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Microemulsion-mediated hydrothermal synthesis of photocatalytic TiO_2 powders

Chung-Hsin Lu [*], Wei-Hong Wu, Rohidas B. Kale

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, ROC

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Abstract

A reverse microemulsion-mediated hydrothermal route has been employed to synthesize photocatalytic titanium dioxide (TiO_2) powders. Nanocrystalline monophasic anatase TiO_2 powders were successfully prepared when the microemulsion-derived precursors were hydrothermally treated. The advantage of using this microemulsion mediated hydrothermal route is the significant reduction in reaction time and temperatures as compared with the conventional hydrothermal process. The oil/water emulsion ratio significantly affected the particle sizes of the obtained TiO_2 powders. The specific surface area of TiO_2 powders was increased with the oil/water ratio, thereby leading to enhanced photocatalytic activity of TiO_2 powders. As the hydrothermal temperature was elevated, the morphology of the TiO_2 particles changed from a rod-like shape into a polyhedral shape. The variation in microstructures decreased the specific surface area of the TiO_2 powders and lowered the photocatalytic activity.

Keywords: Titanium dioxide; Microemulsion; Hydrothermal method; Photocatalytic activity

1. Introduction

The synthesis of semiconductor nanocrystals has attracted significant interest because of their special optoelectronic and physiochemical properties. It is attributed to the quantum confinement of electrons and large surface-to-volume ratio [1–4]. Much effort has been devoted to control the size as well as morphology of the semiconductor nanostructures with improved crystallinity. Since these parameters are the key factors to alter the optoelectronic and physicochemical properties of semiconductors [5,6]. Recently, research has been intensively focused on the various semiconductor oxide materials because of their unique optoelectronic properties and variety of technological applications [7].

Nano-crystalline titania (TiO_2) is considered to be one of the most promising materials due to its excellent physicochemical stability, high oxidation affinity, mechanical hardness, superior photo-reactivity, low cost, novel optoelectronic properties and easy availability [8–10]. TiO_2 has been widely used for various applications including electro-chromic display devices [11], dye sensitized solar cells, [12,13], gas sensors [14], cosmetics [15], and phtotocatalysts [8,16-18].

The photocatalytic activity of titania is markedly influenced by the microstructure, crystal structure, particle shape and size, crystallite size, crystallinity, specific surface area and preparation method [15,19–21]. Titanium dioxide has three polymorphic phases, viz. anatase, rutile and brookite [8]. Rutile is a stable phase, while anatase and brookite are metastable and will be transformed into rutile after thermal treatment [15]. Metastable anatase titania ($Eg = 3.2\,eV$) has higher photocatalytic activity than rutile and brookite phases [15,16]. Well crystallized anatase TiO_2 with small crystallite size enhances photocatalytic performance because of its quantum size confinement, high specific surface area, increased number of active surface sites, short interface migration distance and small crystallite size [21,22]. Therefore, it is important to develop a suitable low-temperature method to synthesize nano-sized anatase TiO_2.

Numerous techniques including chemical precipitation [23], sol–gel [24–26], chemical vapor deposition [27], and hydrothermal crystallization [9,12,13,16,18,22] were used to synthesize nano-crystalline TiO_2. These methods suffer the problems of high-temperature processing, long aging time, grain growth and vigorous stirring. The high processing temperatures and long

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[*] Corresponding author.
E-mail address: chlu@ntu.edu.tw (C.-H. Lu).

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reaction time result in the formation of large sized particles with a wide size distribution. To overcome the above drawbacks, a new microemulsion-mediated low temperature hydrothermal route has been employed in this study to synthesize crystalline nano-sized TiO_2 powders. The main advantage of the proposed route is low reaction temperature and short processing time that prevents agglomeration in the formed particles. Varying oil/water microemulsion ratio, nano-sized TiO_2 nano-particles with large surface area and a rod shape were successfully synthesized at low temperature within short reaction period. The effects of hydrothermal processing temperature on the microstructures and photocatalytic behavior of the obtained TiO_2 powders were also investigated in detail.

2. Experimental

Nano-sized titanium dioxide powders were synthesized using a microemulsion-mediated hydrothermal route. The microemulsion is an admixture of cyclohexane, *n*-hexanol, and polyoxyethylene (10) octylphenyl ether (OP-10) in the ratio of 10:3:2. Here cyclohexane was used as a continuous oil phase, *n*-hexanol act as a cosurfactant and OP-10 as a surfactant. Two types of microemulsions were separately prepared and named E_A and E_B, respectively. The oil phase remains invariant for both microemulsion systems. The main difference is that the E_A was prepared by mixing the oil phase into an appropriate amount of $TiOCl_2$ (0.2 M) aqueous phase. E_B contained aqueous solution of NaOH (1 M) mixed with oil phase to form a dispersed microemulsion aqueous phase. The oil/water volume ratio in both microemulsions varied from 5 to 20. Microemulsion E_B was used as a precipitating reagent. Appropriate amounts of dispersed E_A and E_B aqueous media were mixed together with continuous stirring at room temperature for 30 min. The pH value of the mixed microemulsion was adjusted to 7, by adopting the appropriate E_A and E_B microemulsion volume ratio. The resultant mixed microemulsions were transferred into a Teflon container and hydrothermally treated at different hydrothermal temperatures from 150 to 190 °C for 1 h. The autoclave heating rate was almost 3 °C/min. The nano-sized TiO_2 powders were recovered from vacuum filtration and washed several times with deionized water and ethanol to remove any organic residue present in the powders. The suspensions were washed with acetone to prevent particle agglomeration. The obtained white powders were then dried at 60 °C in a vacuum oven.

The X-ray diffraction (XRD) technique was used to determine the crystal structures and phase purity of the as-prepared powders. The average crystallite size of the TiO_2 powders was calculated using Debye–Scherrer's equation using full width half maximum (FWHM) of diffraction peak. Transmission electron microscopy (TEM) technique was used to examine the microstructures and particle sizes of the obtained nano-size TiO_2 powders. UV–vis spectra were recorded by a UV–vis spectrometer (Hitachi U-3410). Brunauer–Emmett–Teller (BET) nitrogen adsorption method was used to measure the specific surface areas of the powders. The photocatalytic activities of TiO_2 powders were determined using methylene blue decomposition in an aqueous solution. The prepared powders (0.01 g) were dispersed in 20 ml (30 μM) of methylene blue solution, in order to satisfy the Bill's law restrictions. Prior to the photocatalytic measurement, the colloidal solution was magnetically stirred in dark for 20 min to establish adsorption–desorption equilibrium condition. The reactant solution was irradiated for 90 min under UV light at 365 nm wavelength. The suspensions were centrifuged to separate out the catalyst from the solution. The methylene blue solution concentrations were analyzed via an UV–vis spectrometer (at 664 nm).

3. Results and discussion

3.1. Oil/water ratio effects on the microstructures and photocatalytic activities of TiO_2 powder

The microemulsion derived precursors were hydrothermally treated at 150 °C for 1 h to obtain nano-sized TiO_2 powders. The oil/water ratio was varied prior to the hydrothermal treatment. The XRD patterns of TiO_2 powders synthesized at different oil/water ratios are displayed in Fig. 1. The XRD patterns are identical for all samples and all peaks were in good agreement with the data reported in ICDD File No. # 21-1272, and were assigned to the TiO_2 anatase phase. No other peaks corresponding to the rutile or brookite phases were observed, indicating that the obtained TiO_2 powders exhibited a monophasic anatase structure. The crystal structure of the TiO_2 powders was not affected by the change in the oil/water ratio. The X-ray diffraction peaks of the obtained TiO_2 powders became broader with increasing the microemulsion oil/water ratio to 20. The broad diffraction peaks implied a decrease in the particle size of TiO_2 powders.

The microstructures and particle sizes of the obtained TiO_2 powders were examined via TEM. Fig. 2(a)–(c) shows TEM

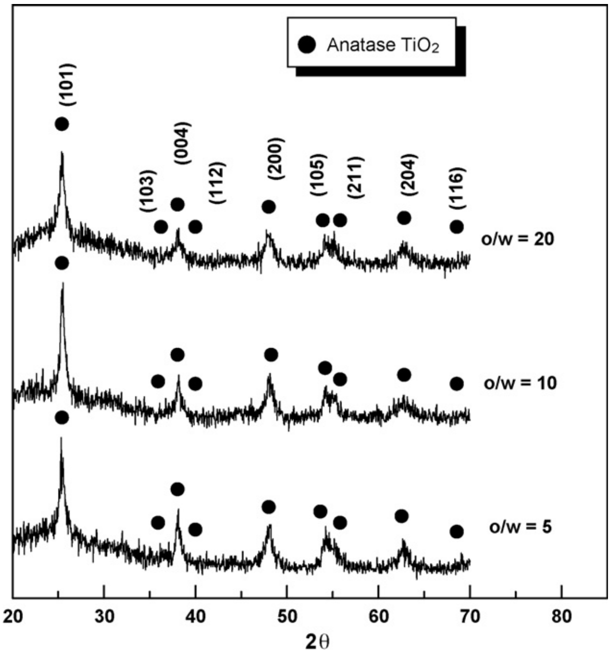

Fig. 1. X-ray diffraction patterns of TiO_2 powders prepared with different oil/water ratios at 150 °C for 1 h.

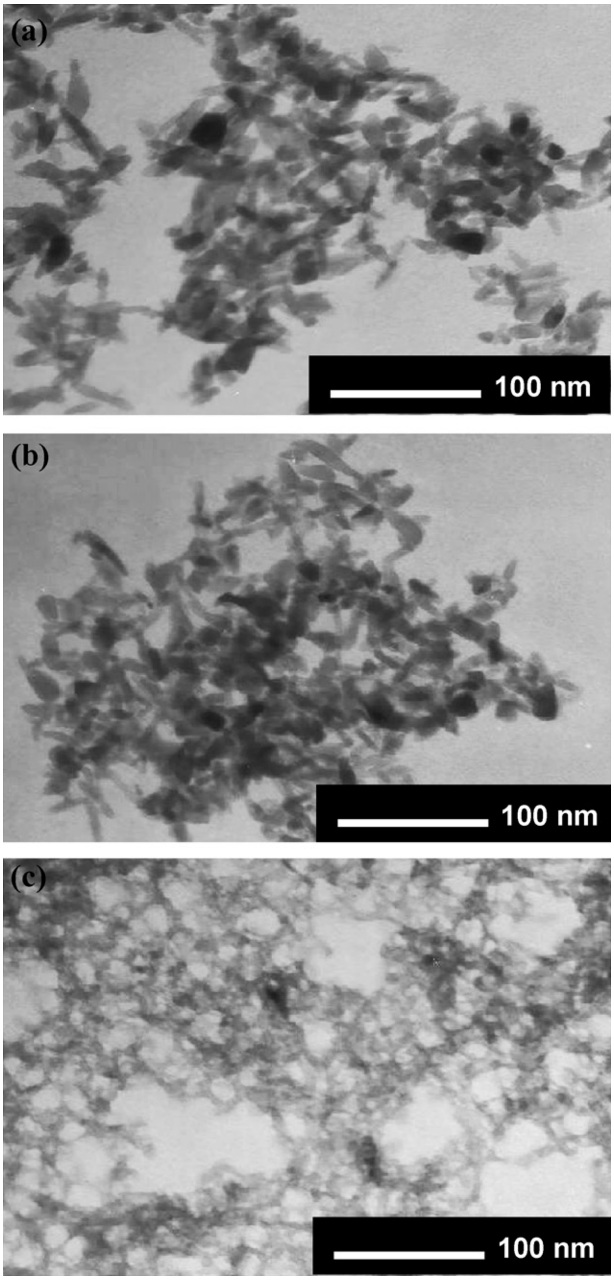

Fig. 2. Transmission electron micrographs of TiO_2 powders prepared at 150 °C with different oil/water ratios of (a) 5, (b) 10, and (c) 20.

micrographs of the TiO_2 powders prepared at oil/water ratios equal to 5, 10, and 20, respectively. It is revealed that the morphology of the obtained TiO_2 particles was mono-dispersed and rod shaped. When the oil/water ratio was increased from 5 to 20, the average particle sizes of the TiO_2 powders decreased from 36.4 to 22.7 nm. This indicated that an increase in the oil/water ratio decreased the particle size of the obtained TiO_2 nano-particles. It was reported that the size of the reverse micelle depends on the amount of water content in the microemulsion solution [28]. Once the oil/water ratio is increased, the size of the reverse micelle is correspondingly decreased. Since the grain growth of particles is limited by the size of the reverse micelles in the microemulsion hydrothermal process, increasing the oil/water ratio ultimately decreases the size of the TiO_2 particles formed therein.

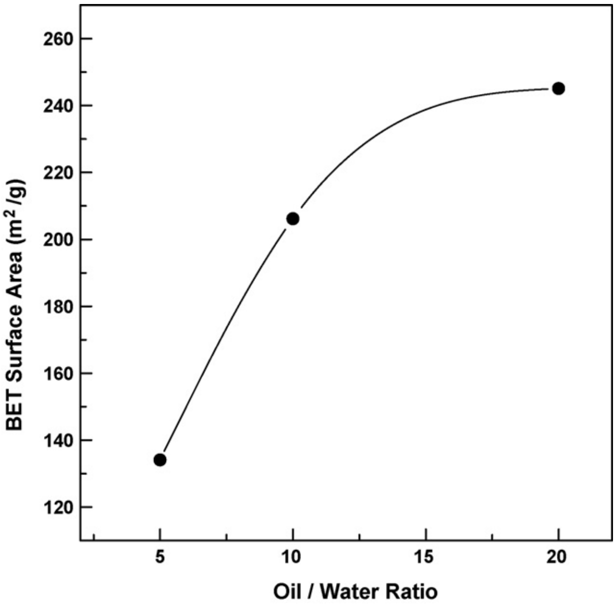

Fig. 3. BET specific surface area of TiO_2 powders prepared with different oil/water ratios at 150 °C for 1 h.

The BET specific surface areas of TiO_2 powders for different oil/water ratios are illustrated in Fig. 3. The BET specific surface areas of TiO_2 powders for oil/water ratios equal to 5, 10, and 20 are 134, 206, and 245 m^2/g, respectively. It is also important to note that the BET specific surface areas of commercially available Degussa P-25 and Aldrich TiO_2 powders are about 50 and 10 m^2/g, respectively. In this study, TiO_2 powders with BET specific surface areas greater than 200 m^2/g were successfully obtained at relatively low hydrothermal processing temperatures in short reaction periods. The large BET surface area is due to the special rod-shaped morphology of TiO_2 powders. The decrease in particle size and consequent increase in BET specific surface area of TiO_2 powders were observed with increasing the oil/water ratio.

Fig. 4 illustrates the variation in methylene blue concentration with time in presence of obtained nano-sized TiO_2 powders synthesized using different oil/water ratios. It was found that almost all methylene blue was decomposed under UV light illumination for 10 min. It also revealed that the amount of methylene blue degraded by TiO_2 powders was increased when the oil/water ratio was raised. This is attributed to the increase in BET specific surface area of TiO_2 powders as reported by Yu et al. [29]. Compared with commercially available photocatalysts Degussa P-25 and ST-01 (Ishihara Chemical Co. Ltd.), TiO_2 powders prepared via the microemulsion-mediated hydrothermal route have higher photocatalytic abilities.

3.2. *Effects of hydrothermal temperature on the microstructures and photocatalytic activities of TiO_2 powders*

Fig. 5 depicts the XRD patterns of TiO_2 powders synthesized from mixed microemulsion solution after hydrothermally

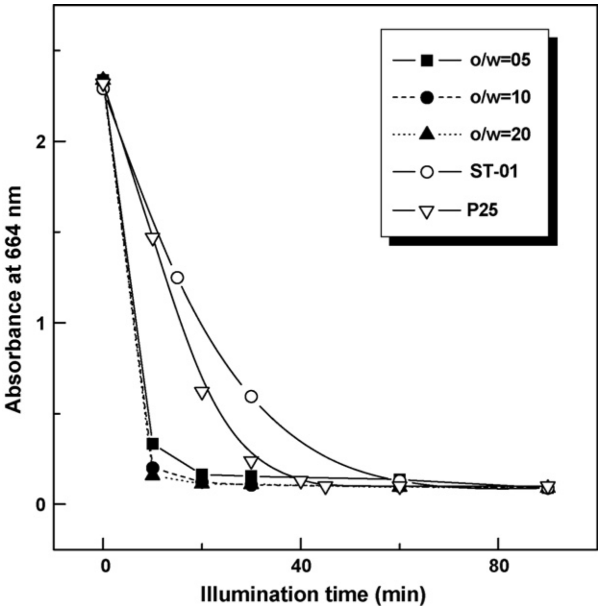

Fig. 4. Relation between photocatalytic activities of TiO_2 powders prepared with different oil/water ratios at 150 °C for 1 h.

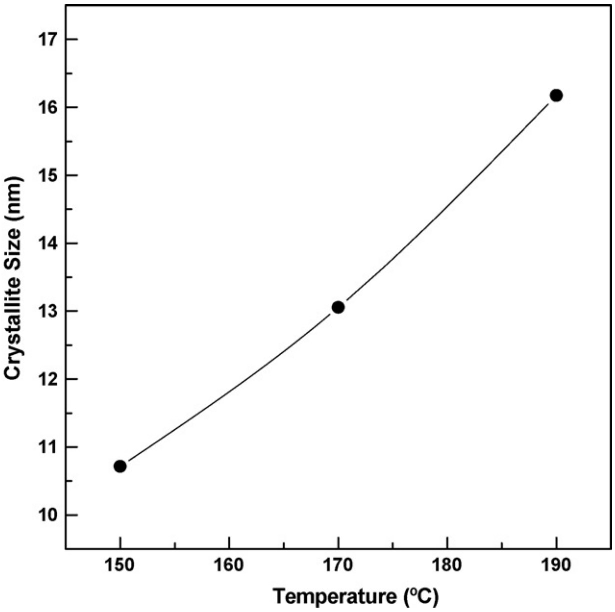

Fig. 6. Variation in crystallite size of TiO_2 powders prepared at different hydrothermal temperatures for 1 h.

treated at (a) 150, (b) 170, and (c) 190 °C for 1 h. The XRD patterns indicate that anatase phase was formed in all samples. It was observed that with increasing hydrothermal processing temperatures, the peak intensities increased and the FWHM of the diffraction peak became narrower. The average crystallite size of the TiO_2 powders was calculated using Scherrer's formula and depicted in Fig. 6. This reveals that the crystallite size increased with increasing hydrothermal temperatures. This indicates the increase in the formation of larger crystallites and anatase phase crystallinity enhancement in the formed TiO_2 powders at elevated hydrothermal temperatures. Yu et al. [22] also reported that the average crystallite sizes and degree of crystallization increase with increasing hydrothermal temperatures.

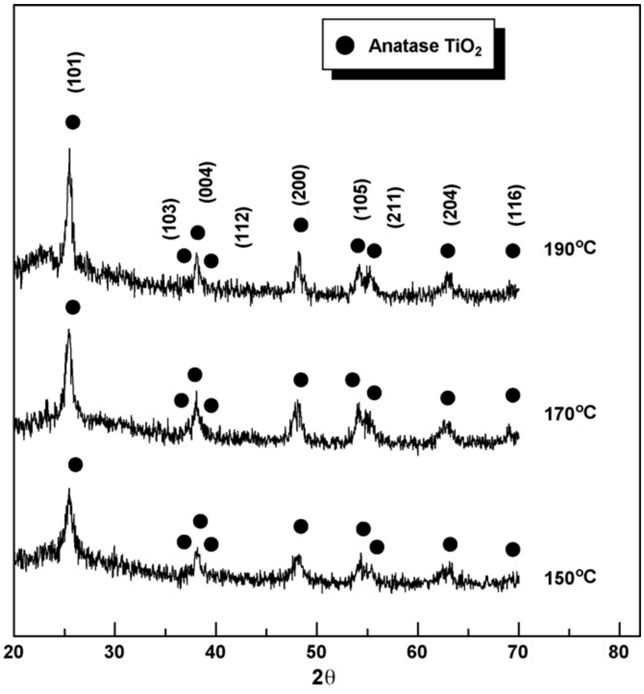

Fig. 5. XRD patterns of TiO_2 powders prepared at different hydrothermal temperatures for 1 h.

Fig. 7 shows TEM micrographs of powders hydrothermally treated at temperatures ranging from 150 to 190 °C. It can be seen (Fig. 7(a)) that the TiO_2 particles formed at 150 °C were monodispersed with a rod-like shape. The length of these rods was around 50 nm and the diameter was in the range of 10 nm, with an aspect ratio of about 5. After increasing the hydrothermal temperature to 170 °C (Fig. 7(b)), the TiO_2 particles retained the rod-like morphology, but the aspect ratio became less (∼2.6). This indicates that the morphology of TiO_2 particles was transformed from a long-axis rod-like shape into a short-axis rod-like shape after the hydrothermal temperature was elevated from 150 to 170 °C. When the temperature was increased to 190 °C (Fig. 7(c)), the morphology of the TiO_2 particles changed from rod-shape to polyhedral particles with a broad size distribution. In addition, the particle size was found to be increased after the hydrothermal temperature was raised. With increasing hydrothermal temperature, the reverse micelles in the microemulsion will not be maintained. This will result in fast cluster nucleation oriented in random directions, thereby forming large particles [30].

Fig. 8 illustrates the variation in transmittance spectra (%T) versus wavelength (nm) of TiO_2 powders synthesized at different hydrothermal temperatures. It shows a decrease in the optical transmittance of TiO_2 powders synthesized at elevated temperatures. This is attributed to the increase in particle as well as crystallite size of TiO_2 and the finding is in good agreement with the results reported by Yu et al. [31]. Fig. 9(a) and (b) represents the BET specific surface area and the amount of degraded methylene blue for TiO_2 powders prepared at vari-

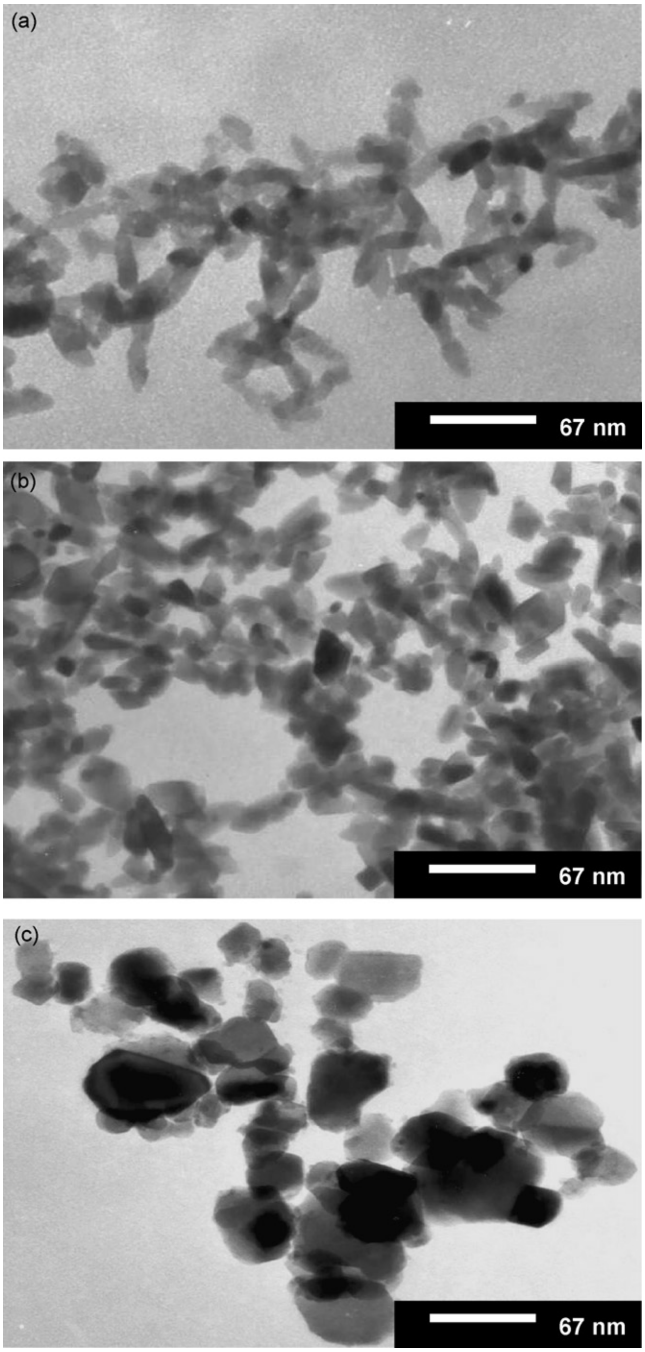

Fig. 7. Transmission electron micrographs of TiO_2 powders prepared at (a) 150, (b) 170, and (c) 190 °C for 1 h.

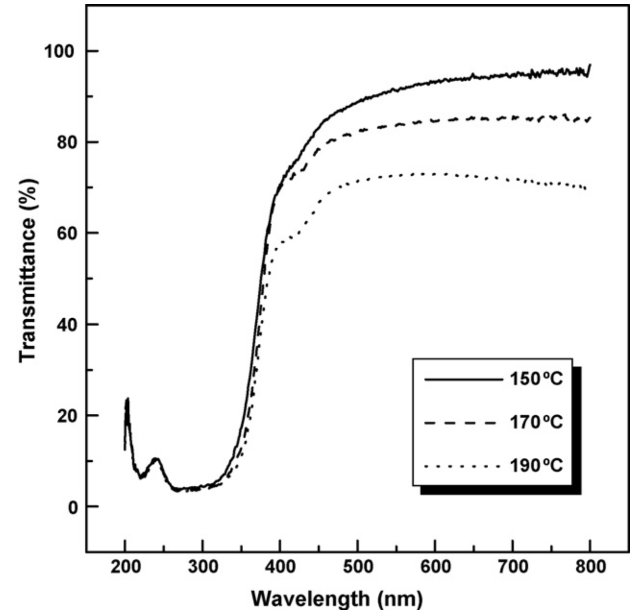

Fig. 8. UV–vis transmittance spectra of TiO_2 powders synthesized at different hydrothermal temperatures for 1 h.

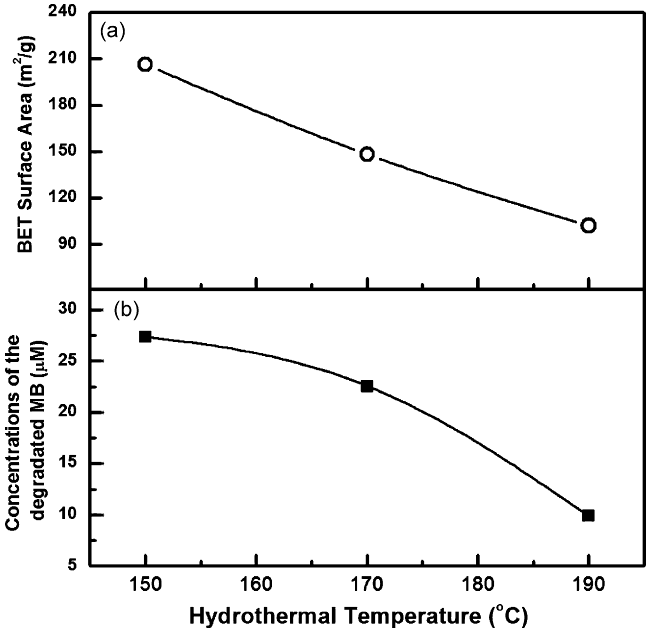

Fig. 9. (a) BET specific surface area and (b) concentration of degraded methylene blue for TiO_2 powders prepared at different hydrothermal temperatures.

ous hydrothermal temperatures. As the processing temperature was increased, the surface area of the TiO_2 powders correspondingly decreased. The rod-like TiO_2 powders prepared at 150 °C had a largest BET specific surface area ($210\,m^2/g$). When the hydrothermal temperature was elevated, the amount of degraded methylene blue was reduced. This is attributed to an increase in the particle size and the decrease in the surface area. The above results indicate that the oil/water ratio and the hydrothermal temperature should be well controlled to obtain nano-sized TiO_2 powders with improved photocatalytic properties.

4. Conclusions

TiO_2 nano-particles with improved photocatalytic performance were successfully prepared via the microemulsion hydrothermal process. Monophasic TiO_2 powders with an anatase structure were obtained after the hydrothermal treatment. Increasing the oil/water emulsion ratio significantly decreased the particle size of the prepared TiO_2 powders, and consequently increased the specific surface area. As a result, photocatalytic activity of TiO_2 powders was significantly improved. When the hydrothermal temperature was elevated, the morphology of the TiO_2 particles changed from rod-shape to polyhedral particles with a broad size distribution. The rod-shaped particles exhibited larger specific surface area than the polyhedral particles. The change in morphology, as well as the grain growth at elevated temperatures, reduced the specific surface area of the TiO_2 powders. Consequently, the photocatalytic activities of TiO_2 powders were reduced with hydrothermal temperature elevation.

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