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Recent advances in syntheses, properties and applications of TiO₂ nanostructures

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TiO₂ is a compound of great importance due to its remarkable catalytic and distinctive semiconducting properties. It is also a chemically stable, non-toxic and biocompatible material. Nano TiO₂ is strong oxidizing agent with a large surface area and, hence, high photo-catalytic activities. With low production cost and a high dielectric constant, it is an inexpensive material. It can be prepared by diverse procedures such as solution and gas phase procedures. Nowadays, TiO₂ is being used frequently for photo degradation of organic molecules and water splitting for hydrogen generation. Most important applications include purification, disinfection of waste water, self-cleaning coatings for buildings in urban areas and the production of the green currency of energy (hydrogen) by splitting water. The review describes the advances in the syntheses, properties and applications of TiO₂ nano structures. Besides, efforts are also made to discuss the working mechanism and future challenges and perspectives.

1. Introduction

Nowadays, nano-structured materials are an important area of research owing to their several unique characteristic features. Among all the transition metal oxides, TiO₂ nano-structures are the most attractive materials in modern science and technology. TiO₂ has been widely used commercially in doughnuts, cosmetics, pigments,¹ catalysts, sunscreens,^{2,3} solar cells,⁴ water splitting *etc.* TiO₂ is being used in plastics, paints, varnishes, papers, medicines, inks, medications, toothpaste, food products, and industries.^{5–10} In 1972 first of all, Fujishima and Honda⁴ reported photo-assisted water splitting under UV light on a TiO₂ photo anode as a semiconductor.^{4,11,12} The diverse claims can be separated into “environmental” and “energy” groups, several of which depend on the TiO₂ properties itself as well as on the changes of the TiO₂ material host (*e.g.* with organic and inorganic dyes). In previous years, the research activity expansion has been observed in nanotechnology and nanoscience.^{13–17} On the modification, preparation and properties of nano-materials, a significant amount of research, reports and reviews have been published recently^{4,11–40} to know and précis the progress in this field. TiO₂ nanostructures in various forms, among the unique characteristics of nano-materials, are gaining broader applications due to their size-related characteristics. For nanometer scale TiO₂ the energy band structure becomes discrete due to its surface,

photochemical and photo physical properties. Consequently, several works have focused on nano crystalline TiO₂ syntheses with a high surface area. As a photocatalyst,^{15,16,27} TiO₂ nano-structures have drawn much attention and are projected to show a significant role in serving to resolve several pollution and environmental problems. Thus, using TiO₂ for H₂ production and photo-assisted water splitting devices offers a way for hygienic and low price production of hydrogen by solar energy.^{13,41}

This review aims to give an inclusive data on the advances in TiO₂ based nanostructure, recent investigation and the development efforts, which tack energy and environmental challenges in consideration. Besides, the crystal structure, optical, electrical/electronic and adsorption, surface area, porosity properties of TiO₂ nanostructure are discussed. The procedures of preparations, fabrications (nanoparticles, nanorods, nanowires, and nanotubes), the conditions of syntheses and accountability for regulation of titanate nanostructures morphology are also discussed. TiO₂ nanostructures applications in electrocatalysis, environment and energy challenges are also highlighted. Finally, the mechanism of action and future challenges are also highlighted.

2. Properties of TiO₂ nanostructures

2.1 Crystal structure of TiO₂

Titanium dioxide [titanium(IV) oxide or titania] has a molecular formula TiO₂ with 79.87 as molecular weight. TiO₂, a non-toxic material, chemically stable, biocompatible and strong oxidizing agent (with large surface area) has very high photocatalytic activity. It is an inexpensive material with high dielectric constant and low production cost. TiO₂ crystal exists in three

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common polymorphs in nature *i.e.* brookite, anatase, rutile,^{42,43} and some few common structures of TiO₂ II *i.e.* columbite,⁴⁴ TiO₂ III: baddeleyite,^{45,46} TiO₂ (R) (ramsdellite),⁴⁷ TiO₂ (B) (monoclinic)⁴⁸ and TiO₂ (H) (hollandite).⁴⁹

Rutile is the most thermodynamically constant among the different polymorphs structures.⁵⁰ From 400 to 1200 °C, it's critical temperature can vary which depends on the grain impurities and size.⁵¹ The optical and electrical properties and crystal structural of rutile, brookite and anatase are given in Table 1.^{51–63} These are discussed in the following paragraphs.

2.2 Rutile

In a tetragonal structure, with 6 atoms per unit cell (Fig. 1), rutile is the most stable having TiO₆ octahedron showing a slight orthorhombic distortion.^{64–66} Rutile phase is stable while at these conditions TiO₂ converts thermodynamically into auspicious phase.⁶⁷ For unit sizes > 14 nm, rutile phase becomes more stable than anatase.⁶⁸ Predominantly, the crystals of natural rutile exhibit (110) surface.⁴² This surface is the most stable stoichiometric rutile surface.⁶⁹ In the unit cell of rutile, 4 oxygen atoms form a partial octahedron about Ti⁷⁰ while 2 titanium atoms (at [0, 0, 0] and $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$) positions, separately are available. Distinctly, octahedron is linked to 10 near octahedra, out of which 2 parts an edge and eight share a bend with it. The octahedral edge shared are aligned along [001] direction as shows in Fig. 1.⁷⁰

2.3 Anatase

TiO₆ octahedron distortion is significantly large for anatase phase while TiO₂ has a tetragonal structure, hence, the symmetry of anatase is lower than orthorhombic (Fig. 1).⁷⁰ The energy change between these 2 phases is minor closely (~2 to 10 kJ mol⁻¹).⁷¹ At 0 K, the rutile phase is not more thermodynamically constant than anatase. The unit cells of anatase



Fig. 1 Crystal structures of the rutile and anatase phases of TiO₂. Small spheres represent Ti atoms, large spheres represent oxygen atoms.

contain 4 titanium atoms (at $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$, [0, 0, 0], $[-\frac{1}{2}, 0, -\frac{1}{4}]$ and $[0, \frac{1}{2}, \frac{1}{4}]$) and 8 oxygen atoms, which form a partial TiO₆ octahedron around Ti;⁷⁰ with division of 4 edges of each octahedron.

2.4 Brookite

It is one of the 3 naturally occurring polymorphs of TiO₂, which belongs to orthorhombic crystal system. It contains a larger cell volume with 8 TiO₂ groups per unit cell (Fig. 2).⁵³ Brookite is also the least dense form compared to anatase and rutile.⁶⁵ Besides, it displays photocatalytic activity.⁷² Liu *et al.*⁷³ investigated principled metal free photocatalytic water splitting. For this investigation the authors modified these surfaces by high pressure. Before and after modification, water splitting on usual anatase single crystal facets and on wafer slices of the [001] plane was investigated. Fig. 3 shows phase transition in TiO₂

Table 1 Comparison of the crystal structural, optical and electrical properties for TiO₂ nanostructures

| Properties | Rutile | Anatase | Brookite |
|---|--|---------------------------------------|--|
| Crystal structure | Tetragonal | Tetragonal | Orthorhombic |
| Lattice constant (Å) | $a = 4.5936$ $c = 2.9587$ (ref. 312) | $a = 3.784$ $c = 9.515$ (ref. 312) | $a = 9.184$ $b = 5.447$ (ref. 312) $c = 5.154$ |
| Space group | $P4_2/mnm$ ⁵² | $I4_1/amd$ | $Pbca$ |
| Molecule (cell) | 2 | 2 | 4 |
| Volume/molecule (Å ³) | 31.21 (ref. 54) | 34.061 | 32.172 |
| Density (g cm ⁻³) | 4.13 | 3.79 | 3.99 |
| Ti–O bond length (Å) | 1.949 (4) ⁵³ 1.980 (2) | 1.937 (4) 1.965 (2) | 1.87–2.04 |
| O–Ti–O bond angle | 81.2° 90.0° | 77.7° 92.6° | 77.0–105° |
| Band gap at 10 K | 3.051 eV (ref. 54) | 3.46 eV (ref. 313) | |
| Static dielectric constant (ϵ_0 , in MHz range) | 173 (ref. 314 and 315) | 48 (ref. 55) | |
| High frequency dielectric constant, ϵ_∞ ($\lambda = 600$ nm) | 8.35 (ref. 56) | 6.25 (ref. 57) | |
| Nature of conductivity at room temperature (undoped) | n-type semiconductor ^{58–75} | | |
| Mott transition | Not observed ⁶⁰ | Observed ³¹³ | |
| Electron effective mass | 9–13 m, ⁶¹ 10–30 m, ⁶² 12–32 m ⁶³ | ~1 m (ref. 313) | |





Fig. 2 Lattice structure of brookite TiO_2 .

with the change in pressure and temperature.⁷⁴ The temperature for transformation can be improved by accumulation impurities into TiO_2 . Anatase phase for powder samples containing V, Mo, & W respectively completely disappeared⁷⁵ at temperature about 530, 680, and 830 °C.

2.5 Optical properties of TiO_2

In the range from IR to visible spectra, the rutile is more anisotropic than anatase. Contrarily, anatase shows important anisotropy in the band gap region.⁷⁶ At about 0.75 to 1.18 eV (ref. 77–80) for rutile, a blue color appearance dependent on the amount of reduction of TiO_2 , arises from the visible part infrared absorption band peaking. The blue color appearance in IR has also been observed in anatase too.^{81,82} Besides, at 3.0 eV an oxygen vacancy causing a yellow color is a color center.⁸¹

2.6 Electrical/electronic properties of TiO_2

The electrical/electronic properties of TiO_2 nanostructures are dependent on the crystallographic directions. Titanium dioxide nanostructure (titania) is an important photocatalytic material, which exists in to 2 chief polymorphs *i.e.* rutile and anatase with tetragonal coordinations. Table 1 shows the several TiO_2 electrical properties. A semiconductor, TiO_2 has high resistivity ($\sim 10^{15} \Omega \text{ cm}$),⁸³ titanium interstitials and bulk oxygen vacancies. These are considered to generate low electron donor levels that donate to the electric conductivity of TiO_2 .⁸⁴

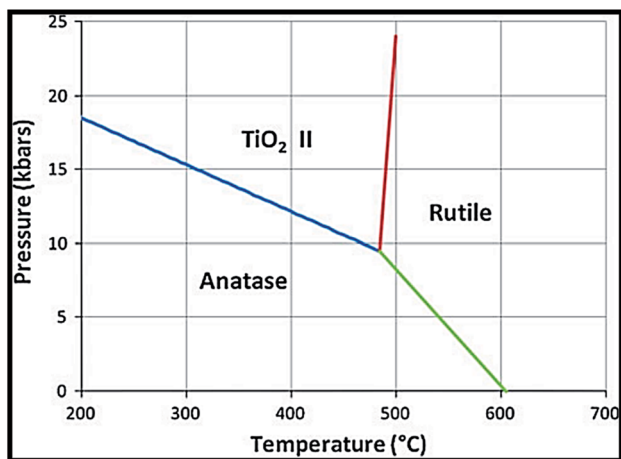


Fig. 3 Reaction boundaries of phase transitions in TiO_2 .⁷⁴



Fig. 4 Influence of gas cycle of sequence on electrical conductivity of 0.5% Pt/ TiO_2 doped with (A) W^{6+} (B) Ta^{5+} (C) undoped and (D) Mg^{2+} .⁸⁵

Vacancies for oxygen are the main fault in TiO_2 .⁷⁰ The absence of oxygen introduces electrons excess in the solid ensuing in a rise of conductance of electricity.⁷⁰ Fig. 4⁸⁵ shows the influence of gas cycle of sequence on electrical conductivity of 0.5% Pt/ TiO_2 doped with (A) W^{6+} (B) Ta^{5+} (C) undoped and (D) Mg^{2+} . Another thing to be added is that Nb (niobium) or tantalum atoms act as electron donors⁸⁶ when incorporated into TiO_2 . Besides, Nb (niobium) or tantalum atoms increase the electrical conductivity. On the other hand, chromium, manganese, and iron act as electron acceptors,⁸⁷ decreasing or increasing the TiO_2 electrical conductivity. On the ratio between the oxygen vacancy concentration and their concentration, the augment or reduction in electrical conductivity depends.⁸⁸ To the electrical conductivity, the point defects typed imperfection plays a crucial role. It is reported that the ionization energies for titanium interstitials⁸⁹ is 0.007–0.08 eV. To the electronic conduction, the contribution of oxygen vacancies is also important.⁹⁰ Several reports recommended the presence of both phenomena, with an activation energy of carrier generation around 4 meV.⁹¹

After studying the formation energies and the electronic states of 4 types of lattice point defects in rutile, it was found that in the forbidden band, the existence of vacancy for oxygen leads to a deep donor defect level. Moreover, to establish that the band gap is ~ 2.86 eV, the band building of the pure rutile TiO_2 was studied.⁹² The valence band (VB) of wide gap rutile and anatase are formed by O_{2p} states, while titanium 3d states forms the conduction band (CB).⁷⁰ On these states, the detailed calculations can be found.⁴⁵ Recently, several researches have been reported that the electronic structure of rutile bulk can also be described by means of additional techniques used in the experiment such as electrical resistivity, electroabsorption,^{93,94}



photoconductivity and photoluminescence,^{95,96} X-ray absorption spectroscopy (XAS),⁹⁷⁻¹⁰² resonant Raman spectra^{96,103} and photoelectrochemical analysis.^{58,104}

3. Synthesis of TiO₂ nanostructures

There are some methods of making TiO₂ nanostructures. Gas phase and solution routes methods are the main ones. The solution route is able to coat complex shapes, to govern on stoichiometry, and preparation of composite materials. The presence of carbon as an impurity is an expensive precursor, and long processing times are the difficulties of solution route. There are two methods of synthesis (i) physical and (ii) chemical methods. Both methods have disadvantages and advantages. Physical procedures produce large quantities of material, but their resolution is inadequate to nanometers. The chemical procedures can approach the atomic layer limit¹⁰⁵ through the preparation of minor (e.g., <100 nm and often <10 nm) structures. Hence, at a smaller scale, chemical procedures are typically completed.

3.1 Solution procedures

3.1.1 Sol gel route. In materials science and ceramic engineering, a wet-chemical technique widely used is sol-gel process. The advantage of sol-gel process is inexpensiveness. With sol-gel method, nanostructured TiO₂ has been synthesized from titanium precursor hydrolysis. Usually, this method involve an acid catalyzed hydrolysis of titanium(IV) alkoxide tracked by condensation.¹⁰⁶⁻¹¹⁹ This process includes 4 steps *i.e.* hydrolysis, polycondensation, drying and thermal decomposition. The sol-gel procedure includes the metal alkoxides usage, which suffer hydrolysis and condensation polymerization reactions to give gels as shown in these equations.¹²⁰

Hydrolysis:



Condensation:



where, R = ethyl, iso-propyl, *etc.* For the change of liquid sol into a solid gel phase, the whole polymerization leads to loss of solvent. The sol particles size depends on the composition of solution, temperature and pH.²⁰ Ti-O-Ti chains development is preferred with little amount of water, additional titanium alkoxide in the reaction combination and stumpy hydrolysis rates.

The advantages of sol-gel method are as follows:

- Product homogeneity.
- Good rheostat above powder particle shape and size and size distribution.
- Easiness of manufacturing multi-component materials.
- No particular apparatus with low price.
- Low processing temperature.
- Synthesis of films with high photocatalytic activity.

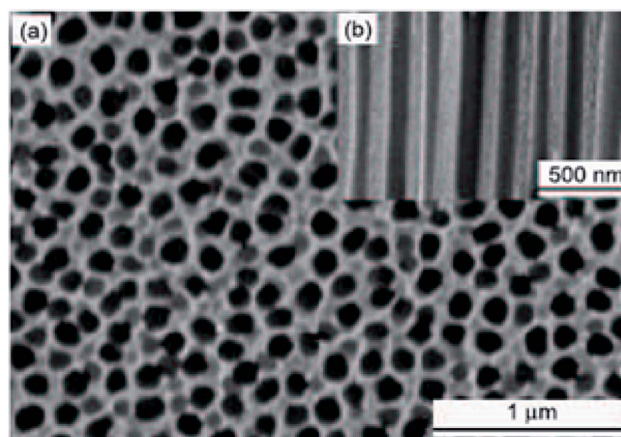


Fig. 5 SEM of AAM template, (a) top and (b) side views.

Utilizing sol-gel template method, the syntheses of TiO₂ nanotubes, nanorod and nanowires has been reported. This synthesis was carried out from the porous anodic alumina membranes (AAMs), supramolecular template and organogel. The first step for synthesis of nanorod is tumbling porous AAMs into a warmed TiO₂ sol following by drying and heating processes.¹²¹ Ghamsari and colleagues¹²² synthesized TiO₂ nanorod by sol-gel Template Process. Briefly, the porous anodic alumina of 60 μm in thickness and pores of 100 nm in diameter were used as templates.

Fig. 5 and 6 show SEM images of AAM template and TiO₂ nanorods grown in the AAM template. By changing the dipping time, nanorods length can be changed. An individual TiO₂ nanorods picture is shown in Fig. 6(b). Through the full length of the rods and continuous yet the rods is uniform. To obtain the nanowire arrays of TiO₂, electrophoretic deposition of TiO₂ colloidal suspensions can be used into the pores of an AAM.¹²³ At room temperature; in another procedure; titanium tetraisopropoxide (TTIP) is dissolved in ethanol followed by the



Fig. 6 SEM of TiO₂ nanorods growth in AAM template, (a) low magnification image, (b) high magnification image.¹²³





Fig. 7 TEM images of TiO₂ nanoparticles after hydrothermal treatment of TBA peptized gel at (a) 210 °C and (b) 270 °C.¹³³

addition of glacial CH₃COOH (mixed with demineralised water and EtOH) using HNO₃ as pH 2–3 controller. AAM is used as the cathode and platinum as an anode. TiO₂ nanowires are obtained after dissolving AAM template in 5% NaOH solution. Using titanium butoxide, titanium isopropoxide [TIPO] and titanium tetrachloride; as Ti precursors in HCl solution; have been synthesized.¹²⁴ Nanotubes were also synthesized by Kasuga and colleagues^{125–127} using sol-gel method with innermost and outside diameters of approximately 5 and 8 nm, respectively. The spine designed products were nanotubes.

3.1.2 Hydrothermal procedures. Hydrothermal syntheses are promising procedures to gain titania nanocrystalline particles. The hydrothermal process is effective to attain the crystalline phase at lower temperatures. Hydrothermal is broadly used for the manufacture of minor units in the ceramics industry. Generally, hydrothermal synthesis is known as crystal synthesis or crystal growth. Below 300 °C, the hydrothermal synthesis is usually carried out. 374 °C is the critical temperature and 22.1 MPa is the critical pressure of water under supercritical conditions.

Some studies indicated application of hydrothermal method to prepare TiO₂ nanoparticles.^{128–132} To synthesize TiO₂ nanoparticles, hydrothermal treatment of titanium precursor (peptized precipitates) was also used.¹²⁹ Besides, reaction of hydrothermal of titanium alkoxide under acidic ethanol-water solution was also used to prepare TiO₂ nanoparticles. Under EtOH–H₂O environment, TiO₂ nanoparticles synthesized were mainly primary structures of anatase. The sizes of the units were in range of 7–25 nm. Besides, TiO₂ nanoparticles¹³³ were synthesized using hydrothermal method. With increasing stirring for 45 minutes into distilled water at 1 : 4 volume ratio, 0.5 M solution of titanium butoxide Ti(OBu)₄ in 2-propanol was gradually added. To prepare nanoparticles for further examination, the gels prepared were treated hydrothermally. TEM images of TiO₂ nanoparticles prepared using hydrothermal method are shown in Fig. 7.

Vijayalakshmi and Rajendran¹³⁴ synthesized TiO₂ nanoparticles using hydrothermal method by making a water

solution of titanium. This solution was made by mingling one molar stoichiometric ratio of TTIP in 50 mL deionized water. TiO₂ nanowire in the solutions of 10 to 15 M sodium hydroxide were synthesized; using TiO₂ white powders; without stirring within an autoclave at 150–200 °C for 24–72 h by Zhang and colleagues.¹³⁵ Fig. 8 shows SEM and TEM images of nanowires of TiO₂ prepared by Zhang and colleagues.¹³⁵ Titania nanotubes¹³⁶ were synthesized *via* hydrothermal process. TiO₂ powders were heated at 20–110 °C for 20 h. TiO₂ nanotubes achieved were washed using a dil. HCl aqueous solution and deionized water. With NaOH aqueous solution, raw TiO₂ material was treated. Besides, titania nanotubes¹³⁷ were synthesized *via* hydrothermal. 5.0 g anatase TiO₂ nanopowders were mixed with 180 mL 10 M NaOH in a perfluoroalkoxy (PFA) bottle and stirred for 1 h. The resultant precipitate was separated by centrifugation after hydrothermal reaction. Until pH value reached approximately 7, precipitate was rinsed with

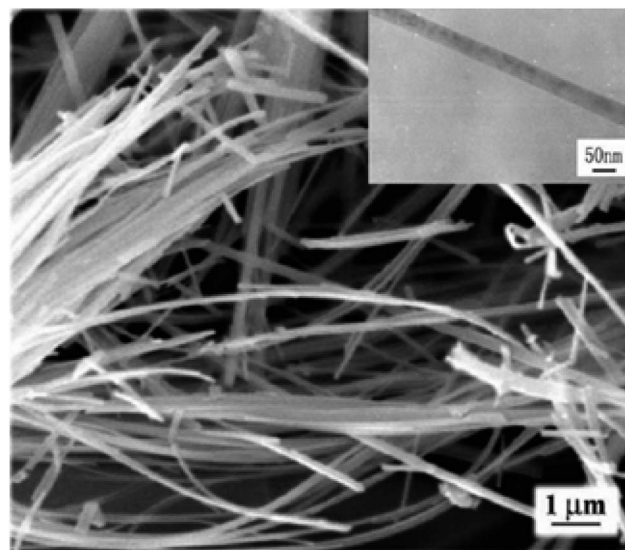


Fig. 8 SEM images of TiO₂ nanowires and a TEM image of a single nanowire prepared by Zhang and colleagues.¹³⁵



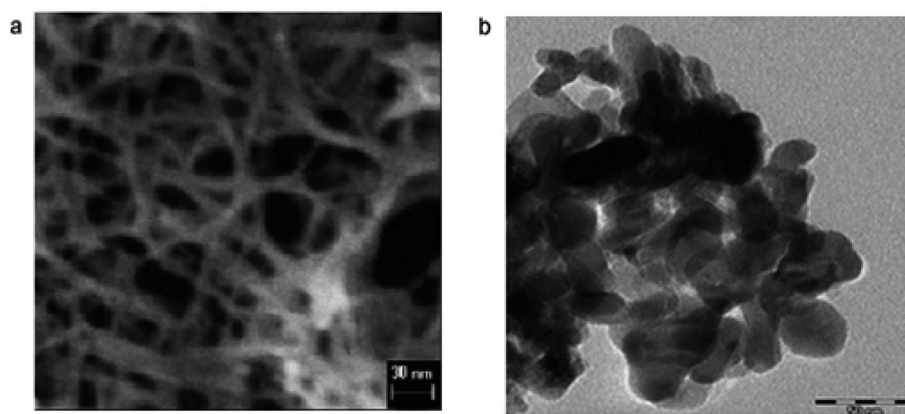


Fig. 9 Electron microscopy images of (a) titania powders and (b) titania nanotubes.³¹²

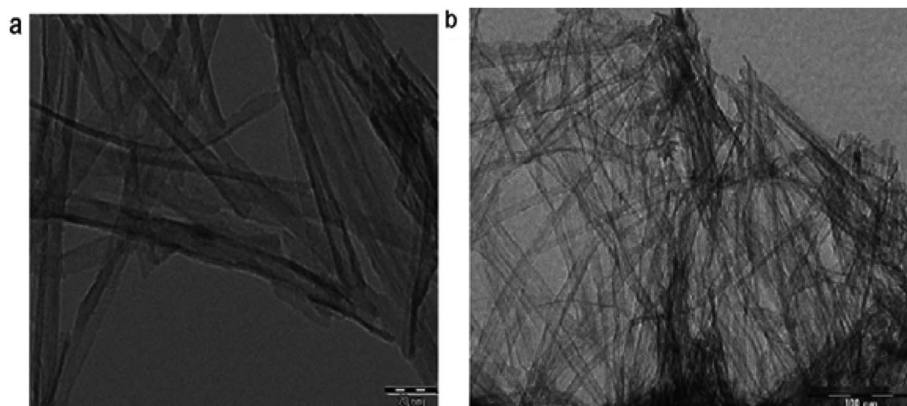


Fig. 10 TEM images of titania nanotubes at (a) low magnification and (b) high magnification.³³⁸

diluted HCl and demineralised water several times. Fig. 9 shows electron microscopy pictures of titania nanotubes and titania powders. Fig. 10 indicates the TEM pictures of TNTs; revealing that the TNTs have tubular, hollow and open structures. 3–6 nm is the inner diameter size of the TNTs and 1.9 nm is the average wall thickness. Besides, some other studies for syntheses of TiO₂ nanowires by hydrothermal are also available.^{110–115}

3.1.3 Electrochemical procedures. To produce advanced thin films such as superlattice, epitaxial, nanoporous and quantum dot ones by anodization, electrochemical procedures provided a diversity and low temperature approach. The distinctive states of the films are measured by electrolysis parameters such as temperature, current density, potential and pH.¹³⁸ In a typical process, the conducting piece (undergoing anodization) is positioned in an electrolytic bath serving as anode. The cathode was a rod of platinum. From electrolyte to positive anode, at power supply the electrons are forced. Drifting through the power source, the electrons return to cathode. With hydrogen ions, these electrons react due to which bubbles off hydrogen gas are occurred. If oxide film is porous, the primary determinant is the electrolyte composition. Fig. 11¹³⁹ shows a representation of an electrochemical anodization cell.

In 2001, TiO₂ nanotube arrays fabrication through anodic Ti oxidation was reported first time.¹⁴⁰ Advanced studies

engrossed on extension of morphology,¹⁴¹ length, pore size¹⁴² and wall thickness¹⁴³ of the nanotube were carried out. Fig. 12¹⁴⁴ shows SEM of TA6V anodised in CA electrolyte under 5 V for 20 min. The usage of different electrolytic diluents permitted the architecture control from well detached, standalone nanotubes to tightly packed arrays. The wall thickness of typical nanotubes ranged from 5 to 30 nm, with 20 to 350 nm pore size and 0.2 to 1000 mm length. Zwilling and co-workers¹⁴⁴ used fluorinated electrolyte to produce a porous surface of TiO₂ films

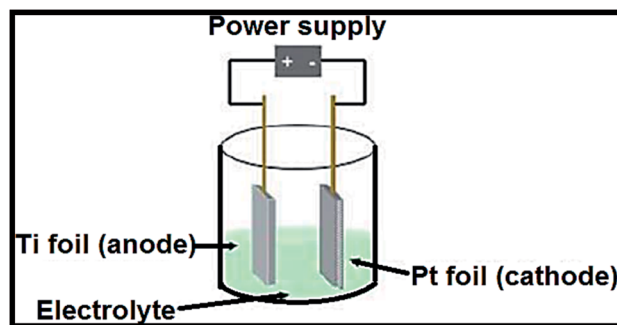


Fig. 11 Depiction of an electrochemical cell in which the Ti samples are anodized. Fabrication variables include temperature, voltage, pH and electrolyte composition.



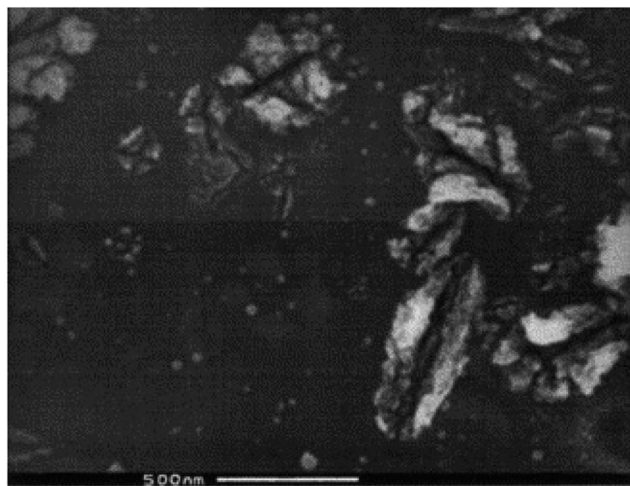


Fig. 12 Scanning electron micrograph of TA6V anodised in CA electrolyte.¹⁴⁴

via electrochemically anodization of titanium. Shimizu *et al.*¹⁴⁵ reported that dil. H_2SO_4 could be used to bond porous TiO_2 thin films. Yamamoto *et al.*¹⁴⁶ observed that the act of dye-sensitized solar cell device was better by cathodically electro-synthesized TiO_2 films; having sealed commercial Degussa P25 nanoparticles. Anodization or anodic oxidation of titanium foils was conducted by Patermarakis *et al.*¹⁴⁷ Platinum and titanium were used as cathode and anode. Using formamide–water mixtures (having fluoride ions), Shankar and co-workers¹⁴⁸ studied the effect of five dissimilar cationic species on development of TiO_2 nanotube array.

In 2006, Ruan and co-workers¹⁴⁹ synthesized titania nanotube by titanium anodization in an electrolyte. In 2006, nanotube arrays of protracted length from DMSO electrolytes was described by Paulose and co-workers.¹⁵⁰ The importance of diethylene glycol (DEG) for nanotube array synthesis was reported by Yoriya and co-workers.¹⁵¹ These authors investigated tube formation. The necessity of tube separation and crystallization in the DEG-based electrolytes were required. The benefit of TiO_2 nanotubes produced by anodization is readily attachment capability in a perpendicular orientation onto the substrate; improving electron transfer pathways as compared to the non-oriented structure.¹⁵² In one study, glycerol pH and water (75–25, v/v) electrolyte having 0.5% NH_4F were modified using H_2SO_4 .¹⁵³ The length of nanotube was 950 nm on adjusting pH 5.6 by H_2SO_4 . Nanotubes of 16 nm were found by anodizing at 20 V for 8 h after adding of 0.1 M CH_3COONa by maintaining pH at 5.6. TiO_2 nanostructured as photoanodes were prepared by nanotubes of TiO_2 by anodic oxidation of foil of titanium^{140,154–156}. In a model experimentation, a plate of clean titanium was anodized in a 0.5% hydrogen fluoride solution under 10–20 V for 10–30 min. The counter electrode used in the experiment was platinum. Crystallized TiO_2 nanotubes were obtained by annellation of plate of anodized Ti at 500 °C for 6 hours in oxygen.¹⁵⁷ The diameter and length of TiO_2 nanotubes may be optimized with the utilized potential between 1.0 and 25.0 V in optimized phosphate/HF

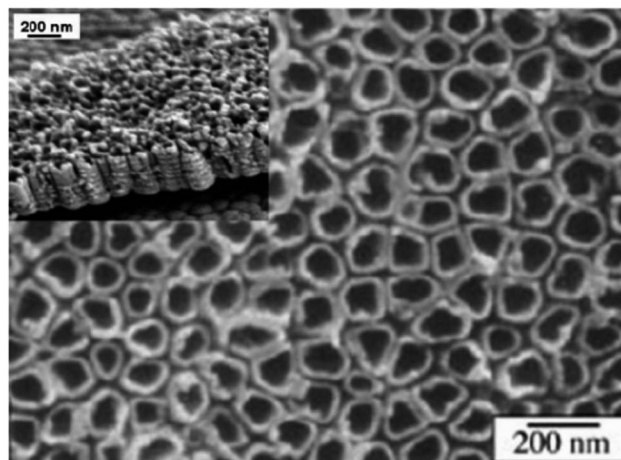


Fig. 13 SEM images of TiO_2 nanotubes prepared with anodic oxidation.¹⁵⁹

electrolytes.¹⁵⁸ SEM pictures of TiO_2 nanotubes produced with this approach are shown in Fig. 13.¹⁵⁹ For the first time, H generation efficiency, phase evolution and electrochemical synthesis of anatase, anatase–rutile and anatase–rutile–brookite (ARB) TiO_2 nanotubes was reported Preethi *et al.*¹⁶⁰ The samples tubular morphology was confirmed by TEM and SEM.

3.2 Gas phase procedures

3.2.1 Chemical vapor deposition. The vapor deposition processes to form coatings to alter the mechanical, electrical are normally used. Also, these methods can be castoff to produce free-stand bodies, fibers and films, or to form fused materials. Recently, chemical vapor depositions have received great attention in the manufacture of nanomaterials. These processes occur in a vacuum space and if chemical reaction doesn't occur, these processes are called physical vapor deposition (PVD). In this process, gases must be heated by suitable thermal. By using liquid precursor and titanium tetraisopropoxide (TTIP), pyrolysis in a mixed gases (consisting of helium/oxygen atmosphere) leads to prepare bushy crystalline of TiO_2 films with sizes below 10 nm.¹⁶¹ Ayllon *et al.*¹⁶² described the synthesis of amorphous nanoparticles of TiO_2 . Pradhan, *et al.*¹⁶³ prepared nanorod arrays of TiO_2 with a length of 0.5–2 μm and a diameter of about 50–100 nm (Fig. 14). Metal organic CVD was used by the authors on a WC-Co substrate using (TTIP) as the precursor. Similarly, on the particle size distribution of aerosol particles prepared by gas-phase chemical reactions, Okuyama and colleagues^{164–166} described the effects of the primary concentration of TTIP vapor and temperature profile of the furnace. They found that in the controlled cylindrical furnace, the thermal decomposition of TTIP vapor led to form 10–60 nm sized ultrafine TiO_2 nanoparticles. Likewise; using TTIP as precursor; the formation of TiO_2 nanoparticles reinforced on porous silica gel (60–100 mesh) via metalorganic chemical vapor deposition MOCVD process was reported by Ding and colleagues.¹⁶⁷ A tubular furnace controlled the reactor temperature. Pretreatment of the support materials, CVD reaction and calcinations process were





Fig. 14 SEM micrograph of TiO_2 nanowires deposited without NH_3 at 500°C ; (a) with 800 sccm argon flow, and (b) with 500 sccm argon flow.¹⁶³

involved in the synthesis of TiO_2 nanoparticle/silica gel photocatalyst. Contrarily, the fabrication of TiO_2 nanorods grown on fused silica substrates was reported by Wu *et al.*¹⁶⁸ Directly, the nanostructures of TiO_2 were grown on the substrates. The only one crystalline anatase and rutile TiO_2 nanorods were formed, respectively, when the temperature ranged between 630 and 560°C at a pressure of 5 torr. Furthermore, for preparing of TiO_2 nanomaterial, the foregoing chemical vapor deposition approaches were also used. These included electrostatic spray hydrolysis,¹⁶⁹ diffusion flame pyrolysis,¹⁷⁰ ultrasonic spray pyrolysis, thermal plasma pyrolysis^{171–173} laser-induced pyrolysis^{174,175} and ultra-sonicated hydrolysis *etc.*

3.2.2 Physical vapor deposition. Among several techniques for the syntheses of TiO_2 nanowires, primary PVD procedures include ion implantation.^{176–178} Before growth of TiO_2 nanowires, a layer of Ti nanopowders deposited on the substrate was

also reported by this group.^{176,177} These authors used gold as catalyst.¹⁷⁶ Fig. 15 displays a model SEM image of nanowires of TiO_2 made by physical vapor deposition method.¹⁷⁶ Xiang *et al.*¹⁷⁹ reported deposit of TiO_2 nanowire on a Si substrate *via* thermal evaporation of Ti powder in a precise furnace. These authors molded $\text{SiO}_2/\text{TiO}_2$ shell-core nanostructures by monitoring the preparation surroundings such as the time of reaction and the substrate position.¹⁷⁹ On a Si substrate, a two-steps thermal evaporation technique was used to grow TiO_2 nanowires. By a radio frequency coil, Ti powder was heated inside a quartz reactor under mixed gases composed of Ar-diluted O_2 atmosphere.^{177–180}

4. Applications of TiO_2 nanostructures

TiO_2 nanostructures have several advantages making them as the most important existing resources with promising usage in the deferent areas. These unique features of TiO_2 include electronic and short diffusion path. Generally, TiO_2 nanomaterials are wide band gap semiconductors containing E_g -values ranging from 3.0 to 3.2 eV with high absorption in the UV region. Titanium dioxide (nanomaterial) is used an important material in high-tech applications. It is the most bio-compatible material. Its optical and biological properties are responsible for UV protection applications.^{181–184} As implant materials, TiO_2 nanostructures are successfully used for dental, orthopedic and osteosynthesis applications.¹⁸⁵ TiO_2 suitable for optical applications.⁷⁰ Besides, photochromism has also been observed in single crystal iron doped rutile.¹⁸⁶ Today, the largest practical research on TiO_2 is its use for photo assisted organic molecules degradation.¹⁸⁷ The applications utilizing this process are purification of waste water, disinfection and self-cleaning coatings in urban areas buildings. The following sub-sections describe different applications of nano TiO_2 structures.



Fig. 15 SEM images of the TiO_2 nanowire arrays prepared by the PVD method.¹⁷⁶



4.1 Photocatalytic applications

Various semiconductor materials such as WO_3 , ZrO_2 , BiVO_4 , Fe_2O_3 and NaTaO_3 have been developed and showed photocatalytic activities over the past few periods. Among of these, TiO_2 is the most photo-catalytically active material used for water splitting as well as decomposition of organic materials.^{65,188–190} Hydrogen is environmental friendly and clean and, hence, it is considered as the future fuel. Numerous studies have been developed to produce hydrogen by splitting water. First of all in 1972, Fujishima and Honda⁴ reported the photocatalytic splitting of water in the occurrence of a TiO_2 catalyst. These materials have also been used to kill bacteria in water treatment¹⁹¹ and tumor cells in cancer treatment.^{14,192} Some reviews are available on the photocatalytic mechanisms.^{11,16,24,33} By the absorption of photon $h\nu_1$, the photocatalytic mechanism is initiated manufacturing an electron–hole pair on the surface of TiO_2 nanoparticle. An electron is encouraged to the conduction band (CB) with formation of a positive hole with the valence band (VB). One or more radicals or intermediate species involved in this photodecomposition process play a crucial role in the photocatalytic mechanisms of reaction. The different factors play significant roles in controlled photocatalytic activities of semiconductors. With constant adsorbents density on the surface, the semiconductors having large surface area lead to faster reactions on the surface.¹⁹³

The size of titanium dioxide particles is much correlated to the fraction of surface located atoms. Due to the decrease in particles dimensions, the atomic fraction enhancing the catalytic activities on the surface increases. The band gap energy depends on the size of nanoparticle. It increases with decreasing nanoparticle sizes, which can be exploited in the optimization of redox potential. The electrons in transmission band and the holes in valence band allow photoredox reactions easily. For high photocatalytic activity, the band gap permits only UV light to be proficiently used. Kormann and colleagues¹¹² investigated the decomposition of 2-propanol using different sizes of TiO_2 nanoparticles. The authors observed that photocatalytic activities of 7.0 nm particles were 1.6 times better than 15–30 nm size.

Wang *et al.*¹⁹⁴ studied the decomposition of chloroform by TiO_2 nanoparticles. They prepared TiO_2 nanoparticles with different size particles and observed the best size of TiO_2 nanoparticles for chloroform photocatalytic decomposition. By decreasing particle size from 21 to 11 nm, an enhancement in activity was observed. Contrarily, by reducing to 6 nm, the activity decreased completely. The authors concluded that the optimal particle size was about 10 nm for this reaction. In different types of TiO_2 nanomaterials, TiO_2 nanorods, mesoporous TiO_2 and nanotubes have revealed high photocatalytic performances under the appropriate circumstances.^{195–197} Rhodamine B was oxidized by mesoporous TiO_2 by Peng *et al.*¹⁹⁶ On the oxidation reaction of desired materials, TiO_2 mesoporous showed significant activity. The nanotubes of TiO_2 treated with H_2SO_4 solutions were prepared by Yang *et al.*¹⁹⁷ The authors observed that the TiO_2 nanotubes treated with different concentration of H_2SO_4 solutions showed photocatalytic

activities for degradation of acid orange II. It was due to small particles having high specific surface areas of TiO_2 nanotubes after treated with H_2SO_4 solution.

To improve the photocatalytic activities under UV irradiation, metal doping TiO_2 nanomaterials have been primarily studied. In current years, wide research work has attentive on visible light tempted photocatalysis by metal doped semiconductor for improved photocatalytic act on the various organic pollutants degradation.^{196–202} As potential dopants, several metal ions including iron^{203–205} nickel^{206,207} vanadium²⁰⁸ chromium²⁰⁹ platinum²¹⁰ ruthenium and cobalt ions²¹¹ have been investigated. There are contradictory consequences on the effects of doping on the visible-light photoactivities of titanium dioxide. Non-metals such as N, C and S (as an impurity) have also been studied for their visible light photocatalytic activities.^{212–221} These studies informed that the non-metallic insertion enhanced photocatalytic actions as related to those for pure TiO_2 nanomaterials; particularly in the visible light region.²¹³ To obtain a charge balance, there are several procedures if an anion is substituted with a high valence anion. In TiO_2 lattice, nitrogen ions substitute oxygen atoms. Titanium dioxide nanotubes photocatalysts have been successfully prepared by Tokudome *et al.*²¹⁹ The author investigated breakdown of gaseous isopropanol into carbon dioxide and acetone by N-doped TiO_2 nanotubes. They observed that N-doped TiO_2 showed high photocatalytic oxidation activity when illuminated with visible light. Other points related to investigated photocatalytic activities of TiO_2 doped sulfur(s) have also been reported.²²² The results exhibited that in region of visible light S doped TiO_2 showed a high photocatalytic activity but lower in UV region. Recently, carbon has received significant interest as a nonmetallic dopant in TiO_2 materials. In visible light region, the decompositions of methylene blue and isopropanol have been demonstrated by C-doped TiO_2 .²¹⁶ Using C-doped TiO_2 nanoparticles, Shen and colleagues²²³ reported the degradation of trichloroacetic acid under visible light. They observed that C-doped titanium dioxide exhibited a remarkable photocatalytic activity for the reaction involved in degradation. Fluoride doped TiO_2 was prepared by Yu *et al.*²²⁴ The obtained F- TiO_2 displayed higher photocatalytic activity than undoped TiO_2 under proper preparation conditions.²²⁴ For acetaldehyde and trichloroethylene decomposition, other comprehensive studies provided the investigated of N/F-doped TiO_2 nanomaterials. It was reported that TiO_2 nanomaterials (N/F-doped) had high visible light photocatalytic activities for decomposition reactions.^{225,226} The different dopants moieties metal and nonmetal doping titanium dioxide and preparation procedures are given in Table 2. On the other hand, this table comprises splitting of water by photochemical cell reaction over numerous photo catalysts (Table 3).

4.2 Photovoltaic applications

Fig. 16 exhibits the principle of a dye sensitized solar cells (DSSC).⁴¹ Dye sensitized solar cells have involved much consideration as reformative low priced substitutes to usual solid state devices.²²⁷ A DSSC composed a nanoporous film



Table 2 The different dopants moieties metal and nonmetal-doping titanium dioxide and preparation methods

| Kind of dopants | Doped elements | Preparation methods | Potential applications | Ref. |
|------------------|----------------|--|---|------|
| Metal dopants | Ag | Silver nitrate was mixed with reduction agent (sodium citrate tribasic dihydrate) and the reaction temperature was raised to 80 °C with continuous stirring. Then TIP and HNO ₃ were added and the reaction was maintained at 50 °C for 24 h. The prepared sol was dried at 105 °C for 24 h and calcined at 300 °C | Degradation of nitrophenol in aqueous phase | 316 |
| | Fe | The reactive magnetron sputtering method: 99.99% titanium target and 99.9% iron pieces were placed in the reaction chamber and mixture of argon and oxygen was introduced into the chamber during discharging | Wastewater decoloring | 317 |
| | V | Sol-gel method: solution 1 (vanadyl acetylacetonate dissolved in <i>n</i> -butanol) was mixed with solution 2 (acetic acid in titanium butoxide) and hydrolyzed (24 h) by the water generated <i>via</i> the esterification of acetic and butanol. The suspension as dried at 150 °C, pulverized and calcined at 400 °C for 0, 5 h | Wastewater decoloring | 318 |
| | Au | Titanium(IV) butoxide dissolved in absolute ethanol was added to solution containing tetrachloroauric acid (HAuCl ₄ ·4H ₂ O), acetic acid and ethanol. The resulting suspension was aged (2 days), dried under vacuum, grinding and calcinated at 650 °C | Wastewater decoloring | 319 |
| | Pt | Photoreduction process: TiO ₂ was suspended in a mixture of hexachloroplatinic acid in methanol. The suspension was irradiated with a 125 W mercury lamp (60 min). Pt-TiO ₂ was separated by filtration, washed with distilled water and dried at 100 °C for 24 h | Wastewater decoloring | 320 |
| Nonmetal dopants | N | Titanium nitride (TiN) oxidation: Heating of TiN at 450–550 °C for 2 h in air (heating and cooling temperature rate: 2 °C min ⁻¹) | Photooxidation of aromatic compounds (<i>e.g.</i> toluene) | 321 |
| | | Treating anatase TiO ₂ powder ST01 in the NH ₃ | Photooxidation of acetaldehyde in gas phase | 322 |



Table 2 (Contd.)

| Kind of dopants | Doped elements | Preparation methods | Potential applications | Ref. |
|-----------------|----------------|--|---|------|
| | S | (67%)/Ar atmosphere at 600 °C for 3 h Oxidation annealing of titanium disulfide (TiS ₂) at 300–600 °C | Wastewater decoloring | 323 |
| | N,S | Hydrolysis of Ti(SO ₄) ₂ in NH ₃ aqueous solution. Precipitate was centrifuged, washed with distilled water and alcohol. Obtained gels were dried under vacuum at 80 for 10 h and were ground to obtain xerogel. The xerogel was calcinated at 400–800 °C in air for 3 h | Photooxidation of volatile compounds in gas phase (e.g. acetone and formaldehyde) | 324 |
| | C | Sol-gel method: TBOT was hydrolyzed in the presence of ethanol, water and nitric acid; precipitated titanium hydroxide was dried at 110 °C and calcinated in air at 150–200 °C | Photooxidation of phenol compounds in aqueous phase | 325 |
| | | Acid-catalyzed sol-gel process. Alkoxidide precursor was dissolved in corresponding alcohol, mixed with hydrochloric acid aqueous solution. Obtained gel was aged for several days and calcinated in air (3 h at 65 °C and 3 h at 250 °C) and grounded | Photooxidation of phenol compounds in aqueous phase | 326 |
| | B | Anatase TiO ₂ powder (ST01) was grinding with boric acid triethyl ester and calcinated in air at 450 °C | Improved photocatalytical activity | 327 |
| | P | Sol-gel method: TIP was hydrolyzed in the presence of isopropanol and water, after hydrolysis phosphoric acid was added. Dispersion was stirred for 2 h, centrifuged at 3500 rpm and dried at 100 °C. Obtained powder was calcinated at 300 °C | Photooxidation of phenol compounds in aqueous phase | 328 |

prepared from mesoporous oxide layer of anatase TiO₂. Firstly, through a transparent conducting oxide (TCO) electrode, cell is illuminated where TiO₂ is deposited. Into the metal oxide conduction band, photo excited dye molecules insert electrons. I⁻/IO₃⁻ couple acts as redox species in the electrolyte reducing the oxidized dye molecules back to their inventive state. Overall, the device produces electric power from light.^{4,32} The surface of nanoporous TiO₂ film is bounded by more cations than the electrons. Henceforth, electron transport mechanism is measured to be purely diffusive.^{228,229} From solid-state p-n junction, the process of absorption of light and the transport in

the case of DSSCs are different due to distinct phenomenon. Through eqn (3) to (6), the process is described:

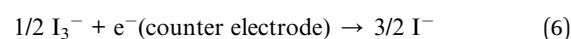
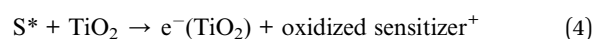


Table 3 Water splitting by photochemical–cell reaction over various photocatalysts

| Photocatalysts | Weights | Reaction solutions | Light sources | Rate of evolutions ($\mu\text{mol h}^{-1}$) | | Ref. |
|---|---------|--|--|--|----------------|------|
| | | | | O ₂ | H ₂ | |
| Pt/TiO ₂ | 0.3 g | 2.17 M Na ₂ CO ₃ | 400 W Hg lamp | 568 | 287 | 329 |
| ZrO ₂ | 1 g | Distilled water | 400 W Hg lamp | 72 | 36 | 330 |
| ZrO ₂ | 1 g | 1.09 M Na ₂ CO ₃ | 400 W Hg lamp | 142 | 75 | 330 |
| Pt/ZrO ₂ | 1 g | 0.94 M NaHCO ₃ | 400 W Hg lamp | 120 | 61 | 330 |
| Ru ₂ O/ZrO ₂ | 1 g | Distilled water | 400 W Hg lamp | 11 | 5 | 330 |
| Cu/ZrO ₂ | 1 g | Distilled water | 400 W Hg lamp | 14 | 6 | 330 |
| NiO/Sr ₂ Nb ₂ O ₇ | 1 g | Distilled water | 400 W Hg lamp | 110 | 36 | 331 |
| NiO/Sr ₂ Ta ₂ O ₇ | 1 g | Distilled water | 400 W Hg lamp | 1000 | 480 | 331 |
| (Tetra)BaTa ₂ O ₆ | 1 g | Distilled water | 400 W Hg lamp | 21 | 10 | 332 |
| (Ortho)BaTa ₂ O ₆ | 1 g | Distilled water | 400 W Hg lamp | 33 | 15 | 332 |
| (Ortho)BaTa ₂ O ₆ | 1 g | 0.0005 M Ba(OH) ₂ | 400 W Hg lamp | 126 | 59 | 332 |
| (Ortho)BaTa ₂ O ₆ | 1 g | 0.001 M KOH | 400 W Hg lamp | 24 | 11 | 332 |
| (Ortho)BaTa ₂ O ₆ | 1 g | 0.0005 M BaCl ₂ | 400 W Hg lamp | 15 | 6 | 332 |
| NiO/BaTa ₂ O ₆ | 1 g | Distilled water | 400 W Hg lamp | 629 | 303 | 332 |
| Ni/Rb ₄ Nb ₆ O ₁₇ | 1 g | Distilled water | 400 W Hg lamp | 936 | 451 | 333 |
| Ni/K ₄ Nb ₆ O ₁₇ | 1 g | Distilled water | 400 W Hg lamp | 403 | 197 | 333 |
| Pt/TiO ₂ , TiO ₂ | 12 mg | 2 M KBr, 6.5 mM FeCl ₂ | 500 W Hg | 2.8 | 1.3 | 334 |
| Pt-TaON, Pt-WO ₃ | 0.2 g | 5 mM NaI | 300 W Xe lamp with filters: $\lambda > 420$ nm | 24 | 12 | 335 |
| Pt/BaTa ₂ O ₆ N, Pt/WO ₃ | 0.1 g | 5 mM NaI | 300 W Xe lamp with filters: $\lambda > 420$ nm | 6.6 | 3.1 | 336 |
| Pt/SrTiO ₃ :Rh, BiVO ₄ | 0.1 g | 2 mM FeCl ₃ | 300 W Xe with filter: $\lambda > 420$ nm | 15 | 7.2 | 337 |
| Pt/SrTiO ₃ :Rh, Bi ₂ MoO ₆ | 0.1 g | 2 mM FeCl ₃ | 300 W Xe with filter: $\lambda > 420$ nm | 19 | 8.9 | 235 |

From the equations, it is clear that photosensitizer (S) adsorbs light on the exterior of the semiconductor TiO₂ (eqn (3)). Then the photo-excited dye (S*) hand over electrons into titanium dioxide (eqn (4)). After that the reduced species found in the electrolyte (I⁻) recovers electrons losing in the sensitizer (eqn (5)). Finally, by the mediator (I₃⁻) that gains electrons (eqn (6)), the circuit is closed.

4.3 Photocatalytic water splitting

Photo-electrochemical and photo-catalytic water splitting to produce hydrogen are considered as potential procedures to achieve hydrogen. These are discussed below.

4.3.1 Fundamentals of photocatalytic water splitting. At semiconductor electrodes, breakdown of water is the main aim of lively research in current years. First, on a TiO₂ electrode, photocatalytic splitting of water was reported by Fujishima and Honda⁴ in 1972. For green and sustainable energy sources,²³⁰ photocatalytic water splitting into H₂ and O₂ using TiO₂ nano-materials remains to be challenge. To drive chemical reactions, the generated electron and hole can be used. Water molecules for overall water splitting^{231–233} are oxidized as well as reduced. The oxidation of water takes place by the holes to form O₂. While the reduction of water takes place by the electrons to form H₂. Of course, there are several features of TiO₂ but under solar energy, its photocatalytic water splitting efficacy is still quite low. Consequently, to activate the photocatalyst, only UV light can be utilized. It enhances its visible light response including upgraded bulk properties of the material. Water splitting mechanism on TiO₂ for hydrogen production is shown in Fig. 17.

4.3.2 Water splitting on TiO₂ nanotube arrays. TiO₂ nanotubes photocatalysts was investigated for water splitting under UV illumination by Shankar *et al.*¹⁴³ By potentiostatic anodization of titanium foil at 10 V in an electrolyte consist of (0.5% hydrofluoric acid, CH₃COOH mixed in a 7 : 1 ratio),¹⁴³ the TiO₂ nanotubes were prepared. Besides, four different electrolyte bath temperatures *i.e.* 5 °C, 25 °C, 35 °C, and 50 °C were tried to obtain the variation in the nanotubes length and thickness. TiO₂ nanotubes having pore diameter of 22 nm and wall thickness of 34 nm (ref. 156) were used to generate hydrogen gas. The total adaptation efficiency was 6.8%.¹⁵⁶ At 320–400 nm (98 mW cm⁻²), the authors also reported that for illumination. The nanotube array of TiO₂ photoanodes may generate hydrogen from water with 12.25% photoconversion efficiency. On titanium foil; nanotube arrays with 570 nm in length and 70 nm in pore size; were prepared in 0.15 M hydrofluoric acid–0.5 M nitric acid by Xie *et al.*²¹⁷ Fig. 18 shows the comparison between the photoelectrochemical current of annealed TiO₂ nanotube array films and that of porous TiO₂. To higher surface area, the nanotube array samples with higher electrochemical current density were also ascribed.

4.3.3 Water splitting on doped TiO₂. Splitting of water has also been studied on TiO₂ obtained after doping with metal-non metals. Exactly doping is the incorporation of foreign elements into TiO₂ crystal lattice. The aim of doping is to enhance photocatalytic activities.²³⁴ With the potential for H₂ evolution, certainly the band gaps of titanium dioxide semiconductor photocatalysts become extensive.

In a photoelectrochemical cell to oxidation and reduction of water to H₂ and O₂, Wrighton and colleagues²³⁵ investigated the





Fig. 16 Operation principles and energy levels of nanocrystalline dye-sensitized solar cell.⁴¹

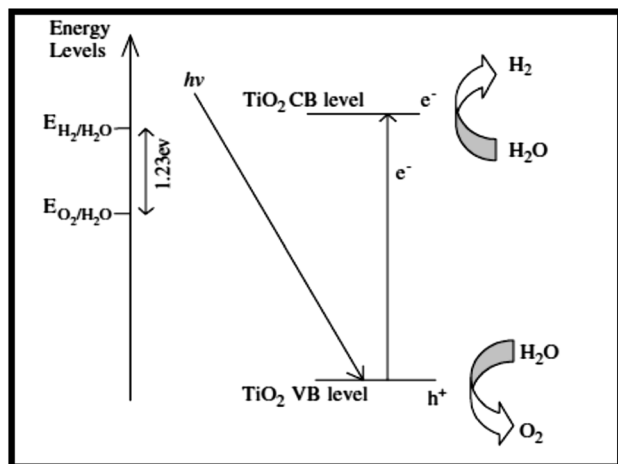


Fig. 17 Mechanism of TiO_2 photocatalytic water-splitting for hydrogen production.²³⁰

use of an n-type semiconductor SrTiO_3 electrode. Without any external bias, decomposition of H_2O can be driven photochemically. Jin and co-workers²³⁶ reported that TiO_2 doped with

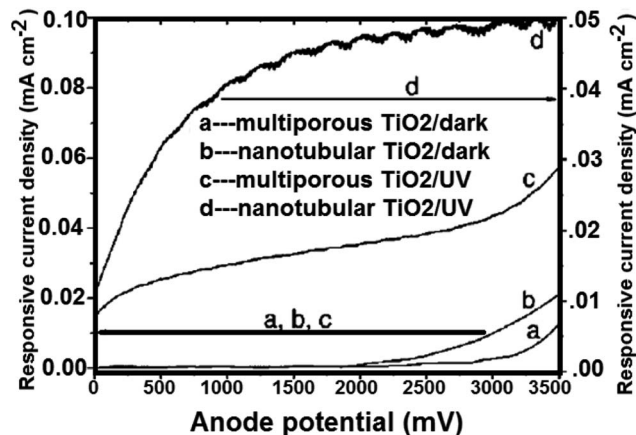


Fig. 18 Measured current of crystallized porous and nanotubular TiO_2/Ti electrodes under linearly swept potential from 0 to 3500 mV vs. SEC.²¹⁷

platinum/boron was a good system for splitting of water. Besides, Khan and colleagues²³⁷ described the response for splitting of water on TiO_2 doped with carbon. The total conversion efficiency was 11%, which had a high water splitting



performance. The authors noted that at 40 mW cm⁻² illumination, an extreme photo-conversion efficiency of 8.35% could be obtained. The synthesis of TiO₂ nanocrystalline thin films; with Pt-loaded through use of radio frequency magnetron sputtering method (RF); was described by Matsuoka *et al.*²³⁸ They investigated that visible light was responsive for water decomposed in the occurrence of TiO₂ nanocrystalline.²³⁹ Bocharov *et al.*²⁴⁰ estimated theoretically the photocatalytic fitness of tinniest single wall fluorite structured titania (4,4) nanotube (NT) possessing three layers each (O–Ti–O) and doped by V, Ni, Mn, Sc, Cr, Fe, Co, Zn and Cu atoms substituted for host Ti atoms. They had associated electronic structure of ground state. For splitting of water, the results were in favor of Sc-doped titania nanotubes only for a potential photocatalytic usage. Using the sol–gel technique, Guayaquil *et al.*²⁴¹ synthesized a series of mesoporous TiO₂ (meso-TiO₂). At 500° and 550°, they were calcined following synthesis. For H generation, the mesoporous 2.50 wt% Pt–TiO₂ had the maximum photo-activity that was displayed by the prepared semiconductors. Alitabar *et al.*²⁴² increased the photocatalytic activity of TiO₂ nanotube arrays used as a photoanode in water splitting by doping it with sodium and carbon.

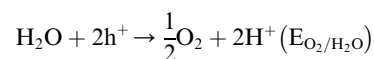
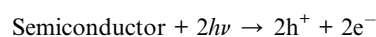
4.3.4 Water splitting on dye sensitized TiO₂. To increase the photocatalytic reaction efficiency, one of the ways is to couple TiO₂ semiconductor nanomaterials to an organic dye to employ visible light for energy change. Some dyes with visible light sensitivities can be utilized in photocatalytic systems and solar cells.^{243–245} Duonghong and co-workers²⁴⁶ studied the effect of using Ru(bipy)₃²⁺ as a dye sensitizer under visible light radiation for hydrogen gas production. They reported water decomposition by using [Ru(bipy)₃]²⁺ and rhodamine B under visible light. Besides, the effect of utilizing [Ru(dcpq)₂(dpq)]²⁺ as a dye sensitizer, Alitabar and Yoozbashizadeh²⁴² carried out a parametric investigation on photocatalytic splitting of water for hydrogen gas manufacture under visible light irradiation. Hydrogen production was increased when dye molecules were adsorbed on to TiO₂. With the help of structure directing surfactant, Sreethawong *et al.*²⁴⁷ prepared mesoporous-assembled TiO₂/Pt. Furthermore, the nitrogen doped TiO₂/Pt (N–TiO₂) was prepared *via* calcination of the hydrolysis product of Ti(SO₄)₂ with aqueous ammonia followed by platinum loading by Li *et al.*²⁴⁸ N–TiO₂/Pt was sensitized and used for hydrogen production in occurrence of triethanolamine using anhydrous EtOH solution of eosin Y. Under comparable experimental conditions, it was observed that eosin Y–N–TiO₂/Pt exhibited advanced photocatalytic activity than eosin Y–TiO₂/Pt.

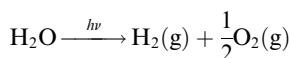
4.3.5 Water splitting on modified TiO₂. Many scientists have modified TiO₂ by different compounds to augment the process of water splitting. Over the surface of TiO₂, when silver oxide nano clusters were impregnated, Mandari *et al.*²⁴⁹ synthesized plasmonic Ag₂O/TiO₂ photocatalysts. Zhang *et al.*²⁵⁰ synthesized (g-C₃N₄) graphitic carbon nitride nanosheets/titanium dioxide (TiO₂) nanoparticles hetero-structure. The prepared g-C₃N₄/TiO₂ hetero-structured composites showed excellent photocatalytic hydrogen generation. Besides, on the g-C₃N₄ nanosheets the TiO₂ nanoparticles were well dispersed.

The as obtained g-C₃N₄ coupled with TiO₂ not only increased the surface area of g-C₃N₄, but also promoted the separation of photo-generated charge carriers. Hou *et al.*²⁵¹ used two typed gold films (i) coated with TiO₂ (ii) and uncoated with TiO₂. After that, they reported measurements of photocatalytic water splitting. For hydrogen gas production with Pt and CoO_x as dual cocatalysts, Zhang *et al.*²⁵² reported a new CoO_x/TiO₂/Pt photocatalyst. This type of catalyst was prepared by template assisted atomic layer deposition (ALD). Under UV light irradiation, the generated electrons and holes transfer to the different surfaces of TiO₂ nanotubes. Photocatalytic efficiency of CoO_x/TiO₂/Pt photocatalysts was 275.9 μmol h⁻¹, while that pristine TiO₂ nanotubes was 56.5 μmol h⁻¹. Xu *et al.*²⁵³ synthesized novel plate like Co(OH)₂ decorated TiO₂ nanosheets for photocatalytic hydrogen generation illustrating Co(OH)₂ decorated TiO₂ samples of high rate of hydrogen generation than native TiO₂ sample. Sui *et al.*²⁵⁴ prepared a Pt/TiO₂ catalyst, where Pt was atomically and selectively dispersed on the (1 0 1) facets of nanosized TiO₂ single crystals. For H₂ production, a remarkably higher photocatalytic activity was compared to frequently used Pt/TiO₂. Si *et al.*²⁵⁵ synthesized anatase TiO₂, thin TiO₂ (B) nanosheets and their composites. The properly aligned structure of band, with the conduction band level of ultra-thin TiO₂ (B) was about 0.6 eV higher than that of the anatase. Wang *et al.*²⁵⁶ reported that very small amount of fluorine inhibited hydrogen and oxygen recombination. The detailed study showed that inhibition was by occupation of hydrogen and oxygen sorption and activation sites by fluorine ion over platinum. Liu *et al.*²⁵⁷ fabricated a composite photoanode having TiO₂ nanotube arrays altered with polyoxometalate (POM) and Co₉S₈.

5. Mechanism of water splitting

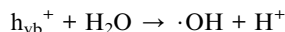
On surface modification of TiO₂, a number of efforts have been made to expand the photocatalytic activities as simple change can eagerly adjust the mechanisms and accelerates the kinetics of photocatalysis.^{258,259} In the UV regime, the band gap for TiO₂ lies. Besides, the latter has lower photocatalytic activities due to the lower ECB of ritual by ~0.2 eV. For modification of TiO₂ nanomaterials, the goals are to improve their optical activities.^{213,214} There are several methods to recover the performance of TiO₂ nanomaterials. In visible light, other colorful compounds sensitizing TiO₂ might be improved optical activity. Second, doping with other elements can also change the optical properties of TiO₂ nanomaterials. At the atomic level, Hussain *et al.*²⁶⁰ explored the interfacial structure between a rutile TiO₂(110) surface pre-characterized and liquid water. The mechanism of splitting of water occurring in the occurrence of semiconductor photocatalyst was explained by Salvador in 1–4 equations as follows.²⁶¹



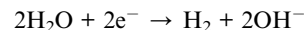
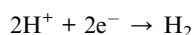
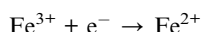


EtOH serves as a sacrificial reagent which also helps to increase the entire process efficiency.⁶⁴ Water splitting mechanism on Ag/TiO₂ was explained by Liu *et al.*²⁶²

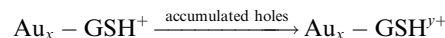
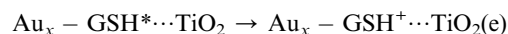
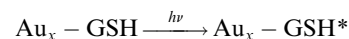
According to Salvador *et al.*²⁶¹ during the process of water splitting, formation of H⁺ and OH⁻ can take place through the reaction of H₂O molecules with holes in TiO₂ valence band. The consumption of ·OH can occur through chemical reaction with CH₃CH₂OH. With enhanced energy, the electrons react with H⁺ at the surface of Ag NPs where H⁺ can take an electron through SPR (surface plasmon resonance) to generate an H atom, and then 2H atoms associate with each other for the formation of an H₂ molecule.



With an I⁻/IO₃⁻ (iodide/iodate) redox-mediator system, water splitting mechanism on TiO₂ was explained by Nishijima *et al.*²⁶³ Besides, they studied the photoassisted oxidation of water continued with impartially high efficiency when Fe³⁺ ions were used as electron acceptors. This whole process of splitting of water on doped titanium dioxide; containing a rutile phase; was compared to that on doped titanium dioxide with an anatase phase. After all, they proposed the mechanism of water splitting in following equations:



Mechanism for water splitting on TiO₂ photosensitized by glutathione capped metal nanoclusters was explained by Chen and Kamat.²⁶⁴ In aqueous buffer solution (pH = 7), a mesoscopic TiO₂ film photosensitized by glutathione capped metal nanoclusters (Au_x-GSH NCs) was utilized as the photoanode with platinum counter electrode. After all, they also proposed the water splitting mechanism as follows:



6. Lithium batteries

As the most promising energy storage technologies, lithium ion batteries (LIBs) are measured as the best for renewable energy, electric vehicles and mobile electronics. In recent years, as a possible anode, TiO₂ (B) has received growing interest for Li ion batteries. As compared to commercialized Li₄Ti₅O₁₂, it offers higher energy storage. From the micron to the nanoscale, it is better than rutile and anatase. The important factors playing an important role and greatly affect the lithium ion batteries (LIB) performance are particle size and crystallographic alignment of the nanostructured.²⁶⁵⁻²⁶⁷ The crystallographic orientations [such as TiO₂(B)] and the theoretical studies^{268,269} confirmed that lithium ion mobility favors the direction in the order of $b > c \gg a$ -axis channel.²⁷⁰

7. Gas sensors

The other application of TiO₂ nanocrystalline is as gas sensor because gas adsorption causes a change in electrical conductivity like ZnO semiconductors.^{155,270-272} Thus, TiO₂ is usually used as an oxygen gas instrument, *e.g.* to gauge the burning process of fuel in car engines to control fuel environmental pollution and consumption. Grimes *et al.*¹⁵⁵ considered the use of titanium dioxide as sensor.



8. White pigments

The pigment being the most abundant component in the coating affects the properties of the coating materials. Because of its highest refractive index of stability, colorless, and relatively low and uniform absorption of visible light, titanium dioxide has newly become a core white pigment source of scattering of light. By two procedures *i.e.* hydrothermal and hydrolysis, Samya El-Sherbiny *et al.*²⁷³ created anatase and rutile. In paper coating, the usage of the prepared nanopigments disclosed that a slight amount of titanium dioxide was satisfactory to attain important improvements in brightness and opacity. It is due to ability of scattering light.

9. TiO₂-based nanocomposites as catalysts

TiO₂ photo catalysts have been widely studied for the uptake of organic contaminants in water and air.²⁷⁴ The present article also concentrated on hybrid nanocrystals based on TiO₂, describing different examples of synthetic methods and deliberating their applications in water treatment. Some papers are reported in the area of hybrid nanocrystals preparation. The papers on the photocatalytic features of nanocatalysts indicated their huge measure applications as challenges. However, these nanomaterials hold good assurance for the dilapidation of organic and inorganic contaminants in water or gas phase. The main features of nano sized TiO₂ materials are enormously high surface to volume ratio and turning into a great density of catalytically surface sites.²⁷⁵ The another fact is the size reliant band gap of nano sized semiconductors. It is likely to finely adjust the redox potentials of photogenerated electron hole couples to selectively control photochemical reactions. Besides, the catalyst surface is occupied easily by charges photo-generated in nano-catalysts.²⁷⁶ The hybrid nanocrystals formed by two or more components hold great promise for the development of multifunctional nanocatalysts among the embarrassment of methods proposed in the literature so far.^{277–281} Indeed, the opportunity is offered by hybrid nanocrystals to merge in one material resulting in countless possible combinations.^{282–285} Under visible light irradiation, spatial separation of e⁻/h⁺ could also be provide by the photoactivity hybrid nanocrystals. Thus, improving is an occasion to magnetically recuperate the photocatalysts or stimulate biocidal utility even in the dark. The surface properties, the particle size of the catalysts, their morphology, the composition, organization of the metal and TiO₂ are the factors, which also affect the photocatalytic efficiency.²⁸⁶ Therefore, for the preparation of metal nanoparticle hybrid hetero-structures, numerous synthetic methods have been described, which include impregnation,²⁸⁷ UV irradiation,²⁸⁸ electrodeposition,²⁸⁹ sonochemistry,²⁹⁰ hydrothermal,²⁹¹ sol-gel,²⁹² and flame-spray synthesis.²⁹³ Wenqing *et al.*²⁹⁴ prepared nanocomposites of titanium dioxide (P25) and reduced graphene oxide (RGO) utilizing numerous methods such as hydrazine reduction, UV-assisted photocatalytic reduction and hydrothermal. Those nanocomposites

were studied as photocatalysts for the progress of hydrogen from alcohol solution under UV-vis irradiation. It was found that the assimilation of RGO into P25 considerably increased the photocatalytic activity for H₂ evolution, and the P25–RGO composite synthesized by the hydrothermal method showed the excellent presentation. Deepa *et al.*²⁹⁵ prepared Au/TiO₂ nanocomposites for photocatalytic hydrogen generation in the company of a sacrificial electron donor like ethanol or methanol under UV-visible and visible light irradiation. These nanocomposites exhibited excellent photocatalytic activity for hydrogen generation under UV-visible conditions. Amount of hydrogen evolved using Au/TiO₂ nanocomposites under dark condition was zero. Anna and Jerzy²⁹⁶ studied the hydrogen generation by water splitting on Pt–TiO₂ catalyst. Besides, they also examine the influence of numerous sacrificial chemicals like MeOH, Na₂S, and ethylene diamine tetraacetic acid (EDTA), I⁻ and IO₃⁻ ions on the photocatalytic efficacy in water splitting reactions in ultraviolet (UV) illumination. Photocatalytic water splitting was achieved at EDTA and Na₂S utilization as the sacrificial reagents. Yatskiv *et al.*²⁹⁷ reported that the photocatalytic systems having mesoporous TiO₂ and Pd/SiO₂, produced extra quantities of molecular hydrogen at keeping in dark after the ending of irradiation. Václav and Daniela²⁹⁸ prepared TiO₂/ZnS/CdS composites by homogeneous hydrolysis of aqueous solutions mixture of TiO₂SO₄, ZnSO₄, and CdSO₄ with thioacetamide for photocatalytic hydrogen production from water. Hydrogen generation was seen in the company of Pd and Pt nanoparticles deposited on TiO₂/ZnS/CdS composites. The excellent photocatalytic activity for H₂ evolution indicated with TiZnCd₇ on surface deposited with palladium, which had 78.5% ZnS, 20.21% TiO₂, and 1.29% CdS–TiO₂/ZnS/CdS. Quanjun *et al.*²⁹⁹ reported new composite material having of TiO₂ nanocrystals *via* two steps hydrothermal process utilizing thiourea, sodium molybdate and graphene oxide as precursors with tetrabutylorthotitanate and MoS₂/graphene hybrid as titanium precursors. TiO₂/MoS₂/graphene composite attained high H₂ generation rate of 165.3 μmol h⁻¹ without a noble metal co-catalyst. Anna *et al.*³⁰⁰ interpreted the development of the quantum yield of H₂ generation using TiO₂/Ag⁰ to TiO₂/Ni⁰ to TiO₂/Cu⁰ in terms of alterations in the electronic interface between the semiconductor surface and metal nanoparticles. They observed a controlled metal amount range for maximum quantum yield of hydrogen generation. Ke *et al.*³⁰¹ examined Pt-loaded nanocomposites, pristine MWNTs and TiO₂ for their photocatalytic activities for water splitting with triethanolamine as an electron donor. Hydrogen was effectively generated on Pt/MWNT–TiO₂ in visible light illumination (λ > 420 nm). Hydrogen production rate up to 8 mmol g⁻¹ h⁻¹ under full spectral irradiation of a Xe-lamp, or more was attained. Takuya *et al.*³⁰² investigated the photocatalytic hydrogen generation in MeOH_n with CuO/TiO₂, SnO/TiO₂, ZnO/TiO₂, CuO/Al₂O₃/TiO₂ and Al₂O₃/TiO₂ nanocomposites. The maximum hydrogen generation was achieved with CuO/Al₂O₃/TiO₂ nanocomposites having 0.3 wt% Al₂O₃/TiO₂/0.2 wt% CuO. Nitish *et al.*³⁰³ demonstrated the higher hydrogen evolution reaction (HER) activity of Pt nanoparticles (Pt NPs) reinforced on titanium dioxide (TiO₂) nanocrystals (Pt–TiO₂) and nitrogen doped



reduced graphene oxide (N-rGO) constructed TiO₂ nanocomposite (Pt-TiO₂-N-rGO). Lu *et al.*³⁰⁴ prepared TiO₂ photocatalysts with nickel sulfide co-catalyst by stocking nickel sulfide on TiO₂ with solvothermal synthesis method. It was reported that NiS was used as a co-catalyst with TiO₂ for the photocatalytic generation of H₂. High hydrogen generation was achieved with NiS as hexagonal structure with content in the composite of 7 at% in relation to TiO₂. The rate of H₂ generation was augmented by 30 times than that of TiO₂ alone. Fuyun *et al.*³⁰⁵ prepared nanocomposite of N-doped TiO₂ with graphene oxide (NTG) to improve the photocatalytic efficiency. NTG exhibited high photocatalytic efficiency hydrogen evolution. It was of 716.0 or 112.0 μmol h⁻¹ g⁻¹ at high pressure Hg or Xe lamp, which was around 9.2 or 13.6 times higher than P25 photocatalyst.

Recently, gold nanoparticles were reinforced on TiO₂-C₃N₄ for CO oxidation in visible light illumination exploiting hydrothermal method; beginning with titanium glycolate and graphitic C as precursors. TiO₂-C₃N₄ microspheres were prepared and then decorated with gold nanoparticles by letting HAuCl reaction at alkaline pH (pH = 10) in the attendance of sodium carbonate. After 2 h, the dried and washed powder was calcinated at 350 °C.³⁰⁶ Besides, visible light dynamic silver modified titania catalyst was described for the utilization in the decomposition of MeOH, CH₃COOH, 2-PrOH and *Escherichia coli*.³⁰⁷ A plasmonic gold silver alloy on TiO₂ photocatalyst was also described that indicated elevated degradation of stearic acid at 490 nm than reported using pristine TiO₂.³⁰⁸ Qiu *et al.*³⁰⁹ have described that Cu_xO/TiO₂ photocatalyst resulted into effective VOCs uptake. Furthermore, Wang *et al.*³¹⁰ prepared and used TiO₂ NRs/Fe_xO_y/Ag core shell nanostructures for photodegradation of rhodamine B in solar light illumination. Recently, a reviews described successful removal of benzene, methylene blue and carbamazepine by photodegradation using CNT/TiO₂ nanostructured composites.³¹¹

10. Future challenges and perspectives

Recently, the applications of TiO₂ nanostructures have been exploited to clean environment and produce hydrogen. But there are certain limitations, which we have to overcome to make the structures applicable in real life problems. The efficiencies of these structures are not excellent; especially for decomposing of persistent organic volatile pollutants and production of hydrogen at large scale. Generally, doped TiO₂ nanostructures result into poor photoactivity. Other challenges are to augment spectral sensitivity of these structures to visible and NIR regions and the bio-compatibility of TiO₂ nanostructures. Therefore, there is a great need of future research focusing constant photoactivity in the long run. These can be achieved by modifying the synthetic routs. Nonmetal doped TiO₂ nanostructures have low photocatalytic activity under visible light UV radiation. Therefore, some materials such as polymers, glass, ceramics, or metals may serve as magical

identities in this area for economic and eco-friendly applications.

Future research needs the development of new synthetic procedures and nanostructures with higher surface states. It may be served by non-lithographic complementary metal oxide semiconductor compatible techniques. This technique may be applicable for new doping materials, dopant incorporation into TiO₂ nanostructures and applications for environmental and alternate energy areas. Besides, visible to near infra-red activated titanium nanostructures should be designed. TiO₂ nanostructures may serve as the ideal materials in biological and medicinal science. Therefore, there is a great need to study the bio-compatibility of these structures at supra molecular level. In a nut shell, the researchers have several challenges to tackle with them in near future. Therefore, there is a great need to improve the structures and properties of these materials. The basic knowledge of chemistry, physics and computer modeling may help to achieve the task.

11. Conclusion

An inclusive review of the syntheses, properties and applications of TiO₂ nanostructures is offered. These nanostructures can be prepared by different synthesis procedures as per the requirements. It was observed that the physico-chemical properties of titanium dioxide nanostructures are responsible for wide applications in several fields such as gas sensors, white pigments, lithium batteries, photocatalytic applications (photodegradation of organic compounds), photovoltaic applications and water splitting. TiO₂ nanostructures play a great role in water purification by degrading biological and organic pollutants. The use in generating hydrogen as a green currency is the biggest asset of nano TiO₂ structures. It was observed that the decomposing and water splitting properties of TiO₂ nanostructures are not good enough, which can be exploited at a commercial level economically. It may be predicted that these materials may be the choice in water purification. Most interestingly, we believe that TiO₂ nanostructures will achieve a great reputation in generation of hydrogen fuel – a need of the next century.

Conflicts of interest

There is no conflict of interest.

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