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Low-temperature synthesis of water-dispersible anatase titanium dioxide nanoparticles for photocatalysis

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ABSTRACT

Water-dispersible anatase TiO_2 nanoparticles were synthesized at a low temperature (80 °C) without using surfactants via the mechanism of electrostatic stabilization. The water-dispersible TiO_2 nanoparticles solution was stable and no precipitation occurred after 3 months. Photocatalytic evaluation demonstrated that the as-synthesized TiO_2 nanoparticles possess excellent quinoline degradation performance (a 2.33×10^{-2} min^{-1} apparent reaction rate constant comparing to 1.22×10^{-2} min^{-1} for P25) and recycle stability (the photocatalytic activity remained 96.6% of the initial activity after four cycles of repetitive uses). These could be attributed to the small size and good water-dispersibility of the as-synthesized TiO_2 nanoparticles that led to large specific surface area and easy photogenerated electron–hole transportation.

1. Introduction

Titanium dioxide (TiO_2) nanoparticles are being intensively studied as catalysts for the photodegradation of organic compounds due to their unique physical and chemical properties [1–4]. Their photocatalytic performance is greatly determined by the particle's crystal phase, crystallinity, size, and surface chemical properties that largely depend on their synthetic routes [5–9]. There are a number of reports [10–13] on the synthesis of anatase TiO_2 nanoparticles attempting to increase their specific surface area and to delocalize the electron–hole carriers in order to enhance their photocatalytic performance. However, it is generally a rule rather than an exception that nanoparticles aggregate if there is no certain surface protection, which is driven by the reduction in the surface energy of the system. TiO_2 nanoparticles with high water-dispersibility usually possess specific surface protection to make the surface energy low, so that the agglomeration can be prevented. Currently, the water-dispersion of TiO_2 nanoparticles has been achieved via organic surfactants such as oleic acid [14], polyethylene glycol [15], and alkylamines [16]. These organic surfactants enable the water-dispersibility of the nanoparticle materials. However, they passivate the particle surface, so that the nanoparticles lose their active sites and therefore affect the photocatalytic properties [17]. Moreover, the general synthesis of TiO_2 nanoparticles usually need high-temperature calcination or complex chemical processes to convert amorphous TiO_2 into crystallines, which generally result in grain growth of the particles and hence the loss of surface area, finally deteriorate the photocatalytic activity. Thus, it would be greatly desirable to synthesize water-dispersible TiO_2 nanoparticles without using surfactants and under mild conditions.

Herein, we report a direct synthesis of water-dispersible anatase TiO_2 nanoparticles at a low temperature (80 °C) without any organic surfactants via the mechanism of electrostatic repulsion between nanoparticles. This synthesis was developed based on the reported low-temperature synthesis of TiO_2 nanoparticles [18–20] and the classical theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) [21,22] in colloid chemistry. The photocatalytic activity of the TiO_2 nanoparticles was investigated for the degradation of quinoline as a model pollutant. Other than being a nitrogenous reference compound for evaluating photocatalysts, quinoline can be found as a water contaminant, especially in industrial wastewaters and the ground surface water. A considerably enhanced photocatalytic activity was found for the water-dispersible TiO_2 nanoparticles in comparison with commercial Degussa P25.

2. Experimental section

2.1. Materials

Titanium *n*-butoxide (⩾97%, TBOT), 2-propanol, and concentrated nitric acid were purchased from Sigma–Aldrich. Quinoline

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(98%) of reagent grade was purchased from Aldrich. Ultrapure water with resistivity of 18.2 MΩ cm from Milli-Q plus, Millipore, was used throughout the experiment. Commercial P25 powder (Degussa, primary crystal size ~30 nm, 75% anatase and 25% rutile, BET surface area 50 $m^2 g^{-1}$) was used for comparison. All chemicals are used without further purification.

2.2. Synthesis of water-dispersible anatase TiO_2 nanoparticles

The water-dispersible anatase TiO_2 nanoparticles were synthesized by a modified sol–gel method with excessive water at 80 °C using TBOT as titanium precursor. In the synthetic process, the molar ratio of TBOT, water, 2-propanol, and concentrated nitric acid was 1:155:1.5:0.1. For example, 3 mL TBOT was mixed with 0.96 mL 2-propanol; this mixed solution was added dropwise (1 mL min^{-1}) into 25 mL nitric acid solution (24.7 mL water and 0.3 mL concentrated nitric acid) under vigorous stirring, providing a final pH of around 1.3. The suspension was continually stirred at 80 °C for 24 h, leading to the formation of anatase crystalline TiO_2 nanoparticles. After being cooled down to 25 °C, the as-synthesized TiO_2 nanoparticles were collected by centrifugation (11,000 rpm, 30 min). Ultrapure water was used to redisperse the TiO_2 nanoparticles, and the particles were separated again by centrifugation. Repeat this one more time to get purified TiO_2 nanoparticles, the particles were dried under vacuum at 30 °C.

2.3. Characterization

The morphology of the as-synthesized TiO_2 nanoparticles was observed using a JEOL 2100 field emission high-resolution transmission electron microscope (HRTEM) operating at 200 kV. A Rigaku X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.154 nm) was used to characterize the crystallographic structure of the nanoparticles with a scanning angle from 20° to 80°; the accelerating voltage and current were 40 kV and 40 mA, respectively. X-ray photoelectron spectroscopy (XPS) data were obtained using PHI Quantera scanning microprobe from Ulvac-Phi. Hydrodynamic size and zeta potential measurements were performed on Malvern Zetasizer Nano ZEN 3600. BET surface area was measured from nitrogen gas adsorption and desorption using Quantachrome Autosorb-3b apparatus; the sample was degassed at 120 °C for 18 h prior to the analysis.

2.4. Photocatalytic activity evaluation

Photocatalytic degradation of quinoline was carried out in a Luzchem model 4 V photoreactor equipped with a magnetic stirrer and 14 UVA lamps with an emission maximum of λ = 365 nm. The intensity of UV light was 3.15 mW cm^{-2} measured by a power meter (serial number E44333). The TiO_2 nanoparticles was mixed with quinoline solution (final volume 80 mL), and the mixture of quinoline (0.55 mmol L^{-1}) and TiO_2 nanoparticles (1.5 g L^{-1}) was stirred for 60 min in dark prior to the experiment in order to allow chemisorption of quinoline on the surface of the TiO_2 nanoparticles. Then, the UV lamps were switched onto start the photodegradation of quinoline under continuous stirring. In the photocatalytic process, 2 mL aliquots were withdrawn from the irradiated solution every 30 min. The aliquots were centrifuged to remove TiO_2 nanoparticles prior to analysis. The quinoline concentration in each aliquot was monitored by UV absorbance using a Varian Cary 5000 UV–Vis-NIR Spectrometer at 313 nm. The degradation efficiency of quinoline is calculated according to the formula below:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$

where η was the degradation efficiency of quinoline in %; C_0 was the initial quinoline concentration in mmol L^{-1}; C_t was quinoline concentration at time t in mmol L^{-1}; and t was the reaction time in min.

Each experiment was repeated at least three times under identical conditions. For the repetitive use experiment, TiO_2 nanoparticles were recycled by centrifuging the reaction solution at 11,000 rpm for 30 min.

3. Results and discussion

3.1. Formation mechanism of the TiO_2 nanoparticles

The synthesis of TiO_2 nanoparticles generally involves hydrolysis and condensation of titanium precursors. Due to the extreme water sensitivity of titanium precursors, in conventional solution-phase synthetic routes, small amount of water is used, and ethanol is employed to inhibit the hydrolysis. This, however, yields amorphous products at low temperature and further high-temperature calcination is required to convert amorphous TiO_2 into crystallines (Eqs. (1) and (2); take tetrabutyl titanate (TBOT) as an example). By analyzing the hydrolysis and condensation reactions, it can be presumed that TiO_2 might be obtained if sufficient excess water is used.

$$Ti(OC_4H_9)_4 + nH_2O \rightarrow Ti(OH)_n(OC_4H_9)_{4-n} + nC_4H_9OH \quad (1)$$

$$Ti(OH)_n(OC_4H_9)_{4-n} + Ti(OH)_n(OC_4H_9)_{4-n} \rightarrow Ti_2O_n(OC_4H_9)_{8-2n} + nH_2O \quad (2)$$

$$Ti(OC_4H_9)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_4H_9OH \quad (3)$$

$$mTi(OH)_4 \rightarrow (TiO_2)_m + 2mH_2O \quad (4)$$

In our synthesis procedure, TBOT is added to excess water to make the hydrolysis proceed quickly and sufficiently, resulting in fully hydrolyzed intermediates before condensation. In this case, Ti will exist in the form of $[Ti(OH)_n(OH_2)_{6-n}]^{(4-n)+}$, which is beneficial for the formation of $[TiO_6]$ octahedron unit [23,24]. It is reported that anatase TiO_2 is obtained when one $[TiO_6]$ octahedron shares edges with other four $[TiO_6]$ octahedral. Consequently, more O^{2-} ions should be removed from the $[TiO_6]$ in the case of anatase formation [25,26]. It means that more water molecules need to be removed during anatase formation. In our synthesis process, pH is around 1.3, the proton concentration is high, so the Ti-OH is protonated to generate a great number of Ti-OH_2^+, which is beneficial to the loss of water molecules when condensation proceeds. After TiO_2 nanoparticles are formed, there are large amount of H^+ existing on TiO_2 surface; therefore, the as-synthesized TiO_2 nanoparticles are positively charged resulting in electrostatic repulsion between each particle and thus prevents the nanoparticles from aggregation (Fig. 1).

3.2. Properties of the TiO_2 nanoparticles

The morphology and crystallinity of the as-synthesized TiO_2 nanoparticles were analyzed by HRTEM (Fig. 2). HRTEM images show that the TiO_2 nanoparticles appear to be polygon in shape with an average size of 9.8 ± 0.6 nm, and the crystal lattices are clearly visible. The structure and oxidation state of the TiO_2 nanoparticles were characterized using XRD and XPS (Fig. 3). Results demonstrate that the TiO_2 nanoparticles are anatase (Fig. 3A), and the Ti element is in the form of Ti^{4+} (Fig. 3B). Based on the calculation from Scherrer's formula for the diffraction peaks (101), (004), and (200), the average crystal grain size of the TiO_2 nanoparticles is 9.7 nm, which is in good agreement with the TEM result.

The water-dispersed TiO_2 nanoparticles solution was found to be purely white, and no precipitation occurred even after 3 months