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Controlling the Microstructure and Properties of Titanium Dioxide for Efficient Solar Cells

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Abstract

In this chapter, we review the controlling of the microstructures, the properties, and the different methods to obtain titanium dioxide and the application of these materials on solar cells. We will concentrate on the application of efficient solar cells including dye-sensitized solar cells (DSSCs). In the first section, we provide a background on energy, including its sources—photovoltaics and titanium dioxide—and the advantages of their application in solar cells. The second section outlines the different methods to obtain TiO_2 nanoparticles. The shapes of titanium dioxide are explored in the third section. In the fourth section, we discuss the use and effect of the titanium dioxide in the efficient dye-sensitized solar cells, and the last section is a summary of the current state of the art and perspectives of titanium dioxide for efficient solar cells.

Keywords: titanium dioxide, nanoparticles, solar cells, dye-sensitized solar cells, efficiency, applications

1. Introduction

The focus of this chapter is to study a general background on titanium dioxide and explain the different methods of its preparation including dry and wet chemical methods. In this section, the importance of titanium dioxide and the effect of different structural morphologies of titania are depicted with the efficiency of the solar cell applications especially dye-sensitized solar cells (DSSCs).

1.1. Sources of energy

Energy makes change; it does things for us. The cars along the road as well as the boats over the water can be moved by energy. A cake in the oven and the ice frozen in the freezer also are been done using energy. It plays our favorite songs on the radio and lights our homes. Energy enables our bodies grow and make our minds to think. Scientists define energy as the ability to do work. Energy sources are classified into renewable and nonrenewable sources as shown in **Figure 1**.

Most of our energy is extracted from nonrenewable energy sources. Coal, petroleum, natural gas, propane, and uranium are nonrenewable energy sources. The name of nonrenewable energy sources has appeared because their supplies are limited. Petroleum, for example, was formed millions of years ago from the remains of ancient sea plants and animals. A long period of time is needed to deposit more crude oil.

Renewable energy sources include biomass, geothermal energy, hydropower, solar energy, and wind energy. They are replenished in a short time, so they are called renewable. Electricity is mainly produced from renewable energy sources. Sunlight, or solar energy, can be used directly for heating, lighting, generating electricity, and many other applications [1, 2]. Indirectly, sun’s heat also creates winds, whose energy is used to generate electricity by wind turbines, which is called wind energy. Plants are grown by sunlight. Biomass is the organic matter which is composed of plants. It can be used, for example, to produce electricity and transport fuels. Furthermore, geothermal energy absorbs the Earth’s internal heat and can be used for a large variety of applications such as building heating and electricity production. Ocean energy draws on energy of the ocean waves, currents, and tides which can under favorable conditions be used for the production of electricity. Global energy consumption consists of six primary sources: 44% petroleum, 26% natural gas, 25% coal, 2.5% hydroelectric power, 2.4% nuclear power, and 0.2% non-hydro renewable energy [3]. Between 1990 and 2010, worldwide consumption of petroleum, coal, and natural gas is enhanced by 22, 27, and 71%, respectively.

Figure 1. Renewable and nonrenewable energy sources. From Ref. [4]. Reprinted with permission from WordPress.

1.2. Solar energy

Solar energy develops a large variety of techniques, including photovoltaic systems, concentrating solar power, passive solar systems, solar hot water, and solar process heat [5].

Conversion of the light energy into electricity is the main use of photovoltaic solar cells and has been existing for a long time; many applications like solar panels on satellites and smaller uses as calculator or watch energy supply, which is familiar for everyone, enable them to be famous. The solar energy is instituted on the solar cell (photovoltaic) effect, which allows the conversion of light (photons) to electricity (electrons).

1.3. Photovoltaic (PV) technology

Electricity is a necessity in everyday life. The cheapest and available power plays a very crucial role in the economic development of the industrialized nations. At the beginning of the twenty-first century, more than 80% of electricity is generated by burning fossil fuels (coal, gas, and oil) [6]. Because of the limited supply of fossil fuels and the growing concerns about global warming, the use of more and more renewable energy sources in energy production is being encouraged in different parts of the world [7]. Among the various sources of renewable energy, solar energy has been considered to have great potential because of the virtually unlimited (100 KTW) supply of sunlight on the Earth [8]. The technology which harnesses the solar energy and converts it into electrical energy is called photovoltaic (PV) technology.

1.4. Titanium dioxide

The semiconductor of choice for making dye-sensitized solar cells (DSSCs) due to its good properties is titanium dioxide, TiO_2 , also known as titania. This material is a cheap and harmless water-insoluble inorganic material that is related to the family of transition metal oxide [9]. Although TiO_2 is a chemically inert substance and it does not promote chemical reactions in the absence of light, particular safety measures are needed when handling nanosized titania [10]. Moreover, TiO_2 has a strong ionic character and can be noticed as being constituted of $\text{Ti}^{\text{IV}+}$ and O^{2-} ions. The conduction band is formed by the 3d orbital of titanium, and the valence band is obtained by the 2p orbital of oxygen. TiO_2 is commercially available and widely used in industrial applications [11].

The most common form of this oxide in nature is rutile. Another form is brookite. A third form of this oxide is anatase, which is the thermodynamically stable crystalline form at high pressure. In all of them, each titanium is surrounded by six oxygen atoms, leading to more or less distorted TiO_6^{2-} octahedrons. Crystal structures differ by the distortion of each octahedron and by the assembly patterns of the TiO_6^{2-} units [12]. For the rutile structure, each octahedron is connected with 10 neighbors (two sharing edge oxygen pairs and eight sharing corner oxygen atoms), while for the anatase and brookite structures, every moiety is in contact with eight neighbors (four sharing an edge and four sharing a corner) as shown in **Figure 2**. Three-dimensional TiO_2 network is obtained from a mixture of corner-sharing and edge-sharing octahedral units [13].

Figure 2. Rutile, anatase, and brookite unit cells, all showing octahedral titanium coordination. Gray and red atoms correspond to Ti^{4+} and O^{2-} , respectively. Reproduced from Ref. [14] with permission from American chemical society 2010.

The most stable phase for titania is anatase below the particle size of 11 nm [15]. The structural parameters lead to differences in mass density and electronic band structure, inducing inherent properties to each polymorph. Then, it is widely confirmed that anatase is the most photoactive TiO_2 phase, although a mixture of anatase and rutile is preferred for photocatalytic applications [16].

2. Synthesis of titania nanoparticles

An exponential growth of research activities has been noticed in nanoscience and nanotechnology in the past decades [17, 18]. When the size of the material becomes smaller and smaller, down to the nanometer scale, new physical and chemical properties are obtained. Properties also change by the changing in the morphologies of the shrinking nanomaterials. One of the best features of these materials is the swimming of electrons and holes in semiconductor nanomaterials, which are first organized using the well-known quantum confinement, and the moving features owned to phonons and photons are greatly related to the size and geometry of the materials [19]. The specific surface area and surface-to-volume ratio increase dramatically as the size of a material decreases [20, 21]. Continuously, breakthroughs have been made in the preparation, modification, and applications of TiO_2 nanomaterials. Here, we focus on recent progress in the synthesis, properties, modifications, and applications of TiO_2 nanomaterials. The syntheses of TiO_2 nanomaterials, including nanoparticles, nanorods (NRs), nanowires (NWs), and nanotubes (NTs), are primarily categorized with the preparation techniques. For detailed instructions on each synthesis, the readers are referred to the corresponding literature related to the common major four preparation methods as well as the obtained shapes of titanium dioxide nanopowders.

2.1. Synthetic methods for titanium dioxide nanostructures

2.1.1. Sol-gel method

TiO_2 nanomaterials have been synthesized by the sol-gel method from hydrolysis of a titanium precursor. This process normally happened through an acid-catalyzed hydrolysis step of titanium (IV) alkoxide followed by condensation as shown in **Figure 3**. The improvement of $\text{Ti}-\text{O}-\text{Ti}$ bonds is developed with small amount of water, low hydrolysis rates, and excess amount of

Figure 3. (a) An illustration of the mechanisms of sol-gel processes: (A) acidic conditions, (B) alkaline conditions, and (C) P123-templated, containing weak alkaline conditions in this. (b) SEM images of the surface of the tubular titania membrane. Reproduced from Ref. [25] with permission from The Royal Society of Chemistry.

titanium alkoxide in the reaction content [22]. Polymeric skeletons with three-dimensional structure show close packing result from the enhancement of Ti—O—Ti chains. The $\text{Ti}(\text{OH})_4$ is preferred to be obtained with high hydrolysis rates for a medium amount of water. The existence of a large quantity of Ti—OH and scanty development of three-dimensional polymeric skeletons resulted in freely packed first-order particles. Polymeric Ti—O—Ti chains are improved in the presence of a big amount of water [23]. The different sizes and shapes of highly crystalline anatase TiO_2 nanoparticles could be obtained by the polycondensation of titanium alkoxide in the presence of tetra methyl ammonium hydroxide [24].

2.1.2. Hydrothermal and solvothermal methods

Hydrothermal synthesis includes the different techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures, whereas solvothermal method includes crystallization of materials in alcohol-based solvent such as ethanol, methanol, n-propanol, and n-butanol. The hydrothermal method has been used by many groups to obtain TiO_2 nanoparticles [26, 27]. For instance, hydrothermal treatment of peptized precipitates of a titanium precursor with water is considered to be a good source of TiO_2 nanoparticles [28]. The precipitate materials were fabricated by adding a 0.5 M isopropanol solution of titanium butoxide into deionized water ($[\text{H}_2\text{O}]/[\text{Ti}]$) [29], and then they were peptized at 70°C for 1 h in the presence of tetra alkyl ammonium hydroxides (peptizer). After that, filtration and treatment have been done at 240°C for 2 h; then, the as-obtained powders were washed with deionized water and absolute ethanol and then dried at 60°C. With the same amount of peptizer, the particle size decreased with increasing alkyl chain length. The morphology of the particles is affected by the peptizers and their concentrations. In another example, TiO_2 nanoparticles were prepared by hydrothermal reaction of titanium alkoxide in an acidic ethanol-water solution [30]. Besides TiO_2 nanoparticles, TiO_2 nanorods have also been synthesized with the hydrothermal method [31] that obtained TiO_2 nanorods by treating a dilute

TiCl_4 solution at 333–423 K for 12 h in the presence of acid or inorganic salts [32]. **Figure 4** illustrates the fabrication process of the titania nanorods (TNRs) film on FTO substrate via hydrothermal method as well as the SEM image of TiO_2 nanoparticles.

The solvothermal method has been found to be a versatile method for the synthesis of a variety of nanoparticles with narrow size distribution and disparity [33]. TiO_2 nanoparticles and nanorods with narrow size distributions can also be developed with the solvothermal method [34]. For example, in a typical synthesis from [35], the suspension of TiO_2 powder has been done by keeping 5 M NaOH water-ethanol solution at 170–200°C for 24 h in an autoclave and then cooled to room temperature naturally. After that, the obtained sample is washed with a dilute HCl aqueous solution and dried at 60°C for 12 h in air. Then, TiO_2 nanowires are obtained. The crystal morphology determination is highly dependent on the solvent used.

2.1.3. Chemical vapor deposition and physical vapor deposition methods

Materials in a vapor state are condensed to form a solid-phase material is the meaning of vapor deposition operation. These operations are basically used to form coatings to prevent the mechanical, electrical, thermal, optical, corrosion resistance, and wear resistance properties of various substrates. Lately, they have been exceedingly reconnoitered to prepare different shapes of nanomaterials. A vacuum chamber is a place where the vapor deposition process is taken place. In case where no chemical reaction happens, this operation is named physical vapor deposition (PVD); otherwise, it is named chemical vapor deposition (CVD). In CVD processes, thermal energy heats the gases in the coating chamber and drives the deposition reaction. On the other hand, plasma-enhanced chemical vapor deposition (PECVD) is a chemical vapor deposition process used to deposit thin films from a gas state (vapor) to a solid state on a substrate as shown in the schematic diagram in **Figure 5**. Chemical reactions are implicated in the operation, which happened following the creation of a plasma of the reacting gases. The plasma is generally obtained using radio frequency (RF) (alternating current (AC)) or direct current (DC) discharge between two electrodes, the space between which is filled with the reacting gases. Furthermore, in PVD, materials are firstly evaporated and then condensed to obtain a solid material. The primary

Figure 4. (a) Fabrication process of the TNRs film on FTO substrate via hydrothermal method. (b) SEM photograph of a TiO_2 film resulted from P25 and titanium isopropoxide ethanol solution after hydrothermal treatment at 100 °C for 12 h. Reproduced from Ref. [36, 37, 57] with permission from AIMSpress 2016 and Royal Society of Chemistry 2014.

Figure 5. Schematic diagram of the plasma-enhanced chemical vapor deposition (PECVD). Reproduced from Ref. [39] with permission from IOPScience publishers.

Figure 6. TEM image of TiO_2 nanoparticles with an average size of 21 nm obtained from Evonik (Aerosil TiO_2 P-25). It consists of a mixture of 80% anatase and 20% rutile with a specific surface area of approximately 50 m^2/g . Reproduced from Ref. [37, 41, 58] with permission from Springer Nature publishing 2017.

PVD methods contain thermal deposition, ion plating, ion implantation, sputtering, and laser vaporization. TiO_2 nanowire arrays have been assembled by a simple PVD method or thermal deposition [38].

2.1.4. Organic acid precursor method

The organic carboxylic acid precursor technique includes the preparation of aqueous solution of required cations and the chelation of cations in solution by addition of carboxylic acid then, raising the temperature of the solution until formation of the precursor. The precursor is

calcined at low temperature. The method is also called combustion method, polymeric precursor method, and acid gel method (oxalate precursor, tartaric acid, lactic acid, and citrate precursor method). The process depends on complexation of metallic salts with aqueous solution of organic acid; the formed complex solution was evaporated at low temperature from 60 to 1000°C until viscous resin is formed; the formed polymer resin was dried and then calcined at low temperature from 200 to 1000°C for 1–4 h [40]. **Figure 6** shows TEM micrographs of titania nanopowders synthesized using organic acid precursor.

3. Shapes of titanium dioxide nanopowders for dye solar cells

Nowadays, most of the successful photovoltaic devices are assembled by semiconductor materials such as silicon (Si) [42]. In recent years, different alternatives to Si-based solar cells have become obtainable, and the large research is outstanding toward substantially decreasing the cost of electricity generation. Dye-sensitized solar cells (DSSCs) [43] are attractive alternative in comparison with others as they can be cheap, lightweight, portable, and flexible. On the other side, the attractive and extensive properties of titania (TiO_2) have led to its wide use in many industries, from traditional industries to high-technology industries [44]. The morphology and particle size of TiO_2 play critical roles in the photoelectric conversion efficiency of DSSCs [45]. For example, TiO_2 materials with different morphologies, such as nanoparticles [46], nanotubes [47], nanowires [48], and nanorods [49], have applied to fabricate the porous film electrodes. Nanostructured TiO_2 materials can be prepared by dry and wet processes as mentioned in the previous section. Because different reaction conditions, like reactants, reaction medium, temperature, and pH of solution, can be chosen in the wet processes, the crystallite size, crystal shape, and surface structure of the nanocrystals can be controlled more easily than that in the dry processes [50].

In particular, one-dimensional (1D) TiO_2 nanostructures, including nanorods (NRs) [49], nanowires (NWs) [48], and nanotubes (NTs) [47], have attracted large interest because of their unique microstructure and promising lineaments, like a high aspect ratio, high surface area, higher surface area/volume ratio, enhanced number of delocalized carriers, and increasing the charge transport afforded by dimensional anisotropy with the conventional properties [51]. Their remarkable properties have referred to their use in wide applications including dye-sensitized solar cells (DSSCs), photocatalysis, and photochromic devices [52]. For dye-sensitized solar cell (DSSC) operation, 1D nanostructure-based photoanodes can contribute to rapid electron transport, ensuring efficient charge collection by the conducting substrate in competition with recombination. This point has promoted research on self-ordered, 1D photoanodes stretched on a substrate with enhanced electron transport properties due to their desirable features, namely, highly decreased intercrystalline contacts and a structure with a specified directionality. Kang et al. (2008) confirmed that TiO_2 nanorods (NRs) are believed to have exceptional properties and have been deemed an alternative to nanoparticles (NPs) as shown in **Figure 7** [53]. Furthermore, increasing the delocalization of carriers in rods, where they can move freely throughout the length of the NRs, is expected to decrease the e^-/h^+ recombination probability. However, this is partially recompensed by the traps in the

Figure 7. The TiO_2 photoanodes consisting of the NPs and NRs in the configuration of DSSCs (Kang et al., 2008). From Ref. [53]. Reprinted with permission from Royal Society of Chemistry 2016.

surface sites to guarantee more efficient charge separation [53]. Moreover, NRs can potentially enhance the charge transport in the photoanodes of DSSCs. In addition, NRs offer direct electrical pathways for photo-generated electrons and can enhance the electron transport rate, which in turn may improve the performance of DSSCs.

In the DSSC, the photoanode encompassed of oriented attachment. TiO_2 NRs showed the following two main advantages: (1) confirmation of high surface area directly proportional to the light-harvesting yield (dye uptake) resulted from the NRs synthesized from the necking of truncated NPs by recovering the low surface area of the general TiO_2 NRs and (2) fast electron transport rate and degraded charge recombination from the decreased intercrystalline contacts between grain boundaries and specific directionality of NRs, bringing about the improved charge collection efficiency.

4. The architecture of the dye-sensitized solar cell (DSSC)

The architecture of a dye-sensitized solar cell (DSSC) is discussed in **Figure 8**. The DSSC consists of a dye-covered, nanoporous TiO_2 (titanium dioxide) layer and an electrolyte founded in between two glass substrates. Front and back electrodes are decorated with a transparent conducting oxide (TCO). Fluorine doped tin oxide (SnO_2 : F), FTO, is the most widely known. The FTO at the back electrode is covered with few nanometers of atomic layers of platinum (Pt), which enhance the formation of electrons through the redox reaction with the electrolyte. The front electrode is covered firstly with thin layer of TiO_2 as a blocking layer which is responsible to prevent the holes from reaching the anode and then coated with a nanocrystalline TiO_2 layer with an average particle size of 5–20 nm. Considering a layer thickness of 10 μm , the resulting effective surface is about 1000 times larger than the dense compact TiO_2 layer. Three modifications of TiO_2 exist: rutile, anatase, and brookite. In the DSSC preferably only the anatase modification is used [54].

Subsequently, a monolayer of dye molecules (scattering layer) is adsorbed on the surface of the TiO_2 . The huge nanoporous surface allows for an adsorption of a sufficiently huge number of dye molecules for efficient light harvesting. The most widespread dye molecule employed in DSSC is usually a ruthenium (Ru) metal-organic complex, the so-called N719 [56]. The spectral absorption of the dye lies between 300 nm and 800 nm. Sufficient adsorption of the dye to the TiO_2 is critical and is obtained by the two carboxylic groups of the ligand ($\text{L} = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid) of the $\text{RuL}_2(\text{NCS})_2$. Finally, a liquid redox electrolyte is inserted between the two electrodes.

Figure 8. Schematic diagram of a solar cell sensitized by dye. The nanoporous semiconductor (TiO_2) and the redox electrolyte are founded between two substrates, covered with fluorinated tin oxide (FTO). The TiO_2 is filled with a dye, and the cathode is covered with a platinum layer. From Ref. [55]. Reprinted with permission from Springer Nature 2003.

4.1. How does the DSSC work?

When the solar light is irradiated, the dye sensitized it, and the electron excited from the valence band (VB) to the conduction band (CB) of the dye leaving a hole in the valence band. After that, the electron moves from the valence band of the dye to the valence band of the TiO_2 nanoparticles which facilitate the swimming of the electrons to the FTO anode substrate and then to the Pt cathode to generate electricity. On the other hand, the redox reaction occurs in the iodine electrolyte to facilitate the formation of the electron to fill the hole founded in the valence band of the dye to regenerate the electron in the cell, and the process occurs continuously.

4.2. Uses of titanium dioxide in DSSC

TiO_2 is used for DSSCs for the following key properties: (i) is a suitable band that adjusts for electron injection from most commercial dyes, (ii) has a high surface area which is suitable for higher dye loading, and (iii) has high electronic mobility for photo-generated electron collection.

Nowadays, many groups and results mentioned that TiO_2 is the best available choice compared to other metal oxide semiconductors such as ZnO , SnO_2 , and so on due to the internal network structure which is important to achieve high charge collection efficiency and more electron transportation. These features enable a good electrode while fabricating a typical DSSC device.

5. Summary and perspectives

Since many years, titanium dioxide nanomaterials have been highly discussed because of their application in solar to electricity conversion for their matching with modern technologies. The persistent permeation in the synthesis and modifications of titanium dioxide

nanomaterials has imparted novel properties and applications in the photovoltaic field with enhanced performance. Aside from that, recently improved devices depend on a novel concept that have largely expanded the application range of titanium dioxide and also put forwarded new requirements for titanium dioxide properties. In this chapter, the major advances of applying titanium dioxide nanomaterials to photovoltaics have been discussed, including the dye-sensitized solar cells. These steady progresses have demonstrated that TiO_2 nanomaterials play an important role in the search for efficient and low-cost photovoltaic technologies. The charge transfer process in these photovoltaic devices is nearly correlating with the features of titanium dioxide nanomaterials as well as the titanium dioxide interface. The unique physical and chemical properties of titanium dioxide nanomaterials can be controlled through modulation of nanocrystal structure, size, shape, and organization. Furthermore, the properties of titanium dioxide interface can be amended through the interaction between TiO_2 and the surrounding elements, including light harvesters, charge transport materials, additives, as well as interfacial modifiers. Moreover, many efforts have been done to develop large-scale preparation technique for high-quality, low-cost titanium dioxide nanomaterials and transformative technology. In order to realize the marketing economically of solar panels with wide application prospect, many studies have been considered. It is believed that future research efforts on new materials and key interfaces will make the titania-based solar cells as a new PV energy source.

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