamp (300 W) | η = 12.3 % | 0.379 mL/h cm² |
<table>
<thead>
<tr>
<th>Study</th>
<th>Composition</th>
<th>Light Source</th>
<th>Efficiency (η)</th>
<th>Rate (mL/h·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bak et al. [59]</td>
<td>a:TiO₂</td>
<td>Sunlight</td>
<td>0.4 %</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c: Pt</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>e: 0.5 M Na₂SO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Srivastava et al. [60]</td>
<td>a:TiO₂</td>
<td>Xe arc lamp</td>
<td></td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>c: Pt</td>
<td></td>
<td></td>
<td>mL/h·cm²</td>
</tr>
<tr>
<td></td>
<td>e: 1 M NaOH (a) / 5 M H₂SO₄ + 1 M K₂SO₄ (c)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Akikusa and Khan [61]</td>
<td>a: (CM)−n-TiO₂</td>
<td>Xe arc lamp (150 W)</td>
<td>1.6 %</td>
<td>1.087</td>
</tr>
<tr>
<td></td>
<td>c: Pt</td>
<td></td>
<td></td>
<td>mL/h·cm²</td>
</tr>
<tr>
<td></td>
<td>e: 5 M KOH (a) / 3 M H₂SO₄ (c)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Khan et al. [62]</td>
<td>a: TiO₂</td>
<td>Xe arc lamp (150 W)</td>
<td>8.35 %</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c: Pt</td>
<td></td>
<td></td>
<td>40 mW/cm²</td>
</tr>
<tr>
<td></td>
<td>e: 5 M KOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grimes [63]</td>
<td>a: TiO₂ nanotubes / Ti</td>
<td>UV light 320 – 400 nm 98 mW/cm²</td>
<td>16.25 %</td>
<td>1.087</td>
</tr>
<tr>
<td></td>
<td>c: Pt</td>
<td></td>
<td></td>
<td>mL/h·cm²</td>
</tr>
<tr>
<td></td>
<td>e: 1 M KOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Watcharenwong et al. [64]</td>
<td>a: TiO₂ nanotubes / Ti</td>
<td>UV light 270 – 400 nm 11 mW/cm²</td>
<td>12.1 %</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c: Pt</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>e: 0.5 M Na₂SO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mohapatra et al. [65]</td>
<td>a: C-TiO₂ nanotubes / Ti / TiO₂ nanotubes</td>
<td>UV light (300 W) 11 mW/cm²</td>
<td>2.375</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c: Pt-TiO₂ / Ti / Pt-TiO₂</td>
<td></td>
<td>mL/h·cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>e: 1 M KOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Authors</td>
<td>Reagent 1</td>
<td>Reagent 2</td>
<td>Reagent 3</td>
<td>Illumination Source</td>
</tr>
<tr>
<td>------------------</td>
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<td>--------------------</td>
<td>--------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Mohapatra et al. [66]</td>
<td>a: TiO&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;xC&lt;sub&gt;3&lt;/sub&gt; nanotubes/Ti/TiO&lt;sub&gt;2&lt;/sub&gt; nanotubes&lt;br&gt;c: Pt-TiO&lt;sub&gt;2&lt;/sub&gt;/Ti/Pt-TiO&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;e: 1M KOH</td>
<td>UV light (330+/-70nm)&lt;br&gt;13.9 mW/cm²</td>
<td>η = 13.3 %</td>
<td>UV light (520+/-46 nm)&lt;br&gt;5.27 mW/cm²</td>
</tr>
<tr>
<td>Shankar et al. [67]</td>
<td>a: TiO&lt;sub&gt;2&lt;/sub&gt; nanotubes /Ti&lt;br&gt;c: Pt&lt;br&gt;e: 1M KOH</td>
<td>Hg arc lamp&lt;br&gt;320 – 400 nm&lt;br&gt;98 mW/cm²</td>
<td>η = 16.25 %</td>
<td></td>
</tr>
<tr>
<td>Shaban et al. [68]</td>
<td>a: (CM)-n-TiO&lt;sub&gt;2&lt;/sub&gt;&lt;br&gt;c: Pt&lt;br&gt;e: 5M KOH</td>
<td>Xe arc lamp&lt;br&gt;100 mW/cm²</td>
<td>η = 11.31 %</td>
<td></td>
</tr>
<tr>
<td>Gong et al. [69]</td>
<td>a: TiO&lt;sub&gt;2&lt;/sub&gt; nanotubes&lt;br&gt;c: Pt&lt;br&gt;e: 2M Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; + 0.5M ethylene glycol</td>
<td>Xe lamp (300W)</td>
<td>10 mL/h cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
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<tr>
<td>Zhang et al. [70]</td>
<td>a: TiO&lt;sub&gt;2&lt;/sub&gt; nanotubes&lt;br&gt;c: Pt&lt;br&gt;e: 1 M KOH</td>
<td>Simulated Solar light&lt;br&gt;100 mW/cm²</td>
<td>η = 0.49%</td>
<td></td>
</tr>
<tr>
<td>Sun et al. [71]</td>
<td>a: TiO&lt;sub&gt;2&lt;/sub&gt; nanotubes&lt;br&gt;c: Pt&lt;br&gt;e: 1 M KOH + 0.5MH&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Xenon lamp (350) W&lt;br&gt;110 mW/cm²</td>
<td>η = 4.49%</td>
<td>122 µmol/ h cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Liu et al. [72]</td>
<td>a: TiO&lt;sub&gt;2&lt;/sub&gt; nanotubes&lt;br&gt;c: Pt&lt;br&gt;e: 1 M KOH + Ethylene glycol</td>
<td>Solar simulator (300W)&lt;br&gt;(V&lt;sub&gt;Bias&lt;/sub&gt;=0.5 V)</td>
<td>4.4 mL/h cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>
(2) **Fast backward reaction:** Decomposition of water into hydrogen and oxygen is an energy increasing process, thus backward reaction (recombination of hydrogen and oxygen into water) easily proceeds;

(3) **Inability to utilize visible light:** The band gap of TiO$_2$ is about 3.2 eV and only UV light can be utilized for hydrogen production. Since the UV light only accounts for about 4% of the solar radiation energy while the visible light contributes about 50%, the inability to utilize visible light limits the efficiency of solar photoelectrochemical hydrogen production.

In order to solve the above-listed problems and make solar photoelectrochemical hydrogen production feasible, continuous efforts have been made to promote the photocatalytic activity and to enhance the visible light response.

**1.5 Scope of the Present Work**

The scope of the present investigation includes:

- Fabrication of titania nanostructures using four different electrolytes in electrochemical anodization method with linear, pulsed and constant voltage.
- Physico-chemical characterization of the prepared materials by XRD, FEGSEM, EDX, DRUV-Visible, PL and EIS.
Designing a Photoelectrochemical cell for generation of hydrogen and oxygen and photoelectrochemical production of hydrogen by various morphologies of titania nanostructures/tubes with and without the sacrificial agent.

In the present work titania nanostructures are prepared by four different methods using four different electrolytes and also with four different potentials for each one are compared. In the first method the electrolyte consisted of hydrofluoric acid in double distilled (DD) water. In the second method the electrolytes consisted of KF and ethylene glycol solution. In the third method the electrolytes NH$_4$F was dissolved in ethylene glycol + 1% DD water. In the fourth method non-fluoride based electrolytes of HCl + H$_2$O$_2$ in ethylene glycol + 2 vol.% H$_2$O were used for anodization of the photoanode. All the four methods were applied using linearly varying, pulsed and constant anodization voltage.
References


[15] T. Lindgren, H. Wang, N. Beermann, L. Vayssieres, A. Hagfeldt and S. E. Lindquist,


