

Preparation of nano-TiO₂ photocatalyst by hydrolyzation-precipitation method with metatitanic acid as the precursor

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Photocatalytic degradation of toxic waste water has been proposed to purify the drinking water [1–6]. Recently, extensive research has been focused on TiO₂ for the reason that it can show strong photocatalytic activity when irradiated with UV light [7–9], which is resulted from the production of an excited electron in the conduction band of the nanosized TiO₂, along with a corresponding positive hole in the valence band after the absorption of UV radiation. These excited species play an important role in giving rise to various chemical reactions because the resulted radical species exist on the surfaces of the nanosized TiO₂. In addition, because of their relatively long lifetime, the electrons and holes can be allowed to travel to the crystallite surface. Plenty of pollutants, such as NO_x, SO_x and other toxic organic compounds can be detoxified by these species existing on the surface of the nanosized TiO₂ photocatalysts. As a result, there has been growing interest in preparing nano-TiO₂ powders used as excellent photocatalysts in detoxifying the waste water derived from the industry production. In general, the nanosized TiO₂ can be prepared by sol-gel method using Ti(OBu)₄ or TiCl₄ as a precursor [10, 11]. However, there are some inherent drawbacks including using expensive raw materials, the complexity of hydrolysis process and easy agglomerates of the powders prepared by this method, which have greatly limited the application.

In the current study, we try to use a relatively simple approach to prepare nanosized TiO₂ photocatalyst. Metatitanic acid, an inexpensive raw material, is used as the precursor. 10 g of metatitanic acid (H₂TiO₃) powders (CP.Ma AnShan JX Corporation China) are mixed with 100 ml of sulfuric acid (0.5 M) and then heated at 85 °C for half an hour under stirred condition. At last, a transparent solution was obtained. After annealing, a certain content of hydroxypropyl cellulose (HPC) (molecular weight ~100 000, Aldrich Chem) is added to the solution. 300 ml of ammonia (A.R) solution (0.5 M) is added dropwise to the solution until the pH value raises to 3.0. Then continue to stir 6 h at stirring velocity of 600 rp · min⁻¹. The white precipitation formed is aged for 2 h and then dried at 85 °C in the oven. The anatase nano-TiO₂ powders with the diameter in the range of 10–20 nm are obtained after calcining at different temperatures.

The nano-TiO₂ powders obtained are confirmed to be anatase TiO₂ by X-ray diffraction (XRD), as shown in Fig. 1. It is found that the precursor powders are

completely transformed into anatase phase form by heating to 500 °C for 2 h in air (Fig. 1B). When the temperature rises to 850 °C for 2 h in air, rutile phase does not occur (Fig. 1C). In consequence, the anatase phase form can be obtained in a very broad range of temperature and the procedure is easily controlled, which possesses great significance in fabricating photocatalyst powders. According to the Scherrer equation: $D_c = K\lambda/\beta \cos \theta$. Where D_c accounts for the average crystal size, $K = 0.89$ is the Scherrer coefficient, λ denoting the X-ray wavelength is equal to 0.1542 nm. β is the full width at half-maximum (FWHM) and θ is the diffraction angle. The crystals size is 10 nm calcined at 500 °C and 22 nm at 850 °C respectively. The results appears in general agree with the observation from the transmission electron microscopy (TEM), as shown in Fig. 2.

Effect of the pH value of the starting solution to the size of nano-TiO₂ powders is investigated. The results show that the pH value of the solution can affect the crystal size. When pH is 3.0, the nano-TiO₂ powders show serious agglomeration. However, the spherical powders are obtained at pH 4.0 and the average size of the powders is about 10 nm. While the pH increases up to 6.0, the powders having poor dispersity get obviously agglomerated. It can be considered that

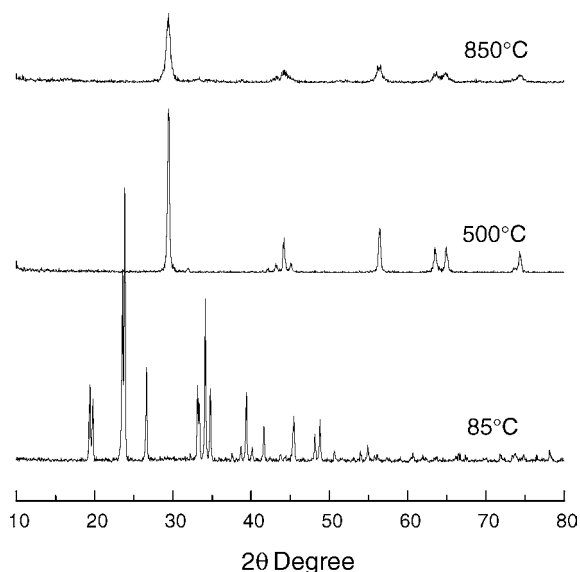
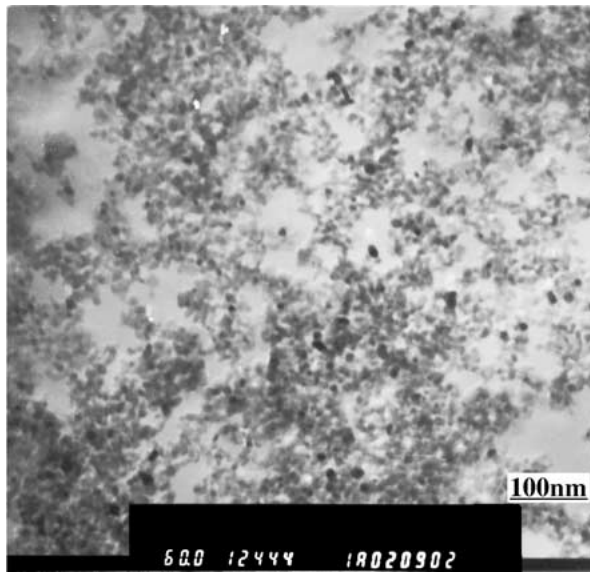
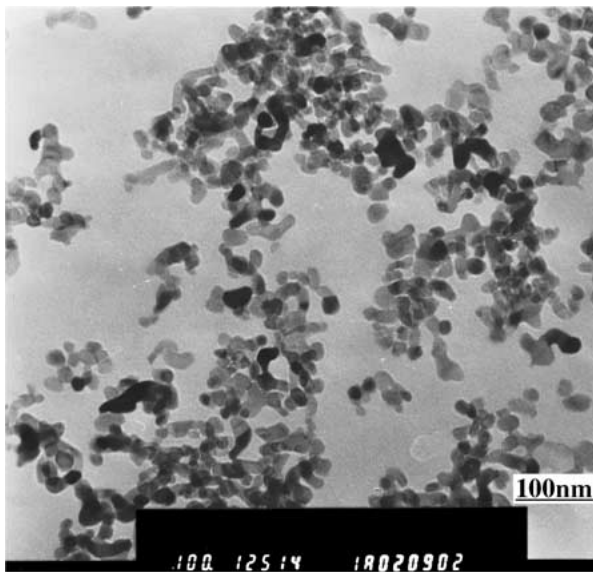


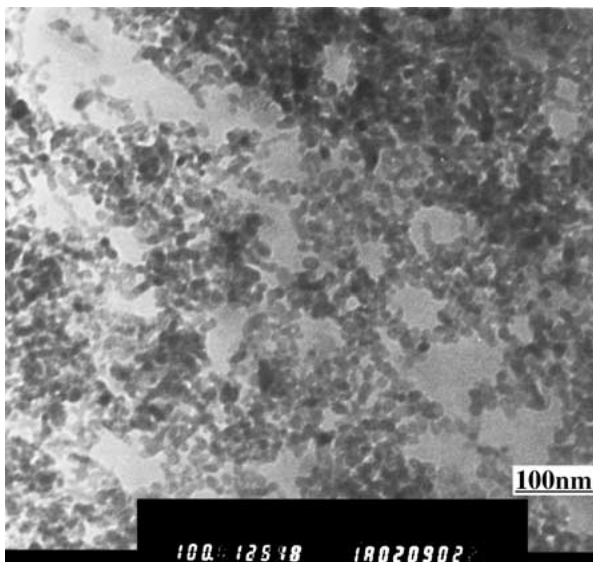
Figure 1 XRD patterns of different nano-TiO₂ powders calcined at (A) drying at 85 °C, (B) 500 °C for 2 h, (C) 850 °C for 2 h.



(A)



(B)

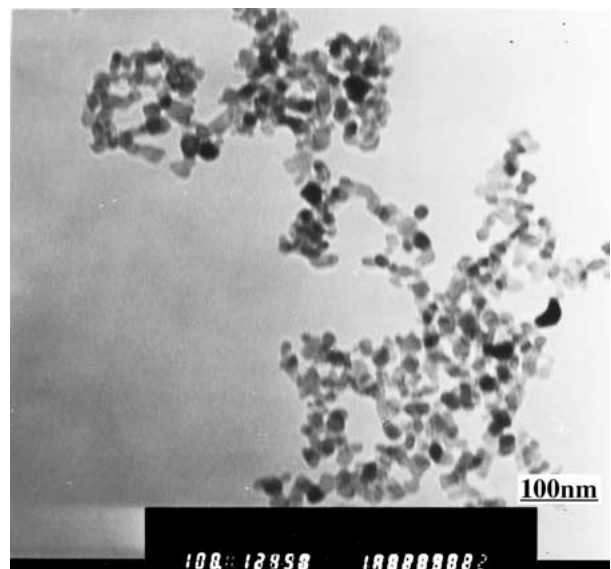


(C)

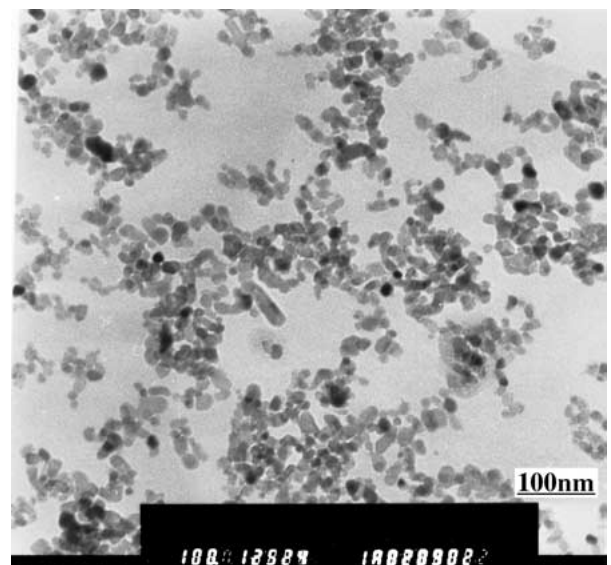
Figure 2 TEM micrographs of nano-TiO₂ powders calcinated at 500 °C for 2 h. (A) pH = 3.0, (B) pH = 4.0, and (C) pH = 6.0.

with the increase of pH value, the concentration of H⁺ decreases and the velocity of the hydrolyzation of Ti⁴⁺ is accelerated resulting in the reuniting of TiO²⁺ in the solution. As a result, the particles flocculated during the process of precipitation and subsequently formed a powder compact with non-uniform distribution.

Steric interaction is caused by the absorption of polymer molecules onto the surface of particles. Hydroxypropyl cellulose (HPC) has been known to provide steric stabilization during the precipitation of TiO₂ [12, 13]. Fig. 3 shows the morphology of precipitates formed with and without HPC as a dispersant. In the absence of HPC, the precipitates consist of agglomerates of discrete particles which have been united. When a smaller concentration of HPC (i.e., $0.75 \times 10^{-3} \text{ g} \cdot \text{cm}^{-3}$) is added to the initial solution, agglomerate formation is greatly reduced and the fine, spherical, and well-dispersed particles are obtained. Fig. 4 shows the effects of HPC concentration



(A)



(B)

Figure 3 TEM micrographs of nano-TiO₂ powders: (A) without HPC and (B) with HPC.

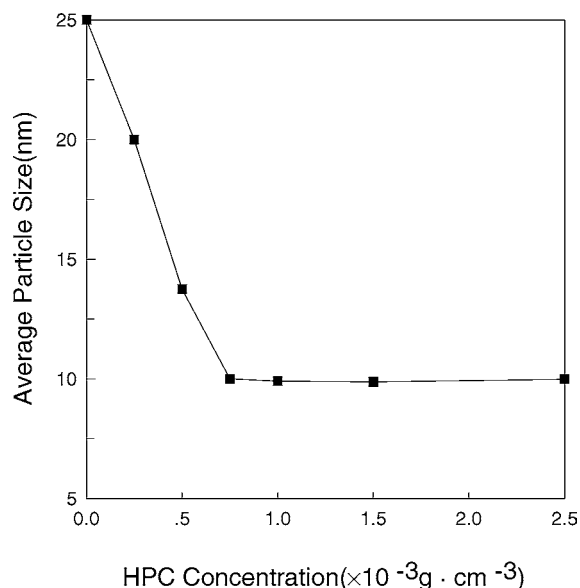


Figure 4 Variation of average particles size with the HPC concentration.

on the size and size distribution of the particles. Because the HPC acts as a nucleation site for precipitation, the higher the HPC concentration, the more the particle size decreases. When the concentration of HPC is more than $0.75 \times 10^{-3} \text{ g} \cdot \text{cm}^{-3}$, the average particle size slightly decreases and the distribution rapidly grows with the increase of the HPC content. The fine, spherical nano-TiO₂ particles with a narrow size distribution are fabricated in the mixed solution from the metatitanic acid as the precursor when the concentration of HPC is $0.75 \times 10^{-3} \text{ g} \cdot \text{cm}^{-3}$, as shown in Fig. 3B.

In conclusion, an anatase phase of nano-TiO₂ is obtained by above procedures. The fine, spherical nano-TiO₂ particles with a narrow size distribution are produced using the metatitanic acid as the precursor at the pH 4.0 of the solution and HPC concentration of $0.75 \times 10^{-3} \text{ g} \cdot \text{cm}^{-3}$. The method is very simple and provides a promising way to prepare nano-TiO₂ photocatalyst.

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Received 11 March
and accepted 9 July 2003