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Synthesis of Titanium Dioxide Microstructures via Sucrose Ester Microemulsion-Mediated Hydrothermal Method

(Sintesis Mikrostruktur Titanium Dioksida melalui Kaedah Mikroemulsi Ester Sukrosa dalam Proses Hidroterma)

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ABSTRACT

Titanium dioxide particles were successfully prepared using microemulsion-mediated hydrothermal processing route, with sucrose ester as a stabilising agent. X-ray diffraction patterns revealed that the particles possessed anatase crystal phase. Scanning electron micrographs showed micron-sized spherical particles with rough and smooth surfaces, which eventually interconnected with one another. The formation mechanism of the titanium dioxide microstructures was postulated. The as-prepared particles were subjected to photocatalytic degradation of methylene blue, which exhibited higher photocatalytic activity compared to their commercial counterpart.

Keywords: Hydrothermal; microemulsion; sucrose ester; titanium dioxide

ABSTRAK

Zarah titanium dioksida telah berjaya dihasilkan menerusi kaedah mikroemulsi dalam proses hidroterma menggunakan ester sukrosa sebagai agen penstabil. Corak pembelauan sinar-X menunjukkan zarah tersebut terdiri daripada fasa hablur anatase. Mikrograf elektron imbasan menunjukkan zarah sfera bersaiz mikron dengan permukaan kasar dan licin yang bercantum antara satu sama lain. Mekanisme pembentukan mikrostruktur titanium dioksida telah dipostulasikan. Zarah yang dihasilkan diuji kuasa penguraian fotokatalitik menggunakan metilena biru dan mempamerkan aktiviti fotokatalitik yang lebih tinggi berbanding dengan zarah titanium dioksida daripada pasaran.

Kata kunci: Hidroterma; ester sukrosa; mikroemulsi; titanium dioksida

INTRODUCTION

Titanium dioxide also known as titanium (IV) oxide or titania, is a naturally occurring oxide of titanium with chemical formula TiO_2. It has a variety of uses and can be found in many products, ranging from paint to food to cosmetics. One of its more well-known uses is as a photocalyst. Its photodegradation activity is spiraled to popularity by Fujishima & Honda (1972) who investigated the decomposition of water on the titanium dioxide electrode. This finding triggers numerous applications of titanium dioxide photocatalysts for the destruction of organic compounds in water or in air. The photocatalytic process breaks down the compounds such as alcohols, carboxylic acids, amines, herbicides and aldehydes into carbon dioxide, water and simple mineral acids (Beydoun et al. 1999).

The photocatalytic efficiency of titanium dioxide is greatly influenced by the crystal structure, particle size, and effective surface area (Mori et al. 2001). Practical application requires maintaining a high surface area of titanium dioxide particles with small dimensions. Several synthesis routes have been developed to accomplish small titanium dioxide particles such as ultrasonic spray pyrolysis (Lee et al. 1991), sol-gel (Sugimoto & Zhou 2002), semi-batch/batch two stage mixed (Kim & Kim 2001) and microemulsion (Kunieda et al. 1993; Li & Wang 1999).

Reverse microemulsion, in which two immiscible liquids, i.e. water and oil, is brought together by means of an appropriate surfactant or surfactant/co-surfactant mixture. This system is formed at high concentration of oil whereby the internal structure of the microemulsion consists of small water droplets in a continuous oil phase.

The surfactants used to stabilise reverse microemulsions can be either charged ionic or nonionic surfactants. In almost all nonionic microemulsions, the nonionic surfactants used are ethoxylated surfactants, such as ethoxylated alcohols, acids and fats, monoglycerides, and sorbitan esters. However, only a limited amount of work was conducted on the polyol type of nonionic surfactants, such as glucoside ethers or sucrose esters of fatty acids. Sucrose esters are biosurfactants which are biodegradable and formed from renewable sources such as fatty acids and sugars (Bolzinger-Thevenin et al. 1999; Thevenin et al. 1996).

In this research, titanium dioxide microstructures were synthesized via sucrose ester microemulsion-mediated hydrothermal method. Hydrothermal method overcomes

the drawbacks of high processing temperatures and long reaction time. The reaction temperature for titanium dioxide falls in the range of 300 to 1200°C (Bakardjieva et al. 2006; Krýsa et al. 2004) whereas the reaction aging time based on microemulsion method usually lasts for 24 hours to 7 days (Lim et al. 2009; Szczes 2009). Upon our investigations, we found that it was appropriate to reduce the reaction temperature and aging time to 200°C and 30 min, respectively with the aid of hydrothermal mediation. The photocatalytic activity of the as-synthesized titanium dioxide particles for degradation of methylene blue was compared with the commercial counterpart under ultraviolet A (UVA) irradiation.

Experimental

Reverse microemulsion was prepared by adding 4.0 mL titanium isopropoxide, $Ti[OCH(CH_3)_2]_4$ (97%, Sigma-Aldrich) dropwise into the mixture of 2.5 mL ethanol (99.9%, R & M Chemicals) and 3.5 mL hydrochloric acid (37%, R & M Chemicals) to obtain a white solution. As titanium tends to form precipitate, the solution was homogenized using a homogenizer. Then, the solution was diluted with 30 mL of distilled water. A given amount of sucrose ester was dissolved into a mixture of a given amount of tetradecane and butanol as shown in Table 1. The sucrose ester used in this work is a commercially available sucrose monoester of stearic acid (S1670, hydrophile-lipophile balance - HLB = 16, at least 70% monoester of stearic acid) in a mixture of di-, tri- and polyesters of stearic acids. The addition of these two phases had a total volume of 60 mL. After stirring for another 30 minutes, the whole mixture was transferred to a 60 mL Teflon-lined stainless steel autoclave and sealed, followed by a heat treatment at 200°C for 30 min. The resulted white powder was centrifuged, rinsed with distilled water and ethanol repeatedly, and finally dried at 50°C overnight. The ratio of water to sucrose ester (W/S) is shown in Table 1. All the chemicals were of analytical purity and were used without further purification. Distilled water was used throughout the experiment.

The crystalline phase of the synthesized titanium dioxide powders was characterized using a Phillips X-Ray Diffractometer (XRD). Measurements were taken from 20 = 15 to 70° at a size step of 0.033°s^{-1}. The Cu anode X-ray was operated at 40 kV and 30 mA in combination with a Ni filter to give monochromatic CuK_α radiation at 1.54 Å. Qualitative analysis was performed with Xpert HighScore using the JCPDS PDF-2 database. Size and morphology of the powders were observed using a LEO 1455 Variable Pressure Scanning Electron Microscopy (VPSEM). Samples for the scanning electron microscopy (SEM) observation were mounted on aluminum stubs using double-sided tape and vacuumed coated with gold in a Polaron SC500 sputter coater.

In order to examine the photocatalytic activity of the as-synthesized titanium dioxide microstructures, the photodegradation of methylene blue was investigated in a photoreactor equipped with UVA radiation. ME1, ME2, ME3 and ME4 (10 mg of each) was dispersed in 100 mL of 5mL/L methylene blue solution. Commercial titanium dioxide (Merck, anatase phase) was used as a reference. The reaction solution was sampled after three hours and the absorbance of the methylene blue solution at 660 nm was monitored using a Shimadzu UV-Visible (UV-Vis) Spectrophotometer.

Results and Discussion

Figure 1 shows the XRD diffractogram of titanium dioxide microstructures. All the peaks at 2θ = 25.00°, 35.50°, 45.50° and 55.00° are attributed to (1 0 1), (0 0 4), (2 0 0) and (1 0 5) crystal planes, respectively. These 2θ values could be well indexed to anatase with tetragonal crystal structure (JCPDS no. 21-1272). No characteristic peaks of other polymorphic phases of titanium dioxide or impurities were found. The broadening of the diffraction peaks is due to the micron size of the particles and indicates that the dimensions of the nanoparticles are small.

Figure 2 shows the SEM micrographs of ME1, ME2, ME3 and ME4, respectively. ME1 and ME2 consist of particles with uneven surfaces. The particle size of ME2 is two-fold that of ME1, which is approximately 2 μm. In contrast, ME3 comprises spherical and smooth particles with narrow size distribution, which is approximately 2 μm. The particle size increases with decreasing W/S ratio. Interestingly, ME4 consists of continuous microstructure. We postulate that the aqueous droplets containing titanium and oxide ions in the sucrose ester microemulsion will continuously collide with each other due to the Brownian

TABLE 1. Chemical ratios for the preparation of titanium dioxide microstructures using microemulsion-mediated hydrothermal method

Sample	Tetradecane + Butanol (1:1) (mL)	Sucrose ester (S) (g)	Water (W) (mL)	W/S
ME1	4	3	3	1.00
ME2	5	3	2	0.66
ME3	6	3	1	0.33
ME4	14	5	1	0.20

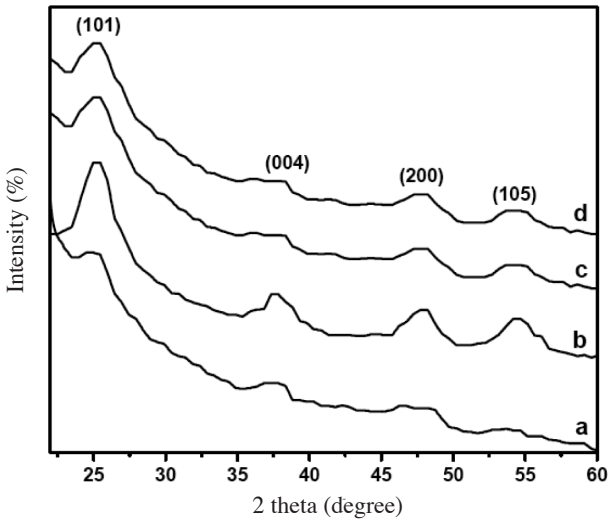

FIGURE 1. XRD diffractogram of (a) ME1, (b) ME2, (c) ME3 and (d) ME4

motion. This will result in the fusion of the aqueous droplets and exchange of the reactants. Then, nucleation and crystal growth happen in the aqueous droplets of the microemulsion. Upon aging, the particles grow larger and adopt the shape of the water droplets. Further growth of the particles resulted in smooth and spherical microstructures due to the maximum growth within the cage-like geometry of the sucrose ester microemulsion (Lim et al. 2009). Meanwhile, the continuous structure was formed due to the Ostwald ripening phenomenon (Ng et al. 1996) under the influence of high concentration of sucrose ester (Glatter et al. 2001).

Among the three main polymorphs of titanium dioxide, which are anatase, rutile and brookite, anatase is believed to exhibit the highest photocatalytic activity (Bakardjieva et al. 2006; Venkatachalam et al. 2007). The degradation of the methylene blue solution by the as-synthesized titanium dioxide microstructures and commercial titanium dioxide particles is shown in Figure 3. Control consisted of only the methylene blue solution.

The UV-Vis absorption of the methylene blue solution was observed after three hours and the absorption peak is detected at 664 nm. Based on Figure 3, ME1 displays the greatest photocatalytic activity as there is almost no absorption of the methylene blue solution after three hours. When titanium dioxide is illuminated with UV light, its electrons are excited to higher energy levels where they can interact with organic chemicals (Shon et al. 2008) such as methylene blue. The interaction degrades the methylene blue molecules causing its blue color to disappear. The high degradation rate is due to its highest surface area contributed by its smallest particle size based on the SEM micrographs.

ME2 and ME3 exhibited rather similar photocatalytic activity, which is degradation of the methylene blue solution by almost half of the initial concentration of the solution.

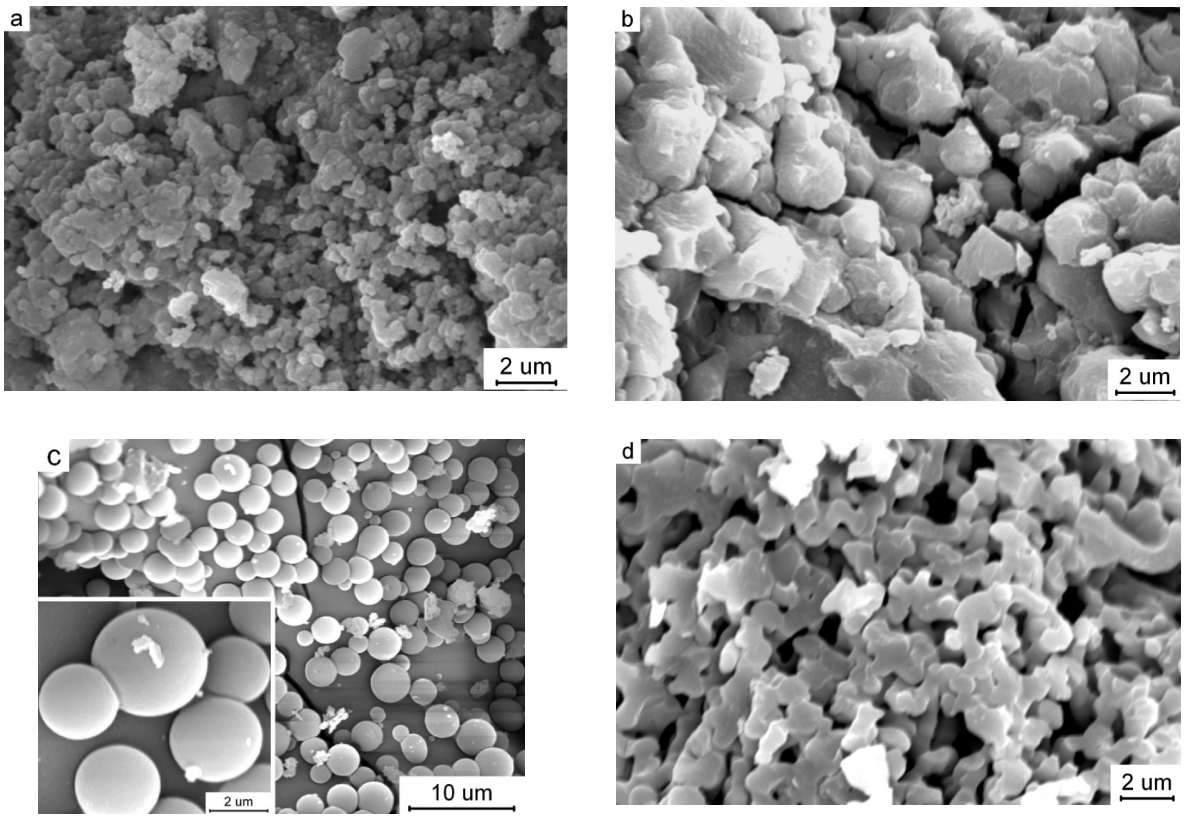

FIGURE 2. SEM micrographs of (a) ME1, (b) ME2, (c) ME3 and (d) ME4

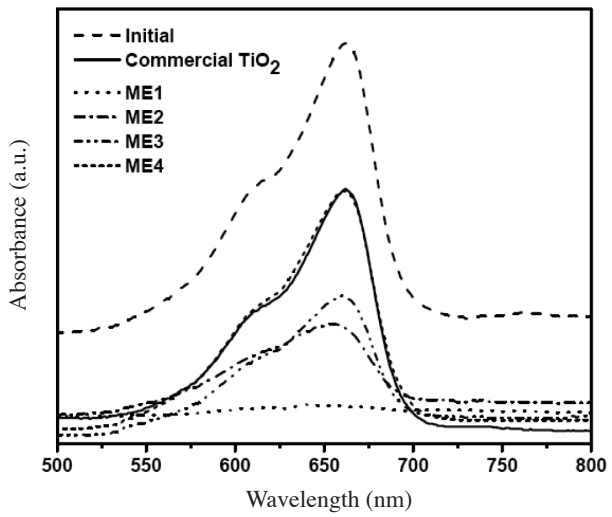

FIGURE 3. Photocatalytic Degradation of Methylene Blue Solution

This is expected as both the samples have almost the same particle size. Surface roughness does not contribute to the rate of photocatalytic activity. The particles produced from ME4 shows the lowest photocatalytic activity and its rate of degradation of the methylene blue solution is almost the same as the commercial counterpart. One plausible explanation to the low photocatalytic activity of ME4 is that there may be remnants of sucrose ester adhering to the surface of the microstructures.

CONCLUSION

Titanium dioxide microstructures were successfully prepared with microemulsion-mediated hydrothermal processing routes. The particles prepared were due to the cage-like properties of the sucrose ester biosurfactant that restricts the particle growth. The as-synthesized titanium dioxide microstructures with significantly enhanced photocatalytic activity underlines their potential as photocatalysts since they provide a good compromise between catalytic activity, economical, easy to obtain and stable in aqueous media.

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