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Tuning the morphology, stability and photocatalytic activity of TiO_2 nanocrystal colloids by tungsten doping

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ABSTRACT

The effects of tungsten doping on the morphology, stability and photocatalytic activity of TiO_2 nanocrystal colloids were investigated. The nanostructure, chemical state of Ti, W, O, and the properties of tungsten doped TiO_2 samples were investigated carefully by TEM, XRD, XPS, UV–vis, PL and photocatalytic degradation experiments. And the structure–activity relationship was discussed according to the analysis and measurement results. The analysis results reveal that the morphology, zeta potential and photocatalytic activity of TiO_2 nanocrystals can be easily tuned by changing the tungsten doping concentration. The tungsten doped TiO_2 colloid combines the characters of high dispersity and high photocatalytic activity.

1. Introduction

In the past several decades, the efforts of scientists and technicians all over the world have realized the application of photocatalytic technology in air and water purification. It has been confirmed that almost all of organic pollutants dissolved in water can be completely mineralized into carbon dioxide, water and mineral acids by photocatalysts [1,2]. TiO_2 nanomaterials with wide bandgap are considered to be the most potential photocatalysts due to the unique size effect, surface effect, quantum effect, chemical stability and excellent photocatalytic activity.

During practical applications, both the photocatalytic efficiency and reusability should be considered. According to these requirements, the immobilized photocatalysts, such as TiO_2 films supported on other substrates, are conveniently for reuse [3,4]. However, the efficiency is usually restricted significantly by the limited catalyst surface area and mass transfer rate. In contrast, TiO_2 nanoparticles usually show high photocatalytic efficiency due to the large surface area. However, it is very difficult for the powder-type photocatalysts to be separated from the purified water and reused. Although magnetic photocatalysts can be recovered easily from the suspension after treatment [5,6], the complicated producing process makes the cost high.

The photocatalysis-membrane processes based on the hybridization of photocatalysis with membrane process can eliminate the conflict between the dispersion and recovery for the powder-type photocatalysts [7,8]. To make better performance, the photocatalyst for the photocatalysis-membrane processes should combine the features of high dispersity, good stability and high photocatalytic activity. The colloidal photocatalyst shows a high potential for the application in photocatalysis-membrane process due to the high dispersity and good stability.

In the past decades, a lot of efforts have been devoted to improve the photocatalytic activity in UV range or visible range by metal ion doping, such as Fe^{3+}, Cu^{2+}, W^{6+}, Cr^{6+}, etc. [9–15]. However, the effects of metal ion doping on the dispersity and stability in solvent is still very interesting and worth to investigate.

Based on our previous research on the colloidal TiO_2 nanocrystal suspension [16–18], we investigated herein the preparation of colloidal TiO_2 nanocrystals with high dispersity and stability by tungsten ion doping. The effects of tungsten doping concentration on the dispersity and stability were discussed. And the photocatalytic activities were evaluated by the photocatalytic degradation of phenol. The results are encouraging that the tungsten doped TiO_2 nanocrystal can possess the advantages of high dispersity in water and high UV-sensitive photocatalytic activity.

2. Experimental

2.1. Materials

Titanium (IV) sulfate ($Ti(SO_4)_2$, CR) was provided by Shanghai Chemical Reagent Co. China. Aqueous ammonia solution (NH_4OH, 25%, AR), aqueous hydrogen peroxide solution (H_2O_2, 30%, AR) and

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tungsten powder (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as received without further purification. Deionized water was used for solution preparation.

2.2. Preparation of tungsten doped TiO_2 nanocrystal

Similar to the previous method synthesizing TiO_2 nanocrystal [16], in a typical synthesis, 0.75 g of titanium (IV) sulfate was diluted in 15.0 ml deionized water to form a 0.2 M $Ti(SO_4)_2$ solution. Under vigorous stirring, 3.0 M of ammonia solution was slowly added, adjusting the pH value to 7.5, which produced a white precipitate in the solution immediately. The precipitate was filtered and washed until the electric conductivity of the filtrate was lower than 100 μs/cm. The filter cake was redispersed in 62.5 mL deionized water to get a suspension by ultrasonic treatment for 0.5 h.

Under continuous magnetic stirring, tungsten powder and 1.25 ml of H_2O_2 (30 wt%) was added to the suspension in an ice-water bath. The mixture was refluxed at 100 °C for 4 h to gain the solvothermal precursor. Finally, the resulting solvothermal precursor was transferred to a Teflon autoclave lined with Teflon 70% filled and tightly closed, and then held at 180 °C for 15 h. After the solvothermal crystallization, the prepared tungsten-doped TiO_2 nanocrystal was filtered again and was redispersed in 125 ml deionized water. The tungsten doped TiO_2 nanocrystal colloid was thus obtained. According to the calculated molar ratio of W: Ti = 0:100, 1:100, 2:100, 3:100, the products are noted as TW-0, TW-1, TW-2, and TW-3, respectively.

2.3. Characterization

The TiO_2 powders were prepared through rotatory evaporation of the TiO_2 colloids at 45 °C. The morphologies of the products were viewed by transmission electron microscopy (TEM). The TEM images were recorded on a JEOL JEM-200 CX microscope at an acceleration voltage of 200 kV. The specific surface area of the prepared sample was measured by N_2 adsorption–desorption on a Micromeritics ASAP 2000 system. The XRD analysis was performed using a Rigaku D/MAX-2000 X-ray diffractometer at room temperature, operating at 30 kV and 30 mA, using Cu kα radiation (λ = 0.15418 nm). X-ray photoelectron spectroscopy (XPS) spectra were recorded by a PHI 5000C ESCA spectrometer using Mg Ka radiation ($h\nu$ = 1253.6 eV). The zeta potential of the TiO_2 nanoparticles was measured on a Zetasizer 3000HS (Malvern Instruments Ltd. UK). The surface area of TiO_2 nanoparticles was determined using a nitrogen adsorption apparatus (model 3H-2000III, China). Diffuse reflectance spectra (DRS) were obtained for the dry-pressed disk samples using a Scan UV–vis spectrophotometer (Varian, Cary 500) equipped with an integrating sphere assembly, using $BaSO_4$ as the reflectance sample. The photoluminescence (PL) spectra were measured through the fluorescence spectrophotometer (Hitachi, F-7000) using 300 nm line of Xe lamp as excitation source at room temperature.

2.4. Evaluation of photocatalytic activity by the degradation of phenol

The photocatalysts obtained were diluted by deionized water to 1.0 g/L. The photocatalytic degradation was performed in an 80 mL test tube with 75 mL of reaction solution. The initial concentration of phenol was 10 mg/L. The suspension was stirred in dark for 30 min to obtain the saturated adsorption of phenol before UV-light irradiation. During the photoreaction process, the mixed solution was irradiated by an UV lamp (16 W, 365 nm) with constant magnetic stirring. The phenol concentration of the solution was measured every 1 h after removing powders by centrifugation at 10,000 rpm for 30 min. The remaining phenol in the solution system was detected by an UV-2501 PC spectrometer at wavelength of 200–400 nm. The efficiency of degradation was calculated from Eq. (1) as follows:

$$\frac{C}{C_0} = \frac{A}{A_0} \quad (1)$$

where A_0 and A are the initial and final absorbance at 269 nm for phenol.

3. Results and discussion

Fig. 1 shows the TEM images of products with different W:Ti calculation molar ratio. For the pure TiO_2 nanocrystals obtained by hydrothermal at 180 °C for 15 h, the length is about 34.2 nm, and the diameter is about 13.2 nm. With the increase of tungsten doping concentration, the shape of nanocrystals changed from rod-like to rectangular, and the aspect ratio of TW-0, TW-1, TW-2, TW-3 are 2.59, 1.76, 1.56 and 1.24, respectively, revealing the tungsten doping really affects the surface energy of the nanocrystal facets and resulting different shapes. The specific surface area of the prepared samples were measured by N_2 adsorption–desorption, and the results are listed in Table 1. Compared with pure TiO_2 nanocrystal, the tungsten-doped samples have larger specific surface area. And the sample TW-2 shows the highest specific surface area 100.2 m^2/g.

The colloidal suspension of tungsten doped TiO_2 in water (Fig. 1c inset picture) shows high transparency, which confirms that the nanocrystals can be dispersed well in water. The stability of water-based colloid depends on the zeta potential greatly. Generally, the colloid with absolute zeta potential value higher than 30.0 mV is a stable dispersion, while higher than 50.0 mV is a good stable dispersion [19]. Table 1 shows the zeta potential of pure TiO_2 colloid and tungsten doped TiO_2 hydrosols at pH value of approximately 7.5. As shown in Table 1, compared with pure TiO_2 hydrosol (−43.7 mV), the absolute zeta potential value of every tungsten doped TiO_2 colloid is a little higher, indicating higher stability of the tungsten doped TiO_2 colloid. The high dispersity of prepared TiO_2 samples should be attributed to the high zeta potential value of nanocrystals, which is favorable for the exposure of large surface area of TiO_2 nanocrystals to the reactants.

The XRD patterns of TiO_2 with different doping concentration are shown in Fig. 2. All the samples are of anatase crystal phase. However, WO_3 phase does not appear in all XRD patterns even if the content of doped W^{6+} is improved to 3%. It is probably that W^{6+} is incorporated into the titania lattice to form W–O–Ti bonds or highly dispersed on the TiO_2 surface [20]. The crystal sizes of TW-0, TW-1, TW-2 and TW-3 calculated by Scherrer formula from the FWHM of the (1 0 1) peak of anatase are 15.3, 16.0, 20.0 and 24.5 nm, respectively [21]. With the increase of tungsten doping concentration, the diffraction angles are shifted to lower degrees. The lattice parameters can be calculated from the diffraction angles according to the Bragg equation (Eqs. (2) and (3)). The lattice parameters are summarized in Table 1. Where $d(hkl)$, θ are the Bragg lattice spacing and angle, respectively. a, b and c are the lattice parameters [22,23].

$$d(hkl) = \frac{\lambda}{2\sin\theta} \quad (2)$$

$$d^2(hkl) = h^2a^{-2} + k^2b^{-2} + l^2c^{-2} \quad (3)$$

The effective ionic radii of W^{6+} and Ti^{4+} with 6-fold coordination are 60.0 pm and 60.5 pm, respectively [24]. Compared with the pure TiO_2, the W^{6+} doped TiO_2 shows higher volume of unit cell. The lattice distortion of TiO_2 should be attributed to the substitution of Ti atom by W atom.