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Research paper

Photocatalyst Nanostructured Tio₂ Powder by Using Hydrothermal Method: a Review

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Abstract

Over the past decades, Titanium dioxide (TiO_2) have been studied extensively that give positive impact to its synthesis and fabrication method that resulting discovery of a simple low-temperature hydrothermal method that makes the nanostructure of TiO_2 easily modified according to the desired application. This paper presents a review of photocatalyst nanostructured TiO_2 by using hydrothermal method as its fabrication method. The TiO_2 powder widely used as a photocatalytic application that mainly for self-cleaning and wastewater treatment. Rutile phase is stable in the high-temperature region compared to anatase and brookite that metastable in high temperature and photo-catalytic activity, PCA could be enhanced by increasing the number of oxygen. By manipulating the preparation method and thermal treatment, a superior photocatalyst with high surface area and crystallinity which correlated to photocatalytic performance was able to produce. In addition to this, photocatalytic activity of TiO_2 is substantially dependent on the crystal size, specific surface area, crystal defects, charge separation capacity and the interface between the photocatalyst and the molecules.

Keywords: *Factor; hydrothermal method; nanostructure TiO_2; photocatalytic application; rutile.*

1. Introduction

Titanium dioxide (TiO_2) has been taken a wide focus on its broad range of application from photocatalysis to wastewater treatment [1-12], solar cell [13-14], cells treatment [15]. Table 1 shows the TiO_2 application. TiO_2 plays the most important role owing to its excellent chemical and physical properties. It can be found mainly in three mineral forms which are brookite, anatase and rutile which has the crystalline structure of orthorhombic, tetragonal with dipyramidal habit, and tetragonal with prismatic habit respectively. For better understanding, Figure 1 illustrates the structure and image of each polymorph [73]. The application of TiO_2 based devices is strongly dependent on its own crystalline structure, morphology and phase dimension [39-43]. Therefore, the controlled synthesis of TiO_2 nanostructures with different shapes and sizes has been developed in recent years. So far, most synthetic efforts have been directed toward monodisperse nanoparticles, nanotubes, nanowires, and nanoribbons. The synthesis of 0-dimensional (0D) and one-dimensional (1D) nanostructures have been widely investigated and well developed. However, reports on the synthesis of complex three-dimensional (3D) titania nanostructures remain uncommon. On the other hand, recent research on the synthesis of 3D nanomaterials shows that this kind of nanostructure may have potential to explore their novel properties [44-47]. For example, flower-like TiO_2 nanostructures, which were synthesized by a hydrothermal method using $TiCl_4$ as raw material, exhibited enhanced light adsorption and photocatalysis [46]. Brookite TiO_2 nanoflowers, which were synthesized by a hydrothermal method from $TiOSO_4$, had larger permittivity than anatase TiO_2 products [47].

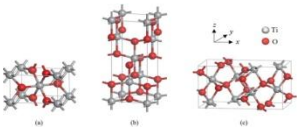


Figure 1: The primitive unit cell of (a) rutile, (b) anatase and (c) brookite TiO_2 [73].

TiO_2 powder has received great attention because of having excellent photocatalytic and antibacterial properties when exposed to UVA light (320-400 nm) and a wide range of applications in various fields like photocatalyst, gas sensing, antibacterial and protective coatings, anti-reflecting coatings, dielectric films, etc [48]. Semiconductor photocatalysis appears to be a promising technology with wide application in environmental systems such as air purification, water disinfection and hazardous waste remediation in addition to hydrogen energy generation [49].

Current methods used to synthesis TiO_2 comprise the assisted–template method [16-18], the sol-gel process [19], electrochemical anodic oxidation [20-25], and hydrothermal treatment [26-38]. The synthesis of TiO_2 powder by hydrothermal method has been studied extensively and the obtained TiO_2 powder offers many advantages compared to other fabrication method. Hydrothermal method is a promising method to obtain nanocrystalline particles. The hydrothermal process generally could take place under auto-generated pressure upon heating. Thus, it is efficient to achieve crystalline phase at a relatively low temperature [7].

The TiO_2 photocatalyst is fabricated using the hydrothermal method because the hydrothermal method is a simple method and may perform in the closed system. Titanium dioxide (TiO_2) or also known as titania is one of the promising catalyst-based material. TiO_2 is a elements combination of titanium and oxygen. This semiconductor photocatalyst already proved for various applications due to its stability, strong oxidizing powers, non-toxicity material, ready availability and low cost [10-13]. In the recent years, TiO_2 powder is extensively studied because of their interesting chemical, optical and electrical properties in photocatalysis. The synthesis of TiO_2 powder via hydrothermal method has been extensively studied, and the obtained TiO_2 powder offers many advantages over that prepared using the calcination method.

Table 1: TiO_2 Application

Author (Year)	Application
Fujihira *et al*. (1981)	Photocatalytic oxidation using anatase TiO_2 in organic suspension [68].
Lakshmi *et al*. (1995)	Methylene Blue degradation by adjusting pH solution [66].
Burda *et al*. (2003)	Methylene Blue degradation by N-doped TiO_2 using direct amination at room temperature [67].
Maneerat and Hayata (2006)	Exhibit antifungal activity of TiO_2 using in vitro and in fruit test.
Fujishima *et al*. (2008)	Antibacterial materials, self-cleaning surface, removing odors and others.
Yaghoubi *et al*. (2010)	TiO_2 coating on polycarbonate for self-cleaning materials.
Ashkarran *et al*. (2011)	Rhodamine B degradation and antibacterial by Ag/TiO_2 doped NP using sol gel and novel arc discharge method [69].
Jiao *et al*. (2012)	Methyl Orange and 2,4-dichlorophenol degradation by anatase-brookite nanoflower synthesized using hydrothermal method for 24 h at 180℃ [70].
Sreethawong *et al*. (2012)	Methyl Orange degradation using various Ti-to-Ni molar ratios band synthesized by sol-gel process aided with lauryl amine hydrochloride as structure-directing surfactant [71].
Gharagozlou and Bayati (2014)	Rh B degradation by Fe-doped TiO_2 NP using sol-gel method and calcined at 400 ℃ for 4 h [72].

2. Titanium dioxide as photocatalyst

Goodeve and Kitchener in their report explain about photo-catalysis study for solid mechanisms using photosensitization [55]. It becomes the first photocatalysis study for that time. Then, Mashio and Kato published their work on the oxidation of different organic solvent by UV radiation [56]. Followed by Fujishima and Honda that reported the success of photocatalytic splitting of water into hydrogen and oxygen on TiO_2 electrodes [57]. While Frank and Bard reported the environmental pollutant treatment with their development of a photocatalyst [58]. In 1994, Amy et al. published their work on photocatalysis on TiO_2 surfaces. Their results show that the mechanisms and principle of TiO_2 support the idea of photocatalysis and suitable for environmental clean-up [59].

Generally, TiO_2 suitable for photocatalysis due to its properties that inert and chemically stable. The presence of light is required when TiO_2 acts as the photocatalyst to decompose organic materials. Brookite, anatase, and rutile are the most important forms of TiO_2. According to Hashimoto et al., the lifetime of charges carriers is high in anatase compared to rutile that directly indicating high photocatalytic activity [60]. On the other hands, brookite that has complicated synthesis procedure makes it seldom studied [62]. But, rutile phase is stable in the high-temperature region compared to anatase and brookite that metastable in high temperature [61]. Photocatalytic activity, PCA could be enhanced by increasing the number of oxygen. Q.Zhang et al., H. Kominami et al., and M.Maeda et al. claimed that by manipulating the preparation method and thermal treatment, a superior photocatalyst with high surface area and crystallinity which correlated to photocatalytic performance was able to produce [63-65].

The applications of TiO_2 become wide since the discovery of semiconductor and emerging of nanotechnology. In 1972, Fujishima and Honda made an important breakthrough discovery for water photolysis by electrochemical using TiO_2 that splitting water on electrodes for photocatalytic splitting. Since then, there is various research group that conducts studies towards the potential uses of TiO_2 based materials as a photo-catalyst. Photocatalytic oxidation of TiO_2 powder on degrading cyanide in aqueous suspension was discovered in 1977b [57]. Besides, various aromatic hydrocarbons were reported by combining the photo-electrochemical production of H_2O_2 at semiconductor electrodes with Fenton reaction. However, the ability or significant potential of TiO_2 towards application for pollutant detoxification for environmental cleaning in air and water only been explored in the nineties [63]. Then, in order to improve the performance of TiO_2 as a photocatalyst, further studies were made by many groups of the researcher and resulting to tuning and modifying the TiO_2 either through preparation method that includes the thermal treatment or dopant introduction during the synthesis system.

3. Mechanism of photocatalyst

Photocatalytic is a process of using light to activate catalyst to initiate a chemical reaction. The mechanism of the photocatalytic reaction in the presence of TiO_2 consists of a free radical reaction initiated by UV light [74-78]. The mechanism may depend on the ability of the degraded compound to be absorbed on the surface of the photocatalyst. The extent of such adsorption depends on many factors and one of it a charge of the degraded compound. It was found that in photocatalytic degradation, the adsorption level on unmodified TiO_2 is higher for dyes with a positive charge (cationic) than for those with a negative charge (anionic) [80]. As the charge depends on the pH of a given solution, it follows that both pH and the nature of particular dyes influence the photocatalyst activity [81-85]. When the catalyst was heated with photon or energy greater than the bandgap of semiconductor, the electron will be excite from the valence band to conduction band leaving the holes that h^+ oxidizing [86].

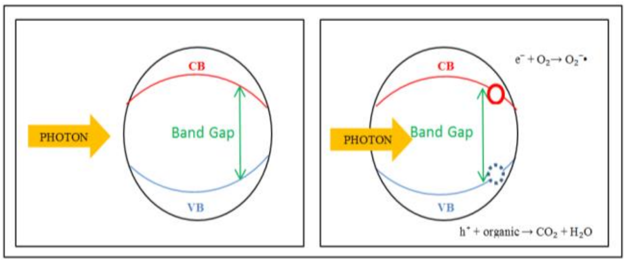


Figure 2 Degradation of organic pollutant [79]

In photocatalyst system, an electron (e^-) from the valence band, VB was excited to the conduction band, CB leaving the hole (h^+) when the photon with energy equal or greater than the band gap energies Eg reach the particle surface. Then it will trigger the heterogeneous photocatalytic reaction due to absorption of radiation that equal or greater than Eg of the targeted semiconductor. The absorbed energy can be dissipated and recombine with the photo-generated electron-hole that generates heat and usable for the redox reaction. Both electron and holes are exploits during redox reaction which is electron (e^-) for reduction process while hole (h^+) for oxidation process on the TiO_2 surface. The most important thing is to make sure the electron and holes are captured the target molecules very quickly because if not it will recombine and there is no reaction and this critical in designing a good photocatalyst. Basically, molecular oxygen in the air reacts with the excited electron in CB to form superoxide radical anions (O_2^-) and water molecules react with photogenerated holes producing hydroxyl radicals (OH•) besides oxidize nearby organic molecules.

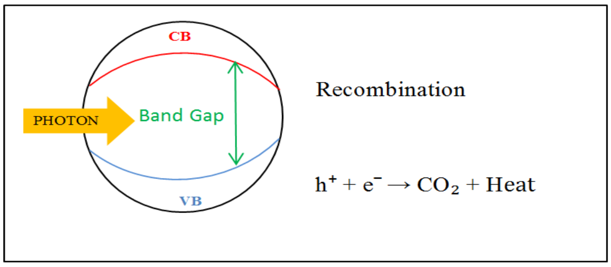


Figure 3 No photocatalysis reaction [79]

The process depends on photocatalyst properties on the electronic, optical, physical and chemical properties. It is important to understand what happened on the surface because the surface reaction is very critical. Light is the most important part. Even there are 100% photonic efficiency materials, no reaction will occur. The photocatalytic breakdown reaction proceeds via intermediate steps ending in the mineralization of the organic to water, carbon dioxide, and mineral acids. The redox potential of the H_2O / •OH couple (-2.8 eV) lies within its band gap energy so that it can be used for water splitting. In the photocatalytic process, the TiO_2 is activated by illumination with UV light having an energy higher than the band gap. Given a band gap Eg = 3.20 eV for anatase and Eg = 3.03 eV for rutile and this corresponds to wavelengths below 387 nm and 413 nm respectively.

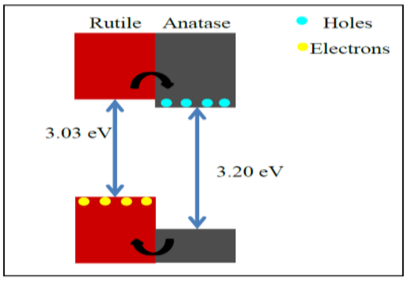


Figure 4 Proposed valence and conduction band alignment mechanism for rutile/anatase interface [87].

4. The principle of the photocatalyst

The photocatalysis word composed of two parts which are photo and catalysis. The prefix photo is defined as “light”. While catalysis is the process of substance speed up or change the rate of chemical transformation of the reactants without being altered in the end. The catalyst is the substance that increases the rate of reaction by reducing the activation energy. Hence, the photocatalysis is a reaction that uses light to activate substance which change the rate of chemical reaction without being altered.

Photocatalysis can be defined as the acceleration of a chemical reaction by either direct irradiation or by the irradiation of a catalyst that in turn lowers the activation energy for the primary reaction to occur [88]. In a heterogeneous photocatalytic process, photo-induced chemical reactions or molecular transformations occur at the surface of a catalyst [89]. This general process can be further divided into catalyzed or sensitized photoreactions based upon whether the initial excitation occurs at the surface of the adsorbate molecule or the catalyst [90]. A catalyzed photoreaction occurs when the initial photo-excitation occurs in an adsorbate molecule, which then reacts with a catalyst substrate. A sensitized photoreaction occurs when the initial photo-excitation occurs in the catalyst substrate and the energy transfer which is often in the form of electron transfer takes place with a ground (non-energetically excited) state molecule.

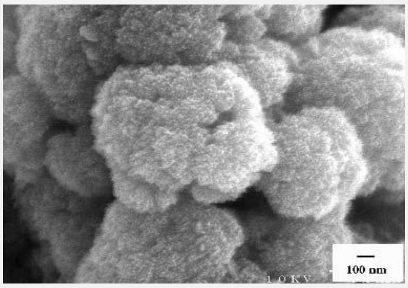
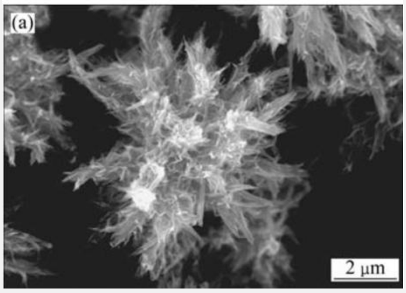
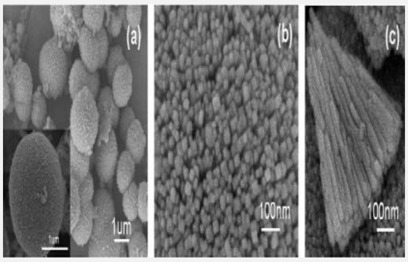
The adsorption of hydrogen on the TiO_2 (110) surface was studied using temperature programmed desorption (TPD), electron paramagnetic resonance (ESR), and measurements of surface conductivity (Ao) and work function (Acp) [56]. The surface defect sites (oxygen vacancies) were found to act as electron donors and are the specific sites for H_2 adsorption. Chemisorption of hydrogen at 300 K forms ionic titanium hydride bonds Ti_4 + -H^- after H_2 dissociative adsorption at the defect sites. This process involves the transfer of two electrons which before adsorption were attributed to one oxygen vacancy site. These two hydrogen atoms can easily recombine during subsequent thermal desorption measurements, exhibiting first-order desorption kinetics. The adsorbed hydrogen atoms also diffuse into the bulk at 300 K, causing a nearly linear increase in conductivity (Ao) when the $Ti0_2$ (110) crystal is exposed to a continuous flow of molecular hydrogen. In the absence of surface defects, the activation energy to dissociate the H_2 molecule is too high, and no adsorption was observed.

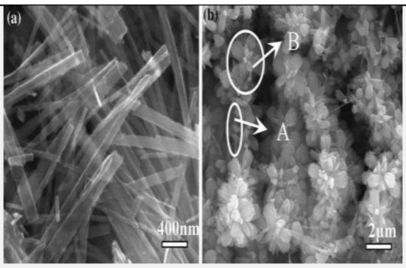
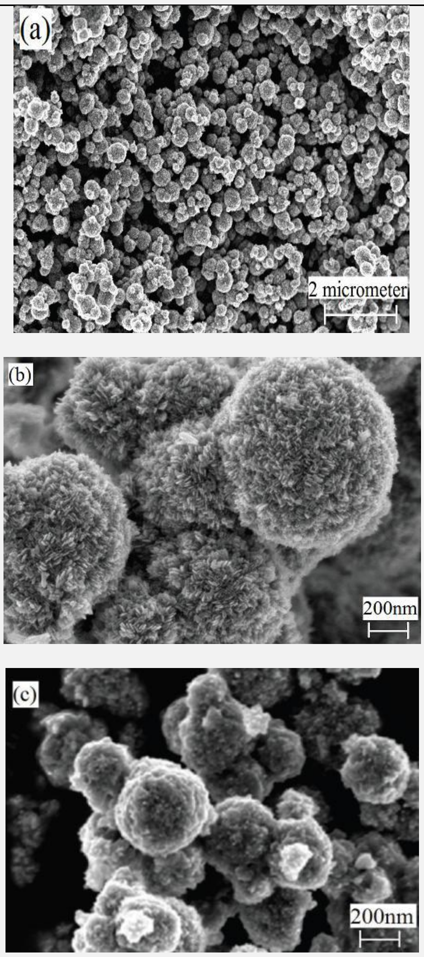
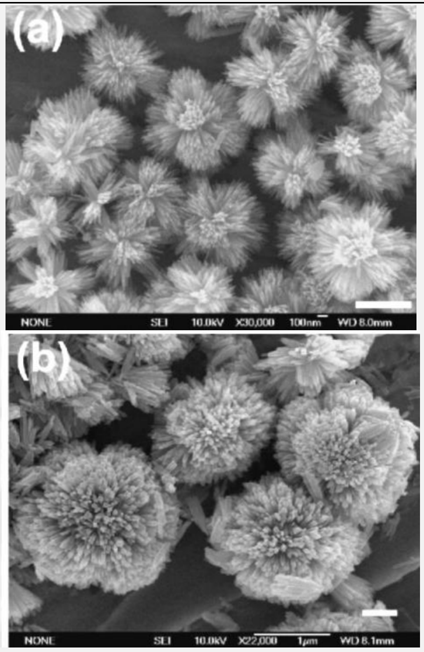
A recent study also reported a very low sticking probability for H adsorption on TiO_2^- (110). Low-energy H_2^+ ion bombardment was employed to enhance the hydrogen adsorption. Surface hydroxyl groups were generated upon hydrogen ion exposures. In addition, the surface Ti_3^+ coverage was found to increase with increasing hydrogen exposures. On powdered $Ti0_2$ surfaces, Beck *et al.* reported TPD spectra typical of weakly adsorbed molecular hydrogen. On both types of $Ti0_2$ powders, chemisorption of hydrogen took place only when hydrogen was introduced above 623 K.

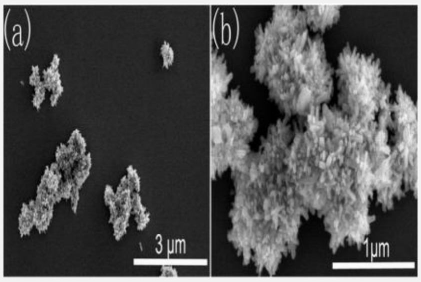
5. Factor that affecting the photocatalytic activity

There are several factors that influence the photocatalytic activity of TiO_2. When photocatalytic degradation of organic molecules is considered, the first demand is that the molecules come in to contact with the surface of TiO_2. However, after the molecules contact the surface of TiO_2, the characteristics of TiO_2 play a significant role in the degradation process. Phase structure is in the center of photocatalytic efficiency of TiO_2. In addition to this, photocatalytic activity of TiO_2 is substantially dependent on the crystal size, specific surface area, crystal defects, charge separation capacity and the interface between the photocatalyst and the molecules [92–93].

Table 2: FESEM images of TiO_2 nanostructured

Details	Method
Cauliflower-shaped, spherical agglomerates of rutile powders are present during the early stage [94].	
Flower-like TiO_2 nanostructures [7].	
(a) SEM image of the TiO2 powder. Inset: an enlarged individual dandelion-like TiO2 sphere. (b) Top image of a dandelion. (c) Crash section of a Dandelion [95].	
(a) TiO2 nanobelts, (b) composite nanostructures composed of a rutile nanobelt framework with anatase nanoflowers: (A) nanobelt as framework, (B) nanoflower grown on nanobelt [10].	

	
(a) Agglomeration of dried TiO2 powder. (b) Needle-like structures of agglomerated particles indicate the formation of rutile phases and (c) Amorphous TiO2 at temperature 50 ˚C [96].	
FESEM images of products derived from (a) benzene (b) oleic acid	

SEM images of TiO_2 nanoflowers at different magnifications [9].	

6. Conclusion

In this review, titanium dioxide was widely used due to its chemical and physical properties that environmentally safe and can easily be modified according to its application. This paper has presented TiO_2 as a photocatalyst, the mechanism involved in photocatalytic activity, the principle of photocatalyst, and factors that affecting the photocatalytic activity. Experimental result regarding titanium dioxide nanostructured also compared.

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