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Synthesis of Titanium Dioxide Nanoparticles via Sucrose Ester Micelle-Mediated Hydrothermal Processing Route

(Sintesis Nanozarah Titanium Dioksida melalui Kaedah Misel Ester Sukrosa dalam Proses Hidroterma)

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ABSTRACT

Titanium dioxide nanoparticles were synthesized via low-temperature sucrose ester micelle-mediated hydrothermal processing route using titanium isopropoxide as the precursor. X-ray diffractometer revealed that the samples possessed a mixed crystalline phases consisting of anatase and brookite in which anatase was the main phase. Upon increasing the hydrothermal reaction temperature, the degree of crystallinity of the nanoparticles improved and their morphology transformed from bundles of needles to rods and to spheres. Photocatalytic behaviour of the as-synthesized nanoparticles was investigated by photodegradation of methylene blue solution in an ultraviolet A irradiating photoreactor. The as-synthesized nanoparticles exhibited higher photocatalytic performance as compared to the commercial counterpart.

Keywords: Hydrothermal; nanoparticles; photocatalyst; sucrose ester; titanium dioxide

ABSTRAK

Nanozarah titanium dioksida disintesis melalui kaedah misel ester sukrosa dalam proses hidroterma menggunakan titanium isopropoksida sebagai pemula. Penyerakan sinar-X membuktikan sampel-sampel tersebut mengandungi campuran fasa hablur yang terdiri daripada anatase dan brokit dengan anatase merupakan fasa utama. Apabila suhu proses hidroterma ditingkatkan, darjah penghabluran nanozarah meningkat dan morfologi berubah daripada jarum ke rod dan ke sfera. Sifat fotokatalitik nanozarah yang dihasilkan diuji menerusi fotodegradasi larutan metilena biru di dalam fotoreaktor sinaran ultralembayung A. Nanozarah tersebut mempamerkan aktiviti fotokatalitik yang lebih tinggi berbanding dengan titanium dioksida yang telah dikomersialkan.

Kata kunci: Ester sukrosa; fotokatalis; Hidroterma; nanozarah titanium dioksida

Introduction

The worldwide annual titanium dioxide use is about 4 million tons and it is the most investigated metal oxides. It is an important material for industrial applications in pigments, semiconductors, photocatalysts, ceramic material, filler, coating and cosmetics (Isley et al. 2008; Wang et al. 2007). The properties of titanium dioxide including high refractive index, light absorption/scattering as well as its chemical stability and relatively low-cost production led to its exploitation in a variety of fields (Baldassari et al. 2005; Kim et al. 2007).

Smaller particle size exhibits better photocatalytic activity because of the higher surface area. With regard to enhancing the catalytic activity and process efficiency in industry, it is important to develop titanium oxide materials with small grain size, high surface area and controlled porosity (Baldassari et al. 2005). Several methods have been utilised for the preparation of nanostructured titanium dioxide such as co-precipitation, sol-gel (Ramaswamy et al. 2008), chemical vapor deposition (Kawai-Nakamura et al. 2008), reverse micelle (Li et al. 2008), microemulsion (Rashidzadeh 2008) and hydrothermal (Kim et al. 2005; Reddy et al. 2004).

Among them, hydrothermal synthesis has been recognised as an environmental friendly process (Kawai-Nakamura et al. 2008; Reddy et al. 2004). This is because the hydrothermal reaction medium uses aqueous as the reaction medium and carried out in an autoclave which is a closed system (Lazau et al. 2007). This method is also known as a powerful method for the preparation of high-purity, highly crystalline, ultrafine and homogeneous powders of various single and multi-component oxide powders (Reddy et al. 2004).

It is important to select suitable surfactant molecules which act as templates or shape controllers, directing the formation of a structure toward a desired target arrangement. Among the surfactants that have been investigated includes dodecanediamine (Wang et al. 2007) and cetylpyridinium chloride (Ramaswamy et al. 2008). Interests in biosurfactants are increasing as they offer several advantages over chemical surfactants such as low toxicity and inherent good biodegradability (Gautam & Tyagi 2006). Sucrose esters are one such biosurfactants as they are prepared from natural and renewable sources such as fatty acids and sugars (Youan et al. 2003).

In this work, titanium dioxide nanoparticles were prepared via hydrothermal processing route, which utilized sucrose ester as a stabilizing agent. The morphology of the as-prepared nanoparticles was influenced by reaction temperature and concentration of sucrose ester. Schematic for the formation of various morphologies of the nanoparticles was postulated. The photocatalytic activity of the nanoparticles for degradation of methylene blue was compared with commercial titanium dioxide under ultraviolet A (UVA) irradiation.

EXPERIMENTAL

Titanium isopropoxide (97%, Sigma-Aldrich) (5.0 mL) was added dropwise into a mixture of 2.5 mL ethanol (99.9%, R&M Chemicals) and 3.5 mL hydrochloric acid (37%, R&M Chemicals) while stirring and a clear solution was formed. Then, the clear solution was added into four different concentrations of sucrose ester solutions (0.1 wt%, 0.3 wt%, 0.6 wt% and 1.0 wt%) under stirring at room temperature for 1 hour. The sucrose ester used in this work is a commercially available sucrose monoester of stearic acid (S1670, HLB = 16, at least 70% monoester of stearic acid) in a mixture of di-, tri- and polyesters of stearic acids. The mixture was than transferred into a Teflon-lined autoclave and the hydrothermal reaction was carried out at 120°C for 24 hours. The resulting particles was centrifuged, washed with water and ethanol, and dried at 60°C for 24 hours. The process was repeated at reaction temperatures of 50, 80 and 105°C. All reagents were of analytical grade and were used as received. Deionized water with electrical resistivity, $\rho \geq 18.2$ MΩ cm was used throughout the study.

The crystallinity of the synthesized titanium dioxide powders were characterised using a Phillips X-Ray diffractometer (XRD). Measurements were taken from 2θ=15 to 70° at a 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 Cu K_α radiation at = 1.54 Å. The XRD data were processed using a PANalytical X'pert HighScore software to examine the peak position and its corresponding intensity data. Samples for TEM observation were dispersed in ethanol and sonicated for five minutes to avoid aggregations. The mixtures were then placed on carbon-coated 400 mesh copper grids and dried at room temperature overnight before examination by Phillips HMG 400 Transmission Electron Microscope (TEM) under 100 kV accelerating voltage.

The photocatalytic activity of the titanium dioxide nanoparticles was determined by the degradation of methylene blue, which was conducted in a 1 L cylindrical Hitachi photoreactor emitting 6 W UVA radiation. Methylene blue was used as a model dye with concentration of 20 mg/L. The solution was immediately analyzed with a Shimadzu ultraviolet-visible spectrophotometer (UV-Vis) to measure its initial absorbance at 665 nm. 2 mg of titanium dioxide sample synthesized using 0.1 wt% sucrose ester at 50°C was added into 20 mL of methylene blue solution and exposed to UVA radiation in the photoreactor for three hours. Commercial titanium dioxide was used as a comparison to the as-synthesized nanoparticles. A blank methylene blue solution was irradiated without the presence of photocatalyst.

RESULTS AND DISCUSSION

The XRD patterns of the hydrothermally prepared titanium dioxide nanoparticles at different reaction temperatures are shown in Figure 1. All the peaks at 2θ = 25.28°, 36.95°, 38.58°, 48.05°, 53.89° and 62.69° are attributed to (1 0 1), (1 0 3), (1 1 2), (2 0 0), (1 0 5) and (2 0 4) crystal planes. These 2θ values could be well indexed to anatase with tetragonal crystal structure (JCPDS no.21-1272) and the lattice parameters are a and b = 3.7852 Å and c = 9.5139 Å. On the other hand, the peak at 2θ = 30.68°, corresponding to (2 1 1) crystal plane, is indexed to brookite with orthorhombic crystal structure (JCPDS no. 76-1937) and lattice parameters of a = 9.2110 Å, b = 5.4720 Å and c = 5.1710 Å. No characteristic peaks of other titanium dioxides and impurities were detected. Therefore, the samples possess a mixed crystal phase consisting of only anatase and brookite in which anatase was the main phase. Upon increasing the hydrothermal reaction temperature, the intensity of diffraction peaks become higher indicating improved degree of crystallinity.

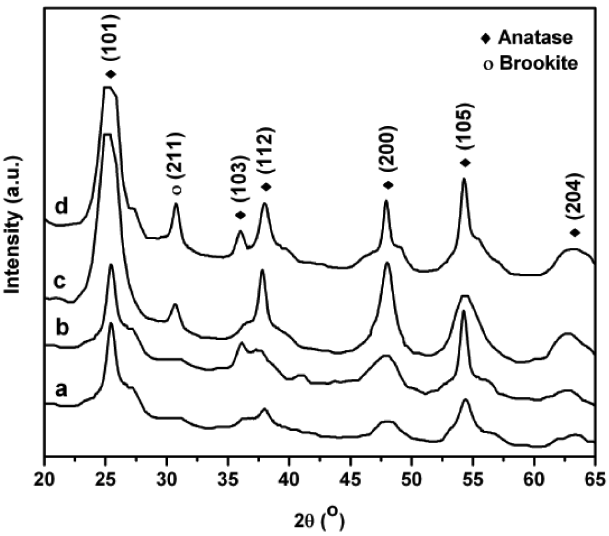

FIGURE 1. XRD patterns of titanium dioxide nanoparticles prepared at (a) 50°C, (b) 80°C, (c) 105°C and (d) 120°C

TEM micrographs in Figure 2 show that at 0.1 wt% of sucrose ester solution, the morphology of the samples changes as the reaction temperature increased from 50°C, 80°C, 105°C and 120°C. At 50°C, the sample consists of bundles of needle-like nanoparticles of 80 nm in length and 40 nm in width (Figure 2a). As the temperature increased to 80°C, the needle-like particles merged to become rod-like with ratio of length to width of 4 (Figure 2b). However, sphere-like nanoparticles were also observed due to separation of needle-like nanoparticles from the bundles. At 105°C, more sphere-like nanoparticles were observed than rod-like particles (Figure 2c) and their number continue to increase at 120°C (Figure 2d). Likewise, the nanoparticles prepared at 0.3 and 0.6 wt% of sucrose ester solutions possess similar morphological formation as the nanoparticles prepared at 0.1 wt% of sucrose ester solution.

One plausible explanation to the formation of sphere-like nanoparticles is that at temperature ≥ 80°C, with pressure rose to above atmospheric pressure due to hydrothermal conditions, the needles were separated from the bundles inadvertently. The separation of needles became more intense as the temperature increased, which resulted in higher amount of needles at higher temperatures. The needles curved at the hydrothermal conditions, which gives rise to the formation of spherical nanoparticles. The size of the spherical nanoparticles increased with increasing temperature of 5 nm (80°C) to 10 nm (105°C) and 20 nm (120°C) because of the increasing rate of crystal growth. The schematic for the formation of the as-synthesised titanium dioxide nanoparticles with various morphologies at hydrothermal conditions is shown in Figure 3. The bundles of needles, formed at 50°C, either merged to become rods or get separated at 80°C. At ≥ 80°C, the separated needles curved to take the shape of sphere.

All the samples which were prepared at 1.0 wt % sucrose ester solution at different temperatures (50, 80, 105 and 120°C) have similar morphology as represented by Figure 4. They possessed ultrafine spherical shape with diameter of approximately 10 nm with narrow size distribution. This indicates that the samples were no longer sensitive to the changes of increasing temperature at the sucrose ester concentration of ≥ 1.0 wt%. Such high concentration of sucrose ester gives rise to gel-like medium, which contributes to ultrafine nanoparticles with narrow size distribution. The gel-like system has significant mechanical rigidity provided by the high surfactant concentration. The high amount of surfactant molecules provides better strength in confining the nucleation and crystal growth within the capacity and orientation of the micelle geometry (Ritzoulis et al. 2005).

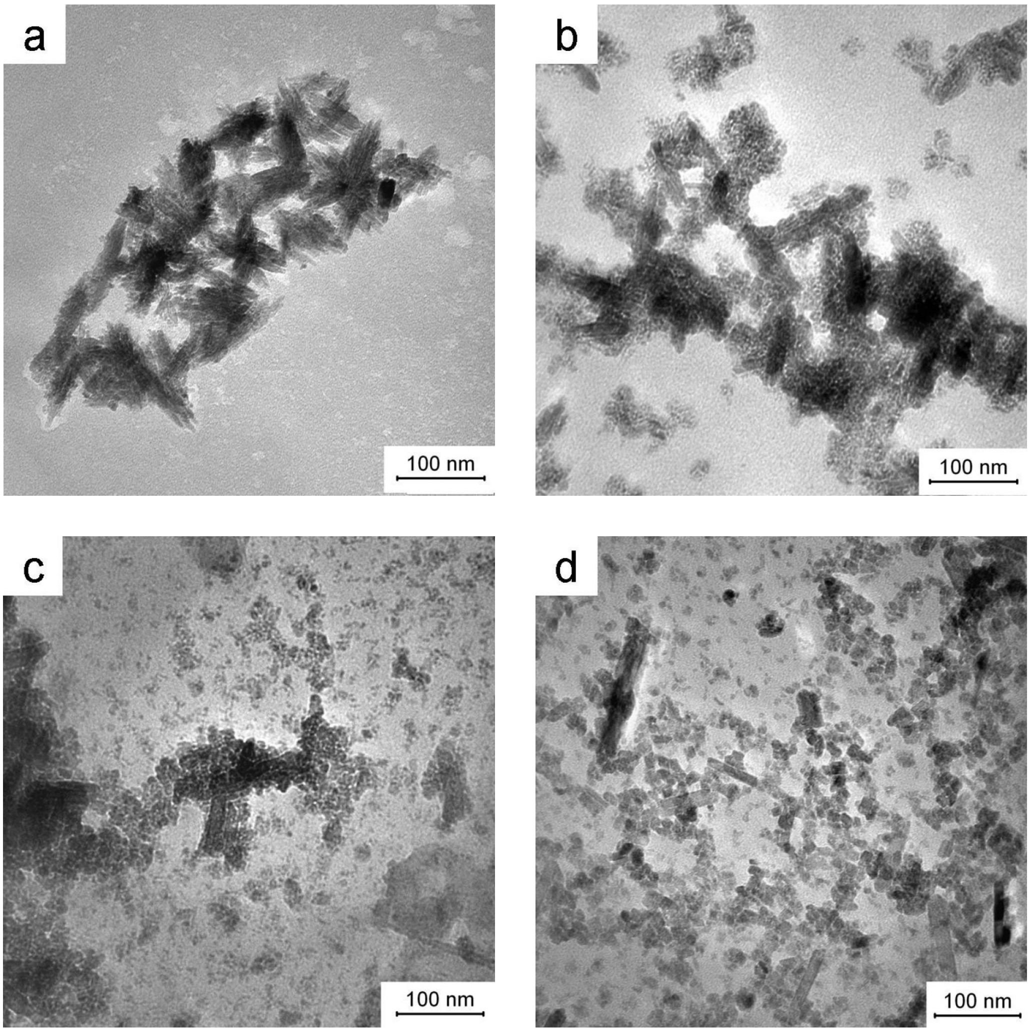

FIGURE 2. TEM micrographs of titanium dioxide nanoparticles prepared from 0.1 wt% of sucrose ester solution and heated at (a) 50°C, (b) 80°C, (c) 105°C and (d) 120°C

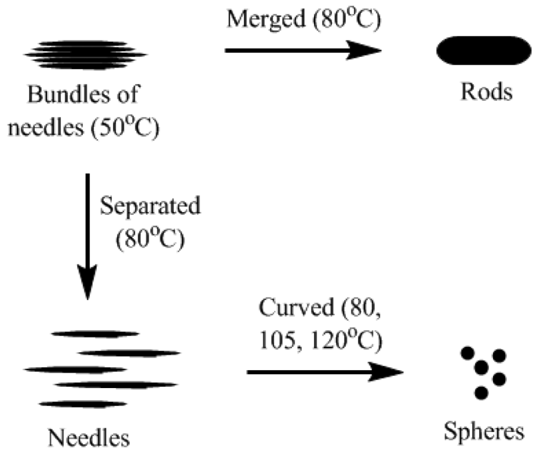

FIGURE 3. Schematic formation of various morphologies of nanoparticles via sucrose ester micelle-mediated hydrothermal method

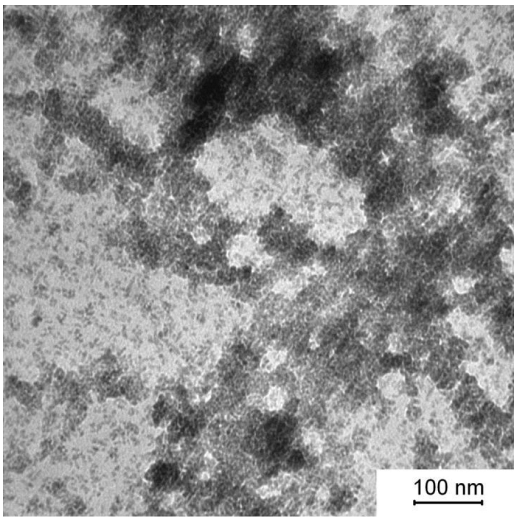

FIGURE 4. TEM micrograph of titanium dioxide nanoparticles prepared from 1.0 wt% sucrose ester solution and heated at 105°C

Photocatalytic activity of bundles of needle-like titanium dioxide nanoparticles prepared from 0.1 wt% sucrose ester solution at 50°C was investigated for their photodegradation activity in methylene blue solution. The photodegradation process was carried out in a photoreactor irradiated by UVA for three hours. Figure 5 shows the degradation of methylene blue solution under UVA irradiation in the absence and presence of as-synthesized and commercial titanium dioxides for comparison. Spectrum a shows the absorbance of the initial methylene blue solution before the irradiation and spectrum b shows absorbance of the methylene blue solution after being irradiated for three hours without the presence of titanium dioxide in the photoreactor. The as-synthesized titanium dioxide nanoparticles (spectrum d) have better photocatalytic activity than their commercial counterpart (spectrum c). The higher photocatalytic activity of the sample may result from the greater surface area contributed by the bundles of needle-like morphology compared to the spherical-like morphology of the commercial titanium dioxide. Moreover, the sample has smaller particle size with narrow size distribution than the commercial titanium dioxide. The latter is about 5-fold larger than the sample as shown in Figure 6. Complete degradation of the methylene blue solution occurred with the addition of the as-synthesized titanium dioxide nanoparticles, which shows that the sample is an efficient photocatalyst.

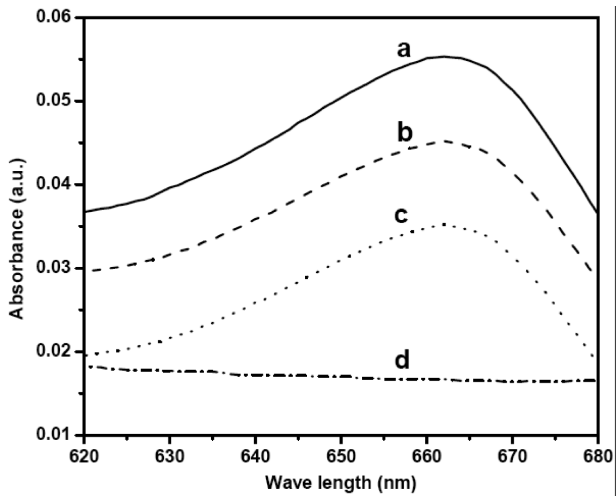

FIGURE 5. UV-Vis absorption spectra of methylene blue solutions after three hours of photodegradation; (a) initial, (b) blank, (c) commercial titanium dioxide and (d) bundles of needle-like titanium dioxide nanoparticles

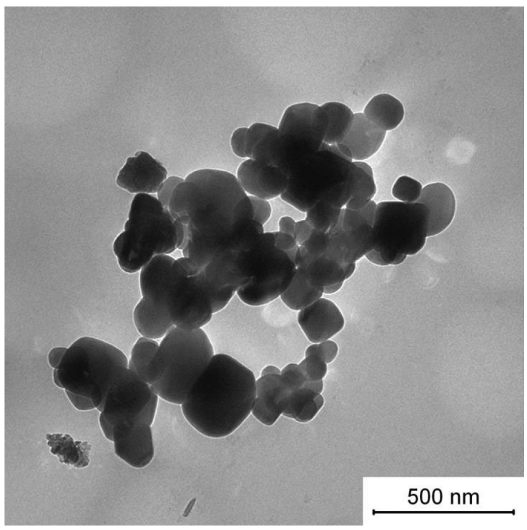

FIGURE 6. Commercial titanium dioxide nanoparticles

CONCLUSION

Sucrose ester-mediated hydrothermal processing route provides a “green” and convenient method to synthesize titanium dioxide nanoparticles at low temperature. At hydrothermal conditions, in which the pressure is raised above atmospheric pressure and the water remains liquid above its normal boiling temperature, there was tendency to produce spherical nanoparticles whose particle size increased with increasing temperature at ≤ 0.6 wt% of sucrose ester solution. Ultrafine nanoparticles of approximately 10 nm with narrow size distribution were formed at ≥ 1.0 wt% sucrose ester solutions regardless of temperature. The promising photocatalytic performance of the as-synthesized nanoparticles underlines their potential as photocatalysts.

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