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One-Step Microemulsion-Mediated Hydrothermal Synthesis of Nanocrystalline TiO_2

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Abstract

Nanocrystalline TiO_2 powders with high photocatalytic activity were prepared by one-step microemulsion-mediated hydrothermal method using tetrabutylorthotitanate ($TiO(C_4H_9)_4$, TBOT) as precursor. The as-prepared TiO_2 powders were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and the Brunauer-Emmett-Teller (BET) specific surface area measurements. The effects of the oil/water ratio and hydrothermal temperature on the microstructures and photocatalytic activity of the TiO_2 powders were investigated. The results suggest that increasing the oil/water emulsion ratio significantly decreased the particle size of the as-prepared TiO_2 powders and improved the photocatalytic activity. With hydrothermal temperature increasing, the average crystallite size increased and the photocatalytic activities of TiO_2 powders decreased.

Keywords

Titanium Dioxide; Microemulsion; Hydrothermal Method; Photocatalytic Activity

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1. Introduction

The excellent performance of semiconducting oxide materials in the photocatalytic realm has attracted scientific interest for ongoing research [1]. As an important n-type semiconductor material, nano-TiO_2 has recently stimulated increasing attention because of their promising applications in many fields, including sensors [2],

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self-cleaning photocatalytic surfaces and devices [3], dye-sensitized solar cells [4], environmental purification and hydrogen generation by water photoelectrolysis [5] [6]. Fundamental researches regarding the preparation of photocatalyst with highly photocatalytic activity, the immobilization of powder photocatalyst, and the improvement of photocatalyst performance are priorities to be considered [7].

Many methods, such as hydrolysis (chemical precipitation) [8], reverse micelles (microemulsion) [9] [10], sol-gel [11] [12] and hydrothermal crystallization [13]-[15], have been used to prepare TiO_2 nanocrystalline photocatalyst. These methods suffer the problems of high-temperature processing, long aging time, grain growth and vigorous stirring. The high processing temperatures and long reaction time result in the formation of large sized particles with a wide size distribution [16]. Consequently, it is in need of developing a novel and environmentally benign approach to preparing TiO_2 nanocrystalline photocatalyst. In this paper, a new one-step strategy by microemulsion-mediated low temperature hydrothermal route has been employed to synthesize crystalline nanosized 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 particles with large surface area and a cuboid-liked shape were successfully synthesized at low temperature within short reaction period. The effects of hydrothermal processing temperature or time on the microstructures and photocatalytic behavior of the obtained TiO_2 powders were also investigated in detail.

2. Experimental Section

2.1. Preparation of the Catalysts

In a typical synthesis, 40 ml cyclohexane, 12 ml n-butanol, 8 ml polyoxyethylene (10) octylphenyl ether (OP-10), 4 ml tetrabutyl titanate and 4 ml HCl (0.1 M) were mixed together to form a dispersed mixture. After stirring for about 30 min, the mixture was finally transferred into a 100 ml Teflon-lined stainless steel autoclave. It was sealed tightly and maintained at 120˚C for 1 h. After that, the autoclave was allowed to cool down naturally. The products were collected and washed three times using deionized water and absolute ethanol, then dried for 12 h under vacuum at 60˚C. The as-synthesized samples were denoted as TX-Y (X denotes the oil/water ratio, and Y denotes the hydrothermal temperature).

2.2. Characterization of the Catalysts

XRD analysis was performed on a D/Max-2550 X-ray diffractometer with monochromatized CuKα radiation (λ = 0.1540562 nm). TEM was recorded on a transmission electron microscopy (TEM, JEOL JEM-200CX). The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) was determined by nitrogen adsorption-desorption isotherm measurements at 77 K on a Micromeritics ASAP 2010 system. The samples were degassed in vacuum at 473 K until a pressure lower than 10^{-6} Torr before the actual measurements.

2.3. Photocatalyst Reaction

The photocatalytic reaction was conducted in the XPA-II photochemical reactor (Nanjing Xujiang Machine-electronic Plant). A 1000 W Xe lamp was used as the simulated solar light source, and a house-made filter was mounted on the lamp to eliminate infrared irradiation. MB (20 mg/L) was used as contamination. 20 mg photocatalyst powder was dispersed in 200 mL reaction solutions by ultrasonicating for 15 min, then the suspension was magnetically stirred in dark for 1 h. Air was blown into the reaction medium at a flow rate of 200 mL/min during the photocatalytic reaction. One 8 mL of the suspension was sampled and filtered. The concentration of the remaining MB was measured by a Hitachi UV-3010 spectrophotometer. The degradation ratio was calculated by $X = (A_0 - A)/A_0 \times 100\%$.

3. Results and Discussion

3.1. Morphology and Structures of the Samples

Figure 1(a) shows the XRD patterns of nano-sized TiO_2 powders prepared by one-step microemulsion-mediated hydrothermal route at 120˚C for 1 h. All samples show pure anatase phase, which was not affected by the change in the oil/water ratio. The anatase crystal sizes were calculated by the Scherrer equation (**Table 1**). The XRD peaks of the obtained TiO_2 powders became broader with increasing the microemulsion oil/water ratio.

Table 1. Experimental conditions, SBET and particle size of the as-prepared samples.

Samples	R = oil/water (volume)	Hydrothermal temperature (˚C)	S_{BET} ($m^2 \cdot g^{-1}$)	Particle size (nm)
T2-120	2	120	232	22.8
T5-120	5	120	294	14.3
T10-120	10	120	300	9.6
T10-140	10	140	287	16.5
T10-160	10	160	259	19.4

The broad diffraction peaks implied decrease in the particle size of TiO_2 powders.

Figures 1(b)-(d) show TEM micrographs of the as-prepared samples T2-120, T5-120 and T10-120. It is revealed that the morphology of the obtained TiO_2 particles was mono-dispersed. When the oil/water ratio was increased, the average particle sizes of the TiO_2 powders decreased, which were consistent with XRD result. It was reported that the size of the reverse micelle depends on the amount of water content in the microemulsion solution [17]. 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.

Figure 2(a) depicts the XRD patterns of TiO_2 powders synthesized from one-step microemulsion-mediated solution after hydrothermally treated at 120˚C, 140˚C, and 160˚C for 1 h. The XRD patterns indicate that anatase phases were formed in all samples. It was observed that with increasing hydrothermal processing temperatures, the peak intensities increased and the full width half maximum of the diffraction peak became narrower. 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*. also reported that the average crystallite sizes and degree of crystallization increase with increasing hydrothermal temperatures [18].

Figures 2(b)-(d) show TEM micrographs of the as-prepared samples hydrothermally treated at 120˚C, 140˚C and 160˚C. It can be seen that after increasing the hydrothermal temperature to 160˚C (**Figure 2(d)**), the TiO_2 particles retained the cuboid-like morphology. 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 [19].

3.2. Photocatalytic Activities of Samples

Figure 3 shows the comparison of photocatalytic activity of the TiO_2 powders synthesized in different hydrothermal conditions. The photocatalytic activity of Degussa P-25 powders, which is recognized as an excellent photocatalyst, was also measured as a reference to compare with that of the as-prepared catalysts. The BET specific surface areas of TiO_2 powders are shown in **Table 1**. It is 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*. [20]. It can be seen that not all of the as-prepared TiO_2 powders had a greater photocatalytic activity than that of Degussa P-25. The photocatalytic activity should be a function of many physical parameters including the BET surface area, pore size and distribution, crystal size, crystalline, etc [18]. Therefore, the highest activities of the prepared TiO_2 powders at 120˚C for 1 h could be attributed to the results of the above mentioned synergistic effects.

4. Conclusion

In summary, TiO_2 nano-particles with improved photocatalytic performance were successfully prepared via a one-step microemulsion hydrothermal process. The advantage of using this microemulsion mediated hydrothermal route is the significant reduction in reaction time and temperatures compared with the conventional hydrothermal process. Nanocrystalline TiO_2 powders with high photocatalytic activity were obtained after the hydrothermal treatment. The oil/water ratio and hydrothermal temperature obviously influenced the microstructures and photocatalytic activity of the as-prepared TiO_2 powders. Increasing the oil/water emulsion ratio

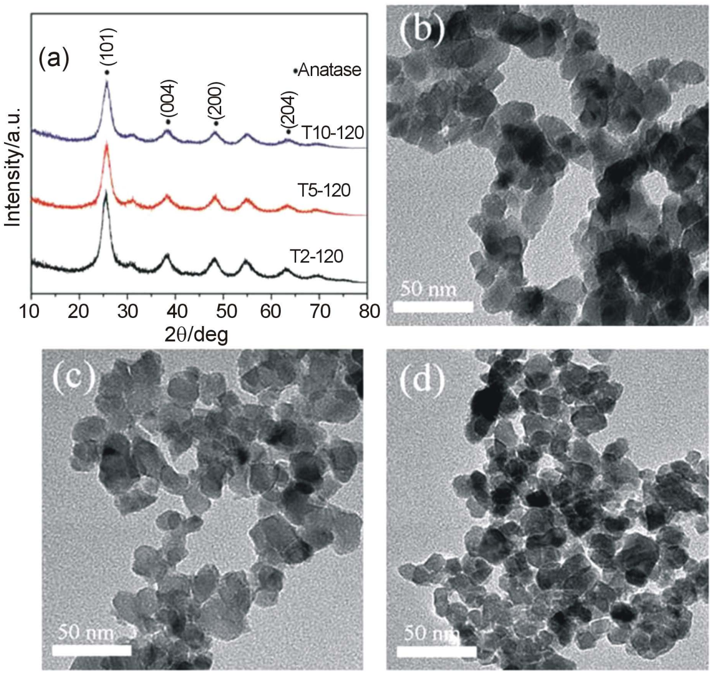

Figure 1. XRD pattern (a) and TEM images of the as-prepared samples: (b) T2-120; (c) T5-120 and (d) T10-120.

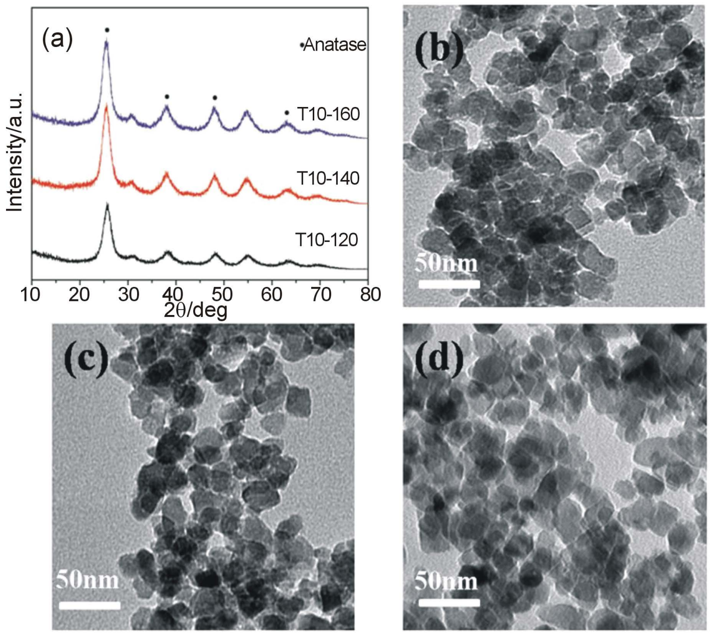

Figure 2. XRD pattern (a) and TEM images of the as-prepared samples: (b) T10-120; (c) T10-140 and (d) T10-160.

significantly decreased the particle size of the prepared TiO_2 powders and improved the photocatalytic activity. With increasing hydrothermal temperature, the average crystallite size increased. In contrast, the BET specific surface areas steadily decreased. Consequently, the photocatalytic activities of TiO_2 powders were reduced with hydrothermal temperature elevation. Our experimental results indicate that the photocatalytic activity of the TiO_2 powders prepared under an optimal hydrothermal condition (T10-120) exceeded that of Degussa P-25 powders.

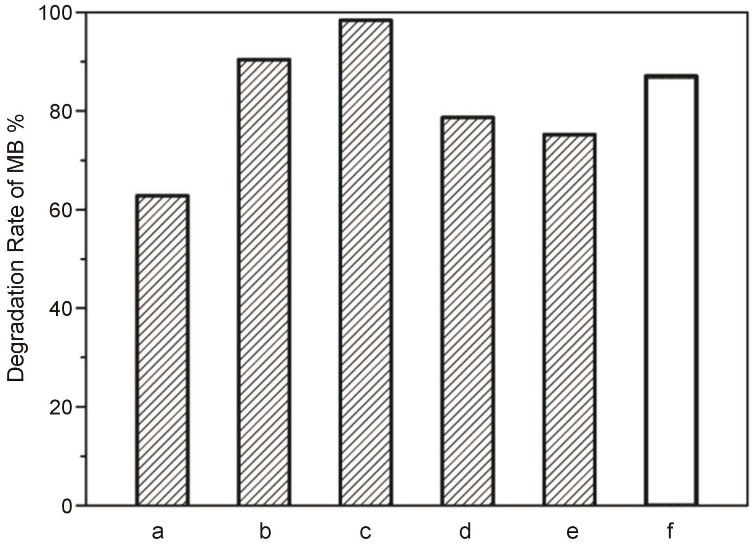

Figure 3. Comparison of degraded methylene blue rate of TiO_2 powders prepared in different hydrothermal treatment for 2.5 h: (a) T2-120; (b) T5-120; (c) T10-120; (d) T10-140; (e) T10-160 and (f) P-25.

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