

One Step Preparation of Highly Dispersed TiO₂ Nanoparticles

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Abstract A facile approach was developed to prepare highly dispersed TiO₂ nanoparticles with selected phase. The crystallization phase of the nanoparticles can be easily tuned from anatase to rutile by the dosage of hydrochloric acid in the reaction system. The crystallite size of the as-prepared anatase TiO₂ nanoparticles was *ca.* 3.2 nm with high dispersion. A transparent TiO₂ colloid was obtained by dispersing the as-prepared anatase TiO₂ nanoparticles in deionized water without any organic additives added. The concentration of TiO₂-H₂O colloid can be as high as 1600 g/L. The optical transmittance of TiO₂-H₂O colloid with a low concentration was nearly 100% in the visible region. Furthermore, anatase TiO₂ nanoparticles (TiO₂-NPs) showed superior photocatalytic performance compared to rutile TiO₂-NPs.

Keywords TiO₂ nanoparticle; Water-dispersible; Colloid

1 Introduction

Over the past decade, titanium dioxide (TiO₂) has attracted considerable attention for its wide applications, such as gas sensors^[1], photocatalysts^[2,3], pigments, optics materials^[4], photovoltaic cells^[5], porous materials^[6–8], and superhydrophobic/superhydrophilic materials^[9–11]. TiO₂ primarily occurs in nature in three distinct crystallographic phases: anatase, rutile and brookite^[12]. Brookite has less been studied due to its typically acting as a transition phase between anatase and rutile^[13,14]. Rutile is the thermodynamically stable polymorph^[15] and has a high density and refractive index. Therefore, this phase has been widely used in white pigments and sunscreen creams. Anatase exhibits excellent photoactivity under UV irradiation, which makes it an amazing functional material for commercial application in the preparation of dye-sensitized solar cells and pollution abatement. The preparation of anatase TiO₂ nanoparticles (TiO₂-NPs) is of great importance in the field of modern nanomaterials research because they are directly related to the inherent properties^[16–18].

Colloid anatase TiO₂ has many commercial applications in energy and environmental areas^[19,20]. Many methods have been used for the preparation of TiO₂-NPs with good dispersion. Solvothermal method^[21,22], reflux method^[23], sol-gel method^[24,25], reverse micelle method, and chemical vapour deposition method^[26] are classical chemical routes. Water-dispersible TiO₂-NP is an important material for the study of optics, electricity and catalysis properties of TiO₂ materials in solution. Meanwhile, TiO₂-NP is easily assembled to objects, which are crucial for practical application due to the formation of ordered patterns of nanoparticles with controlled size and morphology^[27,28]. Usually, nanoparticles should be

modified by organic surfactant to decrease the surface energy and prevent them from aggregation. Ohya and co-workers^[29] prepared aqueous colloidal TiO₂ solutions by a reaction between titanium alkoxide and alkylamines (or tetraalkylammonium hydroxides). However, the alkaline reagents may passivate the surfactivity of TiO₂ and decrease the photocatalytic activity^[30]. Yan *et al.*^[31] synthesized water soluble TiO₂-NPs using polyethylene glycol 400 (PEG 400) as a stabilizer, but their photoactivity became low after the first cycle. It indicates that PEG 400 on the surface would be photo-degraded, which reduced the performance of the catalyst. It is still a challenge to prepare highly water-dispersible TiO₂-NPs at a low temperature and without adding any organic surfactants.

We take the advantage of the reflux method, which operates at low temperatures (<100 °C) and processes a simple separation. In the current study, TiO₂-NPs were prepared by the hydrolysis of tetrabutyltitanate (TBT) in a cyclohexane/alcohol medium under refluxing conditions. TiO₂-NPs can be tuned from anatase to rutile, depending on the amount of concentrated hydrochloric acid (HCl) in the system. As-prepared anatase TiO₂-NPs were well dispersed in deionized water to form a colloid with a concentration up to 1600 g/L. And the TiO₂-H₂O colloid began to gelate when the concentration was higher than 200 g/L. The optical transmittance of TiO₂-H₂O colloid with a concentration of less than 10 g/L was nearly 100% in the visible light region, and the UV absorption edge was gradually red shifted with increasing the concentration. The current approach and materials have a potential application in the fabrication of a variety of macroscopic objects and hierarchically structures based on the high qualitatively homogeneous and disordered assembly of TiO₂-NPs.

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2 Experimental

2.1 Preparation of TiO₂-NPs

All the chemicals used were of analytic grade that were used without further purification. Tetrabutyltitanate [TBT, Ti(OC₄H₉)₄] and concentrated hydrochloric acid (HCl, 36%—38%, mass fraction) were employed as the titanium precursor and the acidic medium, respectively. Cyclohexane (C₆H₁₂) and alcohol (C₂H₅OH) were the solvents. The anatase TiO₂-NPs were prepared *via* a reflux method in a mixture of the solvents. In a typical synthesis, 36 mL of tetrabutyltitanate was dissolved in the solvent (*i.e.*, 90 mL of alcohol and 90 mL of cyclohexane). After the solution was vigorously stirred for 10 min, 9 mL of HCl (TBT/HCl=1:0.25, volume ratio) was added to it followed by magnetic stirring for another 10 min. The final homogeneous solution was heated to reflux (*ca.* 67 °C) for 10 h and then cooled to room temperature. A yellowish transparent TiO₂ solution was obtained. To precipitate the TiO₂-NPs, 600 mL of alcohol was added dropwise to the solution under stirring. After standing overnight, a white precipitate was harvested by centrifugation, washed with alcohol several times, and dried in air at room temperature. To prepare rutile TiO₂-NPs, 54 mL of HCl (TBT/HCl=1:1.5, volume ratio) was used while all the other experimental parameters remained unchanged. A white precipitate was directly acquired instead of the yellowish solution.

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical B.V. Empyrean X-ray diffractometer with graphite-filtered Cu K α radiation at 40 kV, 40 mA and 2 θ angles of 20°—80° with a scanning speed of 3°/min. Scanning electron microscopy (SEM) images were recorded on an SU8020 electron microscope. The detail morphologies of the samples were observed on a Tecnai G2 S-Twin F20 at an accelerating voltage of 200 kV *via* a transmission electron microscopy (TEM) and a high resolution transmission electron microscopy (HRTEM). The samples for TEM analysis were prepared by dispersing TiO₂ onto TEM copper grids that were thinly coated with amorphous carbon. UV-Vis absorption and transmittance spectra were measured on a UV-2450 spectrophotometer, Shimadzu.

2.3 Photodegradation

The photocatalytic activity of TiO₂-NPs was tested by measuring the degradation rate of methylene blue (MB) under UV light irradiation. Typically, 50 mg of the as-prepared TiO₂ catalyst was added to 50 mL of an aqueous solution containing 10 mg/L MB. The mixture was magnetically stirred in the dark at ambient temperature for 1 h to achieve adsorption-desorption equilibrium of TiO₂ with MB followed by exposure to UV light from a 125 W high-pressure mercury vapour lamp. Then 5 mL of the suspension was extracted every 10 min, and the suspended solid was immediately separated by centrifugation. UV-Vis absorption spectra were measured to monitor the

concentration of MB remained in the aqueous system.

3 Results and Discussion

Fig.1 shows the XRD patterns of the as-prepared TiO₂-NP products synthesized under refluxing conditions. When the volume ratio of TBT to HCl was 1:0.25, all the diffraction peaks were well indexed to the pure anatase phase of TiO₂ (Fig.1 curve *a*, JCPDS No. 21-1272). The crystallite size was 3.2 nm, which was determined from the diffraction peak broadening *via* the Scherrer equation^[32]. When the amount of HCl was increased to TBT/HCl=1/0.5 (volume ratio), only the anatase phase was observed (Fig.1 curve *b*). When HCl volume was increased to TBT/HCl=1/1.5 (volume ratio) or higher, a pure rutile phase was achieved, as shown in Fig.1 curves *e* and curves *f*. All the results are in agreement with the rutile TiO₂ phase (JCPDS No. 21-1276). The crystallite size of the as-prepared rutile TiO₂ (TBT/HCl=1:1.5, volume ratio) was 4.1 nm. However, as the volume ratio of TBT to HCl increased to 1:0.75, the XRD pattern (Fig.1 curve *c*) corresponded to both anatase and rutile. Therefore, the products possess a mixed phase consisting of anatase and rutile TiO₂. Fig.1 curve *d* shows the weakened diffraction peak intensity corresponding to anatase TiO₂ and the strengthened intensity corresponding to rutile TiO₂. This result indicates that the content of rutile TiO₂ increased as the amount of HCl increased. The fraction of rutile TiO₂ in the product can be calculated from the XRD intensity *via* the following equation^[33]:

$$w_R = (1 + 0.8I_A/I_R)^{-1}$$

where w_R is the mass fraction of rutile TiO₂ in the product and I_A and I_R represent the integrated intensity of the anatase (101) peak and rutile (110) peak, respectively. Because the anatase (101) and rutile (110) peaks partially overlapped with each other (Fig.1 curves *c* and *d*), the patterns were adjusted by Gaussian fitting. The results for the phase constituents of the products are summarized in Table 1.

It is typically difficult to control TiO₂ phase during the synthesis, and most of the products consist of two or three phases^[34]. A strongly acidic condition favours the formation of the rutile phase^[14]. The transition from pure anatase to pure rutile was performed in this study, and the crystallization phase was controlled by adjusting the added volume of HCl. Hydrolysis and polycondensation are restricted to the interface because TBT is soluble in the organic phase but only sparingly

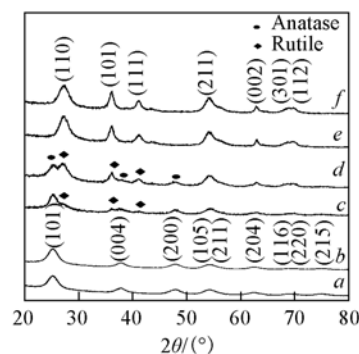


Fig.1 XRD patterns of TiO₂-NPs derived from various HCl volumes

$V(\text{TBT}):V(\text{HCl})$: *a* 1:0.25; *b* 1:0.5; *c* 1:0.75; *d* 1:1; *e* 1:1.5; *f* 1:2.

Table 1 Synthetic conditions and phase constituents of TiO₂-NPs

Sample	<i>V</i> (TBT): <i>V</i> (HCl)	<i>w</i> (Anatase)(%)	<i>w</i> (Rutile)(%)
a	1:0.25	100	0
b	1:0.5	100	0
c	1:0.75	79.2	20.8
d	1:1	60.4	39.6
e	1:1.5	0	100
f	1:2	0	100

soluble in the aqueous phase^[35]. The anatase and rutile phases have the same fundamental structural unit consisted of [TiO₆] octahedron but they are in different arrangements. The structure containing all edge-shared bonding among the [TiO₆] octahedrons results in the formation of the anatase phase. The arrangement of edge-shared [TiO₆] octahedrons along the *c* axis to form chains where the corners are shared among the chains gives rise to the rutile structure^[36]. Ti⁴⁺ is hexacoordinate and exhibits a strong tendency to form [Ti(OH)_{*x*}(OH₂)_{6-*x*}]^{4-*x*} during the reaction^[14]. The linking of [TiO₆] units is due to the dehydration (*i.e.*, oxolation) reaction between the OH⁻ ligands in the [Ti(OH)_{*x*}(OH₂)_{6-*x*}]^{4-*x*} ions, which requires two precursor ions to form one edge-shared bond. When the acidity is lower, there are more OH⁻ ligands in the complex, which favours edge-shared bonding of the octahedrons, with the formation of anatase TiO₂ preferred. In contrast, when the acidity is higher,

there are fewer OH⁻ ligands in the complex, and a portion of the edge-shared bonds would be substituted by corner-shared bonds, which results in a rutile structure. Therefore, the addition of HCl controls the phase change of TiO₂. With various HCl volumes, anatase TiO₂-NPs and rutile TiO₂-NPs were selectively prepared.

Fig.2(A) and (B) show the TEM and HRTEM images, respectively, of the anatase TiO₂-NPs with volume ratio of TBT to HCl being 1:0.25. As shown in Fig.2(A), the as-prepared anatase TiO₂ product is well-dispersed nanoparticles. The average size was 3.0 nm based on *ca.* 100 particles in the sample [the size distribution histogram is shown in Fig.2(C)], which is in good agreement with the XRD result. A higher magnification image reveals more details, as shown in Fig.2(B), and the spacing of the lattice fringe was 0.352 nm, which is consistent with the interplanar distance of the (101) plane of anatase TiO₂. Fig.2(D) and (E) show the rutile TiO₂-NPs with volume ratio of TBT to HCl being 1:1.5. Fig.2(D) shows the scattered arrangement of the obtained rutile nanoparticles with an average size of 4.0 nm [Fig.2(F)]. Fig.2(E) shows the HRTEM image of the sample, and the distance between the adjacent lattice fringes was measured to be 0.324 nm, which agrees well with the interplanar distance of the rutile TiO₂ (110) plane.

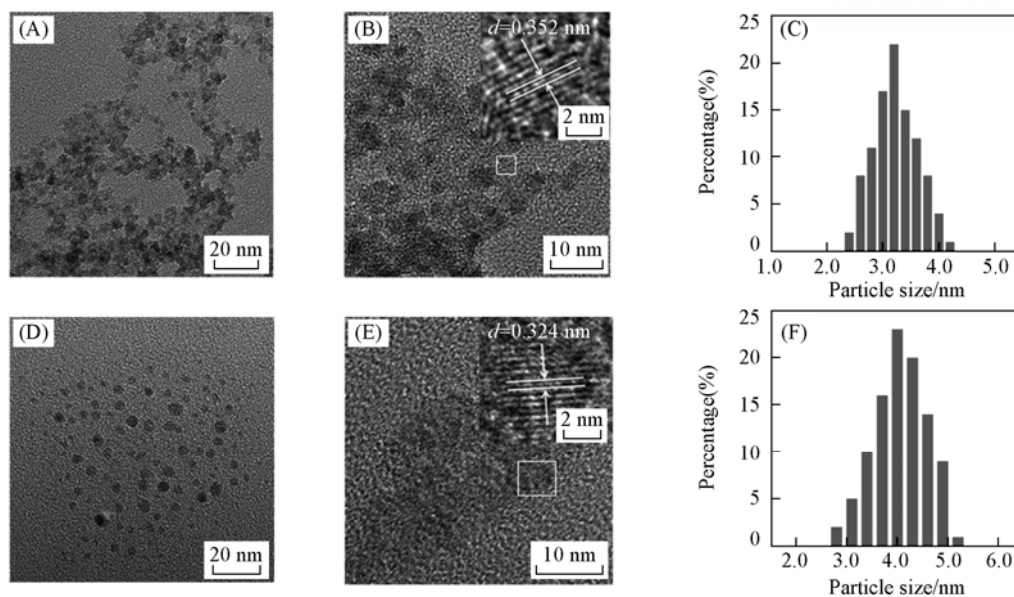


Fig.2 TEM(A, D) and HRTEM images(B, E) and size distribution histograms(C, F) of anatase TiO₂-NPs with volume ratio of TBT to HCl being 1:0.25(A—C) and rutile TiO₂-NPs with volume ratio of TBT to HCl being 1:1.5(D—F)

The insets of (B) and (E) display the spacing of the lattice fringe.

Freshly prepared anatase TiO₂-NPs can be dispersed into deionized water to form a colloid without adding any additives. The stability of TiO₂-H₂O colloid was investigated by changing the concentration. A water colloid with a lower concentration maintains the state of the liquid and is transparent, as shown in Fig.3. Interestingly, having been left statically for a week, the TiO₂-H₂O colloid solidified as an opaque gel when the concentration was higher than 200 g/L. No cloudy precipitates were observed in the colloid even when the concentration was as high as 1600 g/L. Inhomogeneous dispersion of TiO₂-NPs was achieved in the high concentration water colloid due to the

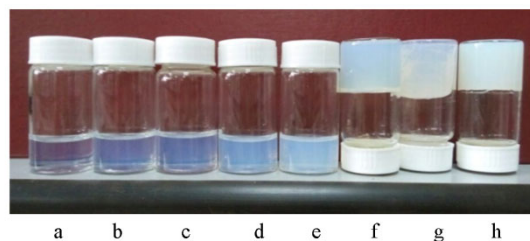


Fig.3 Digital photographic images of TiO₂-H₂O water colloid at various concentrations

c(TiO₂-H₂O)/(g·L⁻¹): a. 10; b. 30; c. 50; d. 100; e. 200; f. 400; g. 1000; h. 1600.

formation of slight aggregates, which scatter visible light^[37,38]. All the colloids were stable for quite a long time(at least six months) without sedimentation or delamination.

The transmittance spectra of TiO₂-H₂O colloid at 1–100 g/L are shown in Fig.4. The optical transmittance of 1 g/L TiO₂-H₂O colloid was nearly 100% in the visible region. The UV absorption edge was gradually red shifted with increasing the concentration, which is due to the aggregation-induced cancellation of quantum localization and electrostatic effects^[39]. In addition, the visible light transmittance decreased as the concentration increased, which indicates the formation of inhomogeneous aggregates in the high concentration colloid.

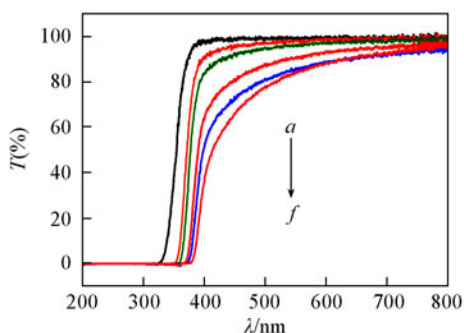


Fig.4 Transmittance spectra of TiO₂-H₂O water colloid at various concentrations

$c(\text{TiO}_2\text{-H}_2\text{O})(\text{g}\cdot\text{L}^{-1})$: a. 1; b. 5; c. 10; d. 30; e. 50; f. 100.

The photocatalytic activities of anatase and rutile TiO₂-NPs were evaluated by the degradation of MB under UV light irradiation. For comparison, the photoactivity of MB solution without any additives was investigated under the same conditions. As shown in Fig.5, MB was almost completely removed in 3 h by anatase TiO₂-NPs, which were superior to rutile TiO₂-NPs in performance. For bulk materials, the band gaps of anatase and rutile TiO₂ are 3.20 and 3.02 eV, respectively. It indicates anatase has a slightly higher redox driving force than rutile although the light absorption range of anatase is slightly less than that of rutile. Furthermore, anatase also enhanced the adsorption capability and even generated much more active sites^[40]. These advantages of anatase lead to its much higher photocatalytic activity than rutile.

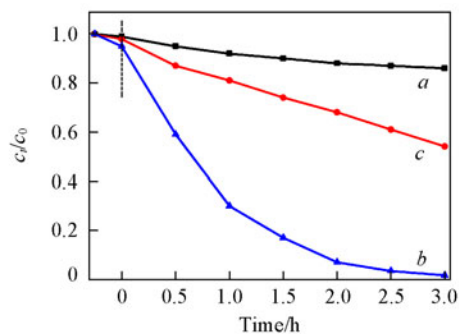


Fig.5 Photodegradation of MB solution without(a) and with anatase(b) or rutile(c) TiO₂-NPs as photocatalysts under UV irradiation

4 Conclusions

In summary, phase-selective crystallization of anatase or

rutile TiO₂-NPs was achieved by low-temperature hydrolysis of TBT under simple reflux conditions. The crystallite sizes of the as-prepared anatase TiO₂ and rutile TiO₂ were *ca.* 3.2 and 4.1 nm, respectively. The facility, reproducibility, and versatility of this synthetic approach will facilitate the development of TiO₂ fine powders. The simplicity of the method suggests that it is amenable to commercial scale-up. Without any surfactant, high-dispersed TiO₂-H₂O colloid was obtained. The TiO₂-H₂O colloid changed from a transparent liquid state to an opaque gel, depending on the concentration. The optical transmittance of 1 g/L TiO₂-H₂O colloid is nearly 100% in the visible region, and the UV absorption edge is gradually red shifted with increasing the concentration. The as-prepared anatase TiO₂-NPs are superior to rutile TiO₂-NPs in photocatalytic performance. The current strategy and resulting materials have potentials for the fabrication of a variety of bulk objects and hierarchical structures based on the assembly of nanoparticles.

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