Chapter

Titanium Dioxide Thin Films for Environmental Applications

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Abstract

The environmental pollution and the rapid depletion of fossil fuel caused by the rapid increase in industrial production became serious problems for humans. These issues have inspired many researchers to found eco-friendly materials, which can degrade pollutants and produce green energy. Titanium dioxide (TiO_2) thin films are one of the important and promising semiconductor materials for environmental and energy applications because of their unique optical and electronic properties. In this chapter, an overview of the background of TiO_2 structure and the different methods of synthesis TiO_2 thin films were carried out. The photocatalytic water treatment and the water split for H_2 production by TiO_2 thin films were investigated. The strong influence on photocatalytic and water split efficiency of TiO_2 thin films by crystal structure, surface area, crystalline structure, average particle size and porosity were summarized.

Keywords: titanium dioxide, thin films, photocatalytic, water splitting, H_2 production, energy and clean environmental

1. Introduction

The industrial revolution has generated the rapid depletion of fossil fuel and the environmental pollution, which have become the most pressing human problems. Nowadays, urgent need to explore environmentally friendly technologies is indispensable to get clean energy and protect the environment.

Titanium dioxide (TiO_2) have been widely investigated in academic research [1, 2] and extensively involved in industrial applications to their abundancy, durability, no toxicity, the high photoactivity and the photoelechemical proprieties.

TiO_2 thin films were successfully synthesis by physical and chemical techniques such as pulsed laser deposition (PLD), molecular beam epitaxy (MBE), RF magnetron sputtering, electrodeposition, sol–gel, hydrothermal, spin-spraying, spin coating, successive ionic layer adsorption and reaction (SILAR), chemical vapor deposition (CVD) and chemical bath deposition (CBD).

Since the discover in the 70's by Fujishima and Honda [3] many research have investigated the production of hydrogen by TiO_2 photoelectrodes under ultraviolet light. For that, TiO_2 semiconductor photocatalysis is considered as the promising material to address both hydrogen production and pollutant degradation.

2. Structures of TiO_2

Titanium dioxide (TiO_2) is an n-type semiconducting material with very interesting properties, such as chemical stability, nontoxicity, low cost, availability, good mechanical flexibility, conductivity and high photocatalytic activity. TiO_2 has three different polymorphs (**Figure 1**) anatase, rutile and brookite [4]. Crystallographic data of TiO_2 structures are summarized in **Table 1**. The most stable form of TiO_2 is rutile. All three polymorphs can be synthesized by many methods.

Anatase is a metastable mineral form of titanium dioxide (TiO_2) which crystallize in the tetragonal system with $I4_1/amd$ space group. Rutile is the most common natural form of TiO_2 and crystallizes in the same system of anatase with $P4_2/mnm$ space group and brookite has an orthorhombic crystalline structure with Pbca space group. In all forms, titanium (Ti^{4+}) atoms are coordinated by six oxygen (O^{2-}) atoms, forming the octahedral TiO_6 were titanium atom (Ti^{4+}) is in the center and oxygen atoms (O^{2-}) are at corners.

TiO_2 is the most crystalline semiconductor used in photocatalytic process, due to the bandgap energy being relatively wide (Eg = 3.2 eV for anatase; Eg = 3.0 eV

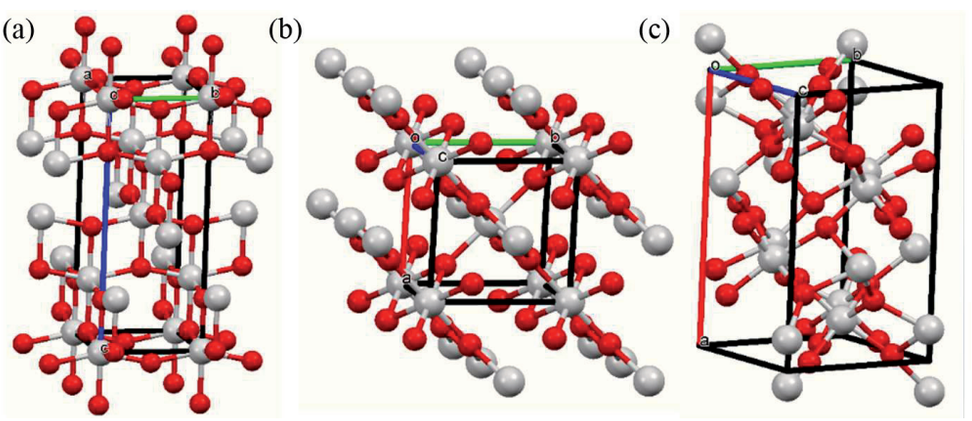

Figure 1.
Titanium dioxide structures (a) anatase, (b) rutile and (c) brookite.

	Anatase	Rutile	Brookite
System	Tetragonal	Tetragonal	Orthorhombic
Space group	$I4_1/amd$	$P4_2/mnm$	Pbca
a (Å)	3.789	4.594	9.184
b (Å)	3.789	4.594	5.447
c (Å)	9.537	2.959	5.145
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V ($Å^3$)	136.93	62.45	257.38
Z	4	2	8
Eg (eV)	3.2	3.0	3.1

Table 1.
Crystallographic data of TiO_2 structures.

for rutile; Eg = 3.1 eV for brookite), the material can only be activated by UV irradiation with $\lambda < 380$ nm.

3. Morphologies of TiO_2

The proprieties of TiO_2 are strongly depends on crystal structure, surface area, crystalline structure, average particle size and porosity. Controlling the morphology of TiO_2 nanomaterials is a highly active area of research. In particular, there is many morphologies of TiO_2 such as nanowires, nanorods, nanotubes and nanosheets.

3.1 Nanowires

Nanowires (**Figure 2**) are one-dimensional nanostructure in cylindrical form. They have lengths in the range of a few micrometers to centimeters and their diameters are in the nanometer range. L. Li et al. [4] have demonstrate that the ITO nanowires coated by TiO_2 have grown by a thermal evaporation method. The high annealing temperatures between 350 and 600°C increase the crystallinity of TiO_2 shell and suppress electron recombination in the core-shell nanostructures. The tin-doped indium oxide (ITO)-TiO_2 core-shell nanostructures are tested as the photoanode for DSSCs. The vertically aligned nanowires are expected to efficiently transport electrons to the substrate where the current is collected. These nanowires have high density, which enables high dye loading and high current density during device operation. The open-circuit voltage decay (OCVD) measurements of (ITO)-TiO_2 core-shell nanostructures show that the electron lifetime increases by quantity of HfO_2 magnitude insertion. ITO-TiO_2 core-shell nanostructures with HfO_2 blocking layers are promising photoanodes for DSSCs.

3.2 Nanorods

Nanorods (**Figure 3**) are one dimensional nanoscale objects. They have a width in the range of 1–100 nm. In the work of J. Ben Naceur et al. [5], the SEM images

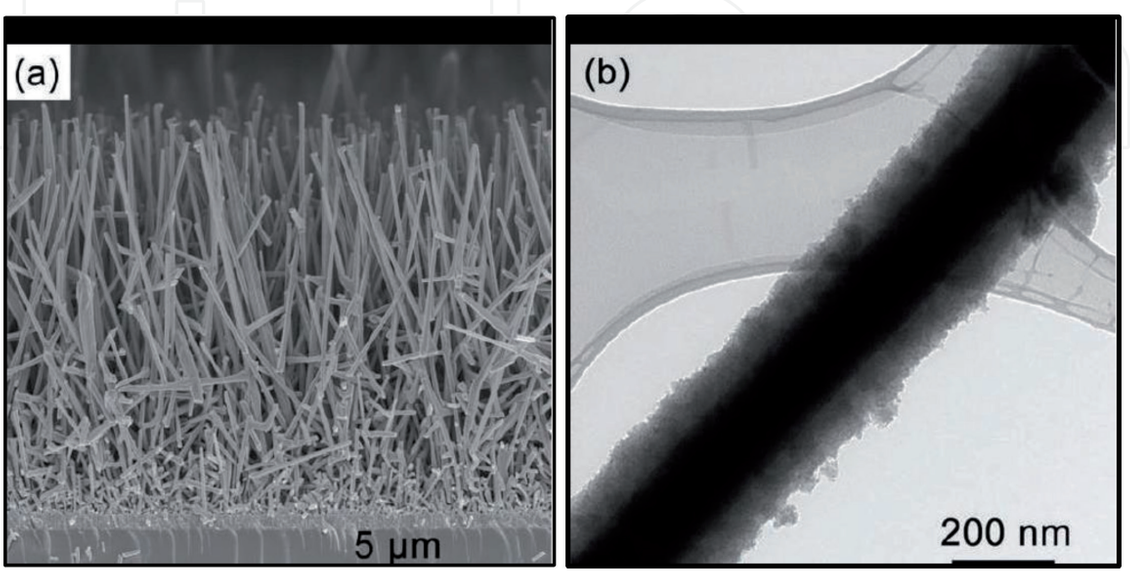

Figure 2.
SEM image of TiO_2 nanowires. (a) TEM image of ITO-TiO_2 core-shell nanostructure (b).

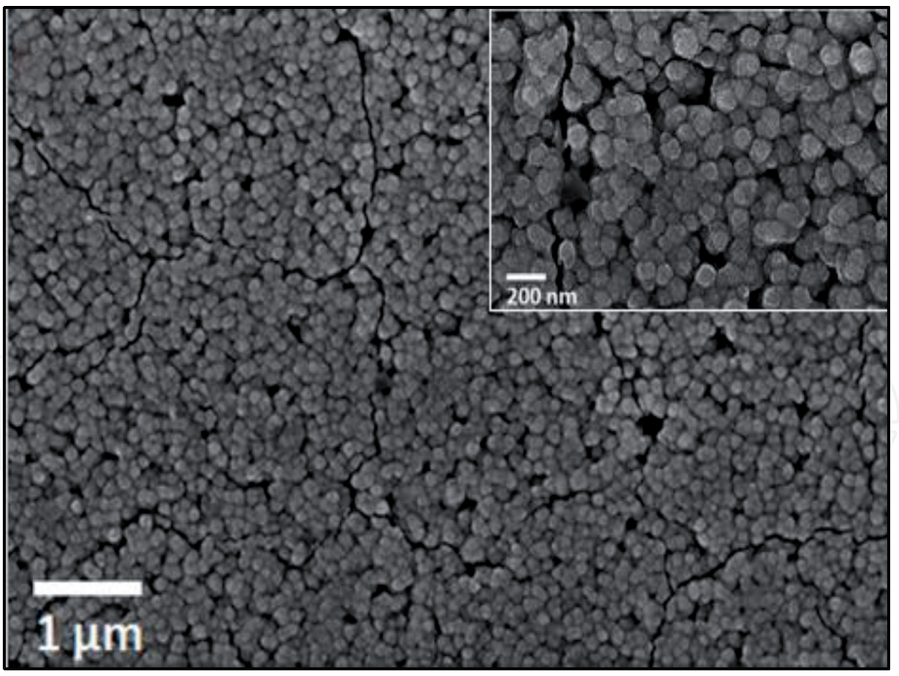

Figure 3.
SEM micrograph of TiO_2 nanorods.

reveal that the entire surfaces of the FTO substrate is uniformly coated by TiO_2 nanorods with an average length and a diameter equal to 1 µm and 60 nm, respectively. Titanium dioxide nanorods arrays (NRAs) photoanodes have been grown by the hydrothermal method on FTO coated glass substrates for different hydrothermal reaction time (5, 10, 15 h). Structural and morphological properties of TiO_2 films confirms the formation of rutile phase with nanorods morphology. The wettability and photoelectrochemical performances of films were investigated. The wettability tests of the sample elaborated at 10 h revealed that this sample is more hydrophilic among all prepared samples for that, it has the best physical properties with a higher photocurrent density equal to 0.22 $mA.cm^{-1}$ at 0.5 V vs. Ag/AgCl.

3.3 Nanotubes

Nanotubes are typically long and thin cylindrical protrusions with sub-micron diameter and lengths in the order of several 100 µm. The SEM images (**Figure 4**), in the work of T-H. Meen et al. [6] show the formation of the TiO_2 nanotubes. To prepared TiO_2 nanotube arrays the electrochemical anodization was used and was tested as photoelectrode of dye-sensitized solar cells. In the SEM analysis, the lengths of TiO_2 nanotube arrays prepared by electrochemical anodization was approximately 10 to 30 µm. After titanium tetrachloride ($TiCl_4$) treatment, the walls of TiO_2 nanotubes were coated with TiO_2 nanoparticles. XRD patterns showed that the oxygen-annealed TiO_2 nanotubes have a better anatase phase. The conversion efficiency with different lengths of TiO_2 nanotube photoelectrodes is 3.21%, 4.35%, and 4.34% with 10, 20, and 30 µm, respectively. The electrochemical impedance spectroscopy analysis, show that the value of Rk (charge transfer resistance related to recombination of electrons) decreases from 26.1 to 17.4 Ω when TiO_2 nanotubes were treated with $TiCl_4$. The treated TiO_2 nanotubes with $TiCl_4$ show that the surface area of nanotubes increase, resulting the increase of dye adsorption and the increase of the conversion efficiency of DSSCs.

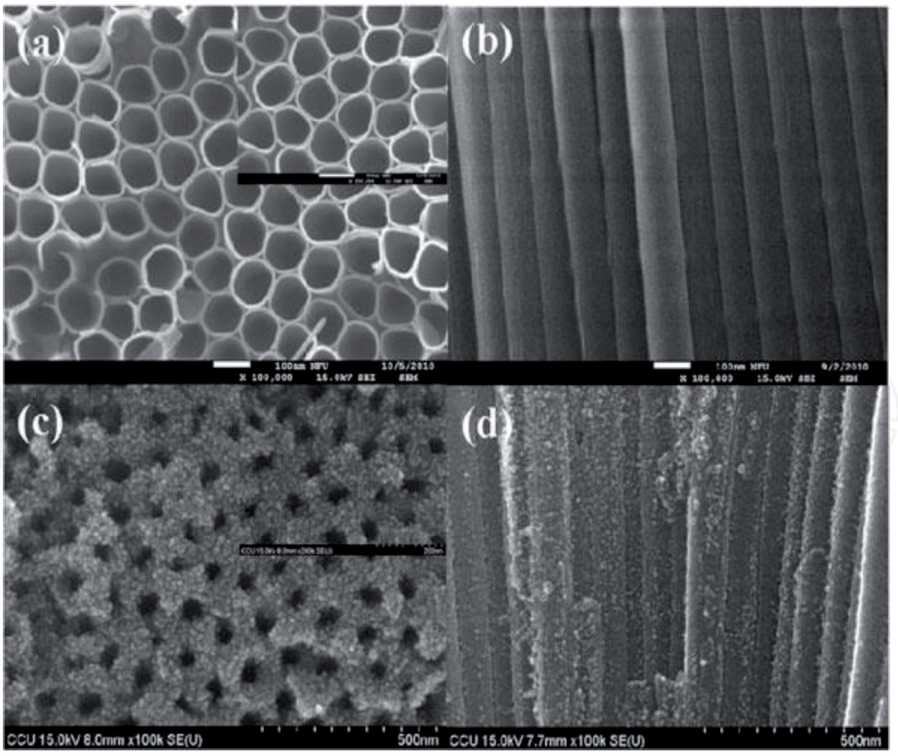

Figure 4.
SEM images of TiO_2 nanotubes (a) top view and (b) side view before $TiCl_4$ treatment, (c) top view and (d) side view after $TiCl_4$ treatment [6].

3.4 Nanosheets

Nanosheet is a two-dimensional nanostructure with thickness in a scale ranging from 1 to 100 nm. As described in work of F. Li et al. [7] the scanning electron microscopy (SEM) image (**Figure 5**) show a single layered 2D morphology of TiO_2 nanosheets. TiO_2 nanosheets are a good carrier of photocatalytic materials and have become attractive materials in the new century because of their high active surface exposure characteristics and special morphology. The preparing TiO_2 nanosheets, was made via hydrothermal calcination method. X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and UV–visible diffuse reflection absorption spectra (DRS) were used to characterize the structure and morphology of the TiO_2 nanosheets. The suitable calcination temperature was 400°C to obtain the TiO_2 nanosheets, with a good hydrogen production rate of 270 μmol/h. The sheet structure of the material was beneficial for improving the photocatalytic water splitting

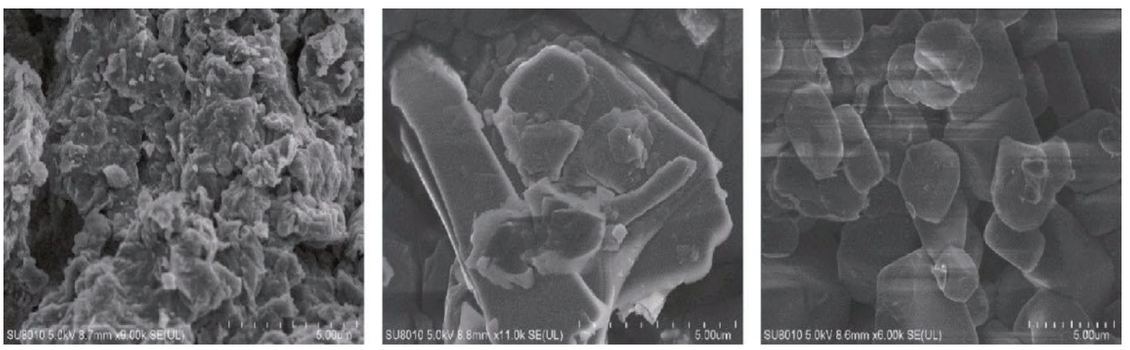

Figure 5.
SEM images of the single-layered 2D mesoporous TiO_2 nanosheets [7].

hydrogen production performance. The research in photocatalytic water splitting of TiO_2 thin films to produce hydrogen are currently a promise topic.

4. Synthesis method of TiO_2

TiO_2 thin films were successfully synthesis by several techniques such as pulsed laser deposition (PLD), molecular beam epitaxy (MBE), RF magnetron sputtering, electrodeposition, sol–gel, hydrothermal, spin-spraying, spin coating, successive ionic layer adsorption and reaction (SILAR), chemical vapor deposition (CVD) and chemical bath deposition (CBD).

4.1 Pulsed laser deposition (PLD) method

The technique of PLD is extremely simple which has been used to deposit high quality films. The technique uses high power laser pulses to melt, evaporate and ionize material from the surface of a target to the substrate (**Figure 6**). *A. Ishii* et al. [8] have elaborated TiO_2 film into glass substrates. For the period of deposition, the pressure of PO_2 in PLD chamber was around 1 to 9 Pa and the temperature was controlled by an infrared lamp heater and a Si plate from room temperature to 600°C for 20 min to make 100–150 nm thick. TiO_2 thin films showed excellent optical properties, with $n = 3.14$ and $k < 0.05$ at $\lambda = 400$ nm.

4.2 Molecular beam epitaxy (MBE) method

The technique of MBE consist to send one or more molecular jets to a substrate with achieve epitaxial growth (**Figure 7**). It makes it possible to grow nanostructured samples of several cm^2 at a rate one atomic monolayer per second. S. Naseem et al. [9] have utilized a Ti electron-beam evaporator and molecular oxygen introduced by a sapphire-sealed leak valve to grown anatase phase TiO_2 doped by Co. The growth of TiO_2 were controlled by a quartz deposition monitor, and under 399.96×10^{-7} Pa of O_2. The 8% cobalt doped TiO_2 film has shown 91% degradation

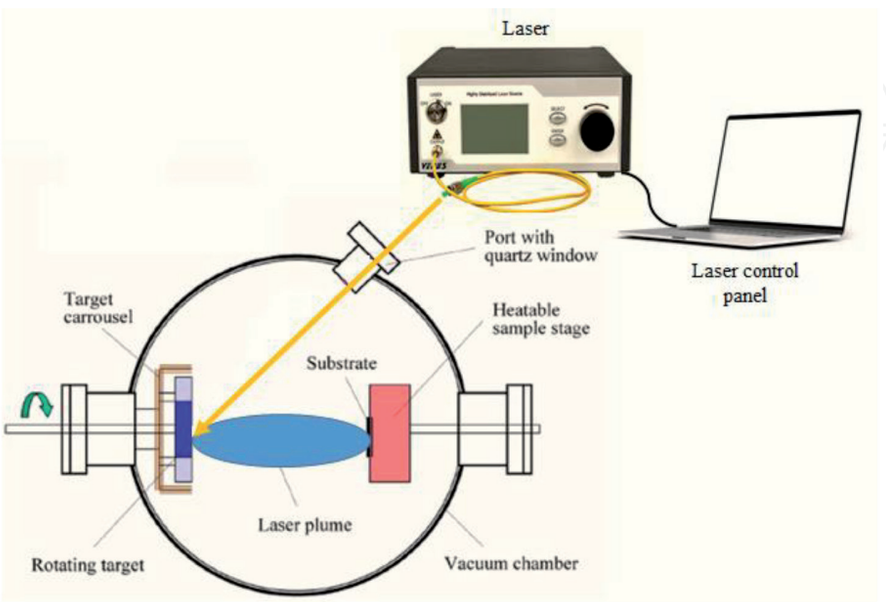

Figure 6.
Pulsed laser deposition (PLD) method.

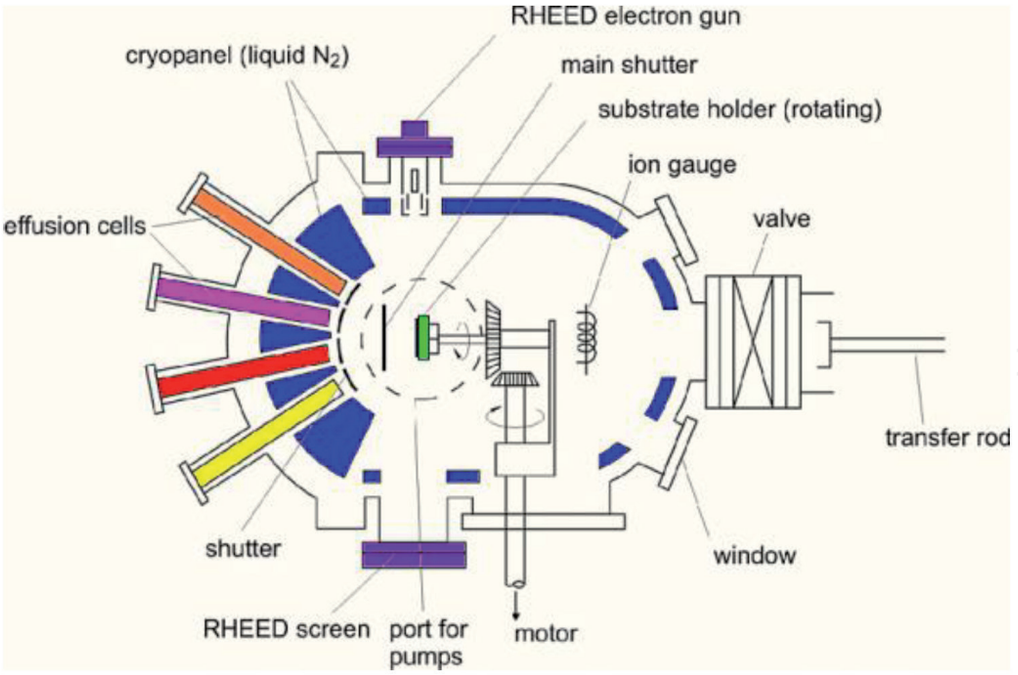

Figure 7.
Molecular beam epitaxy (MBE) method.

with methylene blue and 88% degradation with Azo dye in 70 min under visible light irradiation exhibiting excellent photocatalytic performance.

4.3 Radio frequency magnetron sputtering method

The technique of RF magnetron sputtering (**Figure 8**) has been widely adopted for the high-rate deposition of thin films. This deposition technology involving a gaseous plasma which is generated and confined to a space containing the surface of the target which is eroded by high-energy ions within the plasma, and the liberated atoms travel through the vacuum environment and deposit onto a substrate to form a thin film. J. Singh et al. [10] have prepared TiO_2 thin films deposited on silica glass substrates by RF magnetron sputtering combined with thermal annealing

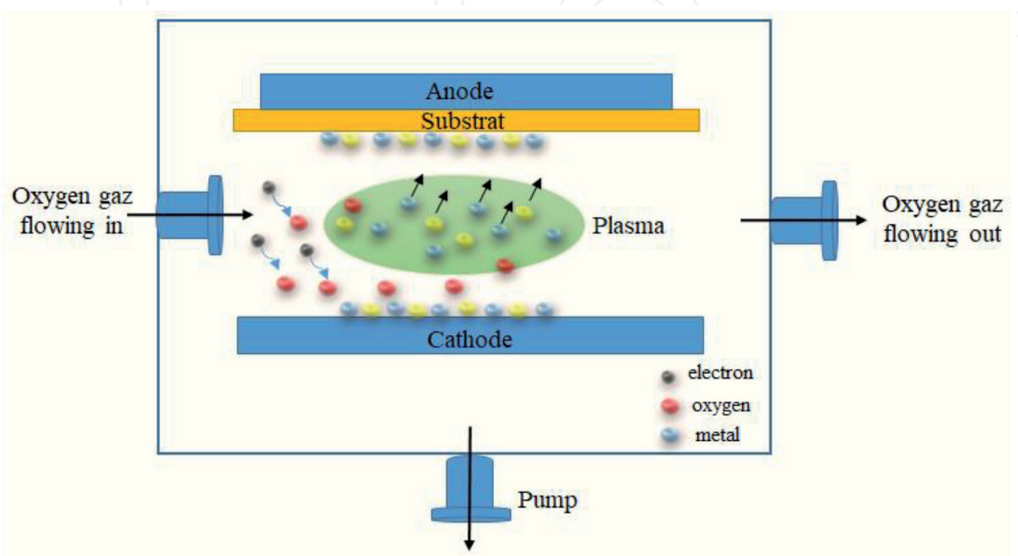

Figure 8.
Radio frequency magnetron sputtering method.

at 2.5×10^{-3} Torr and substrate temperature of 200°C. TiO_2 film exhibits highly enhanced photocatalytic activity leading to complete photocatalytic degradation of 2.1 μM MB in water in only 45 minutes of sun light irradiation, which is very promising for practical photocatalytic applications.

4.4 Electrodeposition method

Electrodeposition (**Figure 9**) is a flexible low-cost method of fabrication of films. The principles of the electrodeposition process are based on principles of electrochemical phenomena associated with the reduction or deposition of electroactive and accompanying species on the cathode surface. H. Wang et al. [11] have elaborated TiO_2 nanotube arrays by the combination of the electrodeposition method and the anodic aluminum oxide (AAO) templating method. A three-electrode potentiostatic system with a saturated calomel electrode (SCE) as a reference electrode and a platinum plate as a counter electrode was used for the electrodeposition method at room temperature. The potential used for the deposition is −0.8, −1.0 V in the electrolyte solution of 0.1 M $TiCl_3$. The pH was maintained at 2.0 by adding a few drops of 2 M Na_2CO_3. After the deposition, the nanotubes in the AAO template were rinsed with double distilled water (DDW), then dried in air at room temperature and finally the samples were heated at 500°C for 2 h under N_2 atmosphere.

4.5 Sol-gel method

The sol–gel technique (**Figure 10**) is a wet low-temperature method that involves the formation of an inorganic colloidal suspension (sol) and gelation of the sol in a continuous liquid phase (gel) to form a three-dimensional network structure. J. Ben Naceur et al. [12] have elaborated TiO_2 on ITO by sol–gel technique. To obtain stable solution, J. Ben Naceur have used 1 mol tetrabutyl-orthotitanate [$Ti(OCH_2CH_2CH_2CH_3)_4$], 1 mol H_2O, 4 mol butanol [CH_3-$(CH_2)_3$-OH], and 3 mol acetic acid [CH_3COOH]. The solution was stirred for 1 h at room temperature, and then a gel film was formed on ITO glass substrate.

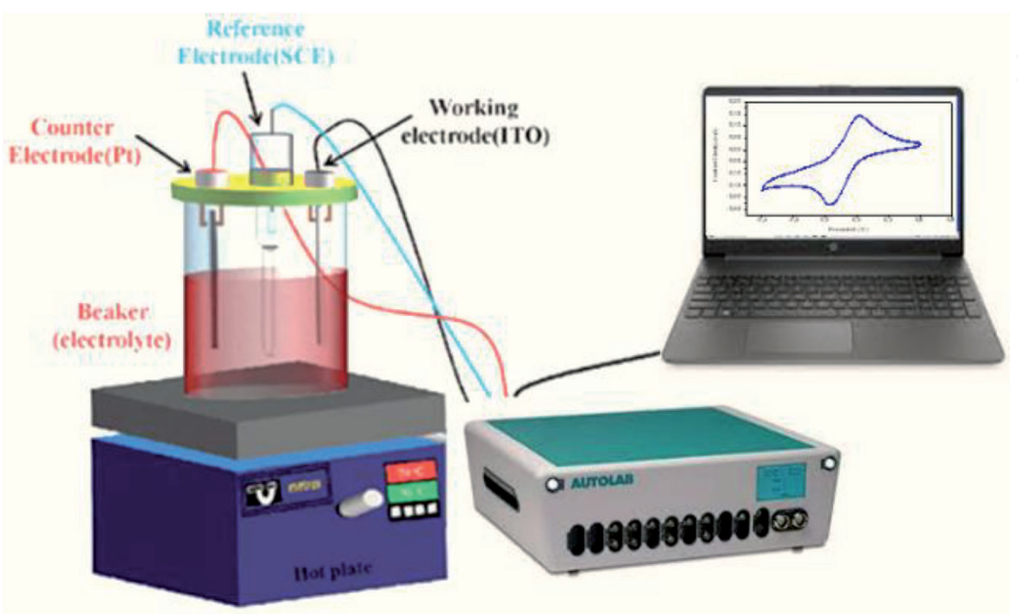

Figure 9.
Schematic of the electrodeposition method.

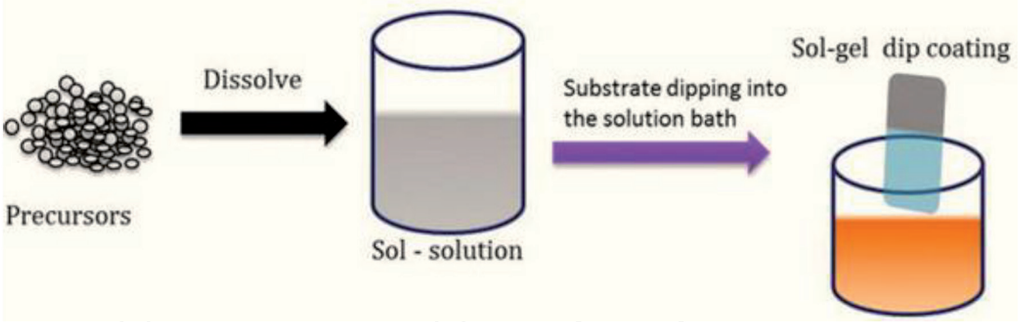

Figure 10.
Schematic of the sol–gel method.

4.6 Hydrothermal method

The hydrothermal technique (**Figure 11**) is a convenient wet way to produce well crystalline materials, with suitably tuned size and shape of particles at temperatures between 180 and 300°C. J. Ben Naceur et al. [13] have prepared TiO_2 nanorods (NRAs) thin film by mixing of hydrochloric acid (HCl), distilled water and Titanium-isopropoxide [$Ti(OCH(CH_3)_2)$]. The mixture was magnetically agitated then transferred to Teflon-coated stainless-steel autoclave. The substrate was placed inside a furnace and kept at 180°C for 5 hours. The hydrothermal method has same advantages such as easy to obtain nanotube morphology, variation in the synthesis method can be implemented to enhance the properties of TiO_2 nanotubes, and it is a feasible method for different applications.

4.7 Spin-spraying method

The spin-spraying technique (**Figure 12**) consists of pulverization of an oxidizing and treatment solutions respectively, onto substrates mounted on a rotating table at a constant temperature. M. O. Abou-Helal et al. [14] have deposited TiO_2 on glass substrates. The solution was prepared by dissolve Titanium (IV) isobutoxide [$Ti((CH_3)_2CHCH_2O)_4$], in a mixture of HNO_3 and methanol solution. The deposition parameters used are 0.1 M of prepared solution, with rate of 1.0 ml/min, at 450–600°C for 5–30 min spray time.

4.8 Spin-coating method

The spin-coating technique (**Figure 13**) is used to deposit uniform thin films onto flat substrates. Usually a small amount of coating material is applied on the

Figure 11.
Schematic of the hydrothermal method.

Figure 12.
Schematic of the spin-spraying method.

Figure 13.
Schematic of the spin-coating method.

center of the substrate, which is either spinning at low speed or not spinning at all. The substrate is then rotated at speed up to 10,000 rpm to spread the coating material by centrifugal force. F. Joudi et al. [15] have prepared TiO_2 thin film by mixing 2 g of P25 in 10 ml of solution of ethanol and acetylacetone under stiring for 10 min. Then the solution was deposited on substrates by spin coating technique. To remove organic solvents from the samples, the films were dried at 150°C and annealed at 450°C for 2 h.

4.9 Successive ionic layer adsorption and reaction (SILAR) method

The SILAR technique (**Figure 14**) is a simple, less expensive, and less time-consuming method for the deposition of binary semiconducting thin films. It is also applicable in the deposition of large-area thin films. V. L. Patil et al. [16] have succeeded to fabricate nanogranular TiO_2 thin films by SILAR. In the initial step, glass substrate was immersed vertically in first beaker contains 2.5 ml $TiCl_3$ (pH = 1)

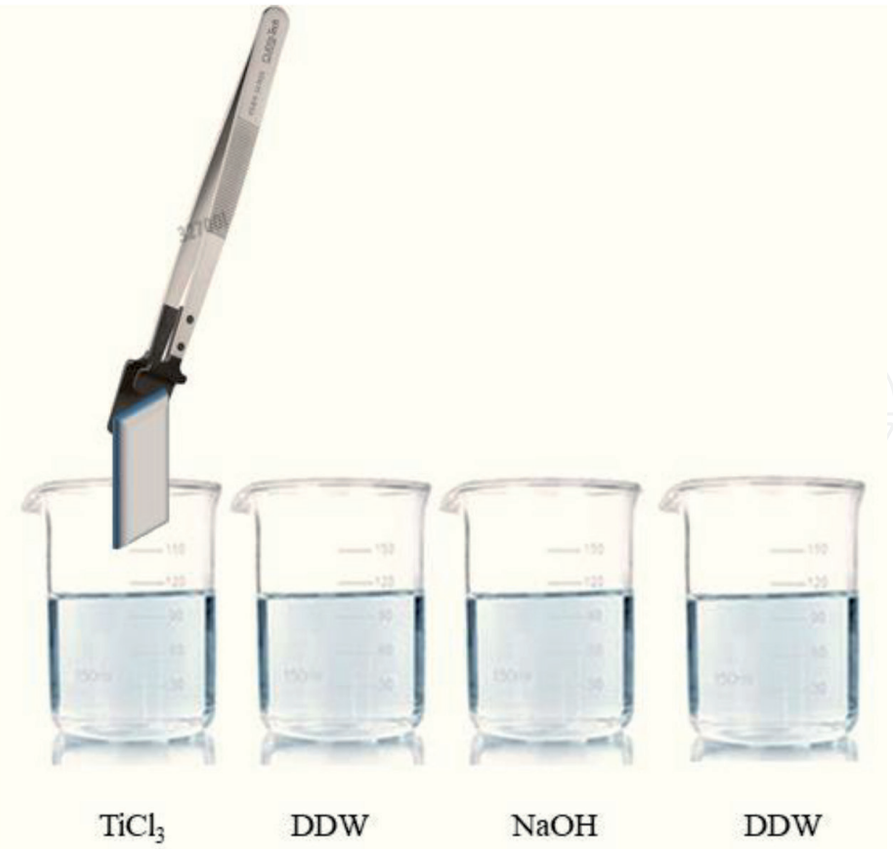

Figure 14.
Schematic of the successive ionic layer adsorption and reaction method.

in 50 ml double distilled water for 10 s, so that a layer of titanium water complex [$Ti(OH)_3$] was adsorbed on the substrate surface. Then the substrate was rinsed using double distilled water (DDW) for 5 s. Then, the substrate was immersed in third beaker contains 0.1 M NaOH solution with pH = 12 for 10 s in which the adsorbed Ti-species with NaOH forms into stable TiO_2 on the substrate. Finally, the TiO_2 and adsorbed hydroxide rinsed in the fourth beaker for 5 s. The nanogranular TiO_2 thin films shows a good gas sensitivity towards NO_2 gas at 50 ppm with good selectivity.

4.10 Chemical vapor deposition (CVD)

The CVD technique (**Figure 15**) is a vacuum deposition method used to produce high quality, high-performance thin films. The substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate

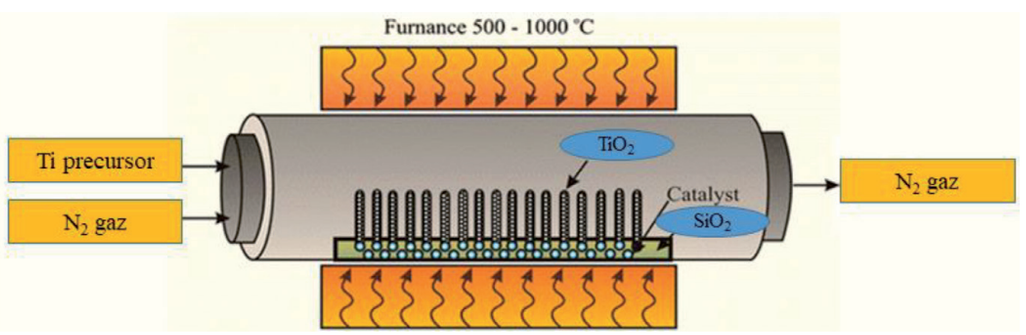

Figure 15.
Schematic of the chemical vapor deposition method.

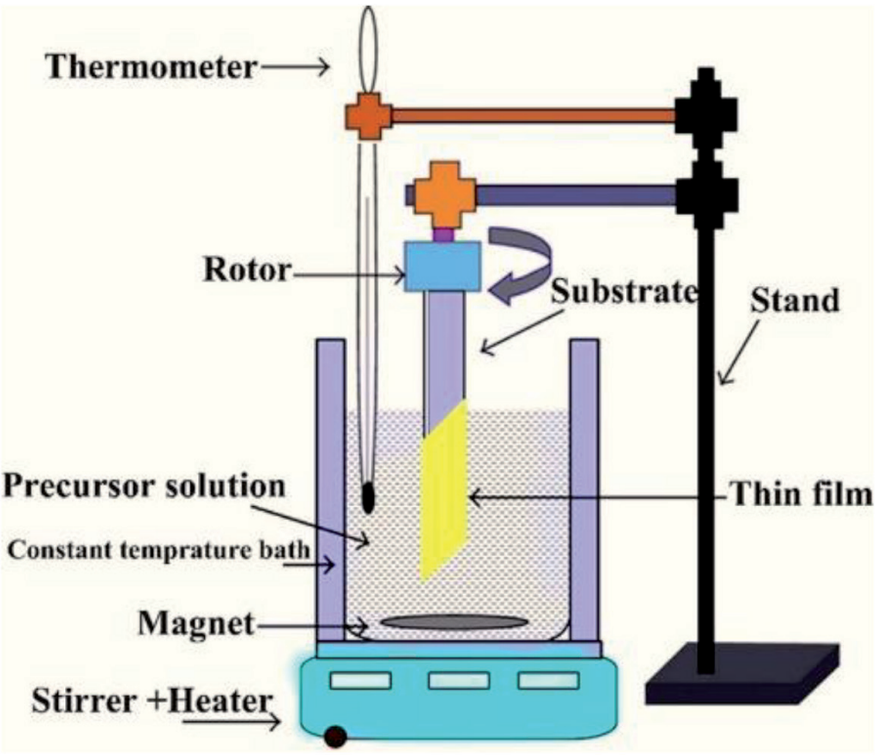

Figure 16.
Schematic of the chemical bath deposition method.

surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber. A. M. Alotaibi et al. [17] have elaborated TiO_2 into SiO_2 substrate by mixing 0.5 g of $[Ti(OCH_2CH_2CH_2CH_3)_4]$ in 20 mL of methanol. The solution was transferred to the reactor and the deposition has been made at 550°C for 40 min. After deposition, the reactor was cooled to room temperature by N_2.

4.11 Chemical bath deposition (CBD)

The CBD technique (**Figure 16**) is one of the cheapest methods to deposit stable, adherent, uniform, and hard thin films by immersing substrate in bath. S.V. Kite et al. [18] have succeed to deposed TiO_2 thin films by simple chemical bath deposition method onto conducting and non-conducting glass substrates. The solution was prepared with ratio of 1: 2: 8 of titanium tetra isopropoxide (TTIP) as a precursor, propan-2-ol (C_3H_8O) and ethanol (EtOH) as solvents respectively. Firstly, the TTIP was mixed with C_3H_8O at constant stirring for 10 min then, EtOH was added. The obtained solution was kept at room temperature with constant stirring to get a clear and homogeneous solution. The substrate was dipped vertically inside the resulting chemical bath for 5 minutes and then substrates pulled out and allowed to dry the step was repeated for 2 to 3 times and finally, the films were rinsed with the distilled water, dried in the oven at 100°C for 2 h then annealed.

5. Water purification by TiO_2 thin films

The conduction band potentials of TiO_2 is near 0 V, which is the reduction potential of H^+ to H_2 and the large bandgap energy of the semiconductors makes them highly promising for photocatalytic and photoelectrochemical water splitting.

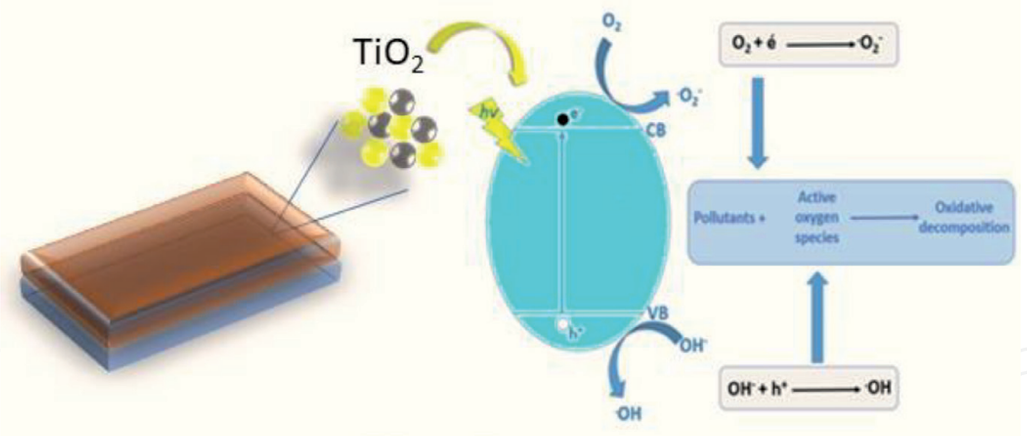

Figure 17.
Schematic of TiO_2 photocatalytic mechanism.

The heterogeneous photocatalysis is widely used for the degradation of water pollutants. The process of photocatalysis can be described as the interaction of incident light with the photocatalyst, causing the formation of electrons and holes (**Figure 17**). The electrons and holes migrate to the surface of the semiconductor without recombining involved the oxydo-reduction reactions. In addition, the holes can also form hydroxyl radicals (·OH) with strong oxidizing properties and the photoexcited electrons can produce superoxide radicals ($\cdot O^{2-}$) and (·OH). These free radicals and e^-/h^+ pairs are highly reactive to decomposed organic substance, environmental pollutants or harmful microorganisms.

The mentioned reactions can be expressed as follow:

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \quad (1)$$

$$e^- + O_2 \rightarrow \cdot O^{2-} \quad (2)$$

$$h^+ + OH^- \rightarrow \cdot OH \quad (3)$$

$$Dye + \cdot OH + \cdot O^{2-} \rightarrow CO_2 + H_2O \quad (4)$$

During the last two decades, researchers have widely studied the purification of water by TiO_2 thin films for their excellent optical and catalytic properties. TiO_2 thin films can act as oxidation and reduction catalysts for organic and inorganic contaminants.

Q. Zhu et al. [19] reported that the synthesis $P/Ag/Ag_2O/Ag_3PO_4/TiO_2$ composite films have degraded 99.9% of rhodamine B (Rh B) after 60 min under simulated solar. J. Singh et al. [20] demonstrated that the synthesized nanocomposite thin films $Ag\text{-}TiO_2$ exhibit a higher photocatalytic activity for the degradation of methylene blue (MB) in water under sun light. S. Yan et al. [21] have determined the photocatalytic performance of $MS@TiO_2@PPy$ through the degradation of soluble organic dye rhodamine B (Rh B) in water under simulated solar irradiation illumination. After being irradiated by simulated sunlight, the degradation efficiency of RhB solution reached up to 90% after 90 min. D. Tekin et al. [22] have reported the efficient application of the ZnO/TiO_2 thin film prepared by the sol–gel method to degrade Orange G dye which show a good performance. K.B. Chaudhari et al. [23] have fabricated TiO_2 film onto glass substrate using a simplified chemical bath

deposition method at moderately low temperature. The photocatalytic activity of the TiO_2 thin film was tested by photodegradation of congo red dye solution which proved enhanced photocatalytic activity under visible light.

6. Water splitting by TiO_2 thin films

The first investigation of water splitting in 1972 by Fujishima and Honda, has attracted a large attention of researchers to developed photoelectrochemical water splitting (PEC) system for the generation of clean and renewable energy from solar light and water.

The hydrogen is produced from water using sunlight and semiconductors materials, which use light energy to directly dissociate water molecules into hydrogen and oxygen. Over the past few years, there is great interest on the evolution of hydrogen by PEC water splitting using various semiconducting oxides such as TiO_2, which is considered as suitable photoanode for water splitting. In the PEC water splitting systems (**Figure 18**), the incident photons, with the energy level of the corresponding material band gap, induce the generation of electrons and holes in the conduction band (CB) and valence band (VB), respectively. In a photoanode, holes are driven to photoelectrode's surface to perform the oxygen evolution, meanwhile electrons are collected by the back contact and close the circuit performing the proton reduction reaction in the counter electrode.

The water splitting reaction can be expressed as below:

$$2H_2O \rightarrow 2H_2(g) + O_2(g) \tag{5}$$

A. Sreedhar et al. [24] have demonstrated that the TiO_2 films grown at a higher ion-beam-energy equal to 110 eV have a photocurrent density of 1.2210^{-5} A/cm^2 under UV light and the TiO_2 films decorated by AgNPs under visible illumination

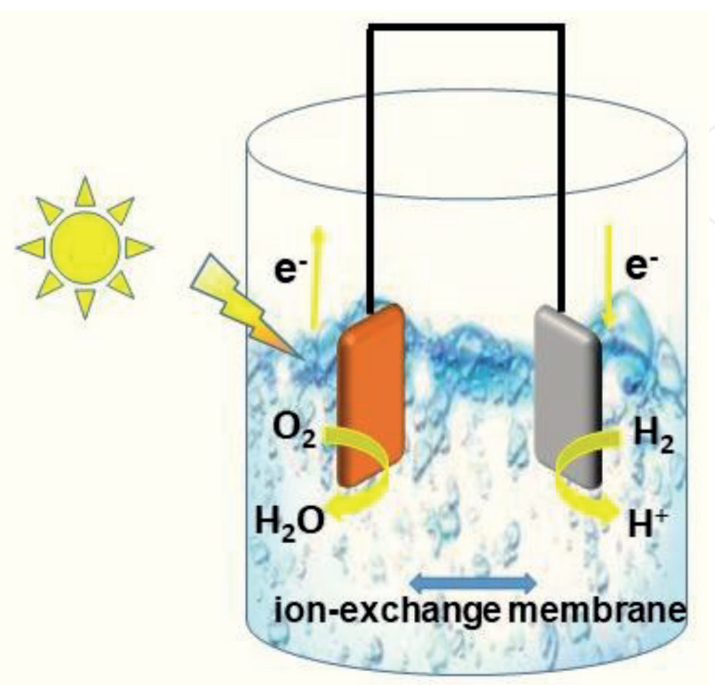

Figure 18.
Schematic of TiO_2 water split mechanism.

have superior photocurrents equal to 6.5310^{-5} A/cm^2, which are a promising photoanodes.

In another work of A. Sreedhar et al. [25] have illustrated that the ZnO/TiO_2 films fabricated at 120 nm yielded with a dominant photocurrent density 4.710^{-6} A/cm^2 is higher ten times than that of ZnO/TiO_2–60 nm films (4.4910^{-7} A/cm^2) and proposed that the film thickness parameter could be a promising pathway to promote the visible-light-driven PEC water splitting activity. C. W. Kim et al. [26] have reported that the TiO_2 photoanode fabricated through hydrothermal method produce 18% of incident photon-to-current conversion efficiency at 0.65 V Ag/AgCl potential under AM 1.5 G illumination and the hydrogen production reached to 0.07 mmol cm^{-2} for 12 hrs. The TiO_2 films with modified morphology synthesis by M. Ibadurrohman et al. [27] have photoconversion efficiency of 1.15% at −0.50 V vs. HgO/Hg, which is an exceptional PEC response and can be considered as promising photoanode.

7. Conclusion

Titanium dioxide TiO_2 is considered as a promising semiconductor for water treatment and H_2 production due to their physical, structural and optical properties under UV and sun light. In this chapter, the structure, the morphology and the synthetic methods of TiO_2 thin films were summarized. The recent researches have confirmed the effect of morphologies of the elaborate nanostructured TiO_2 thin films on proprieties. The photo activity of TiO_2 thin films has been evaluated for the removal of dyes, pharmaceuticals, PCCPs, pesticides, and industrial additives. TiO_2 thin films have the possibility to produce hydrogen from solar energy and water with significant efficiencies. TiO_2 thin films show a good performance to degrade pollutants and can be considered as a promising photoanode for water splitting.

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Conflict of interest

We state that the article is original and all authors are aware of its content and approve its submission. This article has not been published previously, and it is not under consideration for publication elsewhere. I confirm that there is no conflict of interest exists.

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