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Hydrothermal Synthesis of Highly Water-dispersible Anatase Nanoparticles with Large Specific Surface Area and Their Adsorptive Properties

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Abstract. Highly water-dispersible and very small TiO_2 nanoparticles (~3 nm anatase) with large specific surface area have been synthesized by hydrolysis and hydrothermal reactions of titanium butoxide and used for the removal of three azo dyes (Congo red, orange II, and methyl orange) with different molecular structure from simulated wastewaters. The synthesized TiO_2 nanoparticles are well dispersed in water with large specific surface area up to 417 m^2 g^{-1}. Adsorption experiments demonstrated that the water-dispersible TiO_2 nanoparticles possess excellent adsorption capacities for Congo red, orange II, and methyl orange, which could be attributed to their good water-dispersibility and large specific surface area.

1 Introduction

Owing to their excellent physical and chemical properties, titanium dioxide (TiO_2) nanoparticles (NPs) have shown great potential in various applications such as photocatalysts, pigments, solar cells, water photolysis for hydrogen production, ultraviolet blockers and adsorbents [1-5]. For many applications, high quality anatase NPs with large specific surface area are required to satisfy individual demands. Additionally, for water treatment applications, the TiO_2 NPs also required to have good dispersivity in water since highly water-dispersible properties can greatly increase the contact area and contact opportunity between the solid and contaminant ions or molecules. In general, the surface chemical properties of NPs largely depend on their synthetic routes. Therefore, various preparation methods have been developed to produce TiO_2 NPs, such as sol-gel process,

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hydrothermal method, solvothermal method, and electrochemical deposition [6]. Among these, the sol-gel method attracts much attention and is extensively used for the synthesis of TiO_2 NPs owing to its convenience and low cost. However, the NPs synthesized by conventional sol-gel method suffer from problems of aggregation that is driven by lowering the surface energy of the system. Consequently, as-obtained precipitate is not able to be re-dispersed in water to form stable colloidal solution. For this reason, in recent years, some modified sol-gel methods have been developed, and it has been demonstrated that water-dispersible TiO_2 NPs can be prepared via controlling particle size and preventing particle agglomeration [7].

In the present work, we report the synthesis of water-dispersible TiO_2 NPs with a large specific surface area using a combination of hydrolysis and hydrothermal reactions of titanium butoxide (TBOT). This method is initiated by the hydrolysis of TBOT in the presence of excess water and moderate amount of nitric acid. Subsequently, the dehydration of –TiOH groups obtained in the previous step was activated under hydrothermal conditions to produce TiO_2 NPs. The facile method adopted in this study was found to be an efficient technique for the synthesis of water-dispersible TiO_2 NPs with a large specific surface area up to 417 $m^2 g^{-1}$. To our best knowledge, there is no any reported TiO_2 NPs with such a higher specific surface area. In addition, for the first time, we report the enhanced adsorption of Congo red (CR), orange II (O II), and methyl orange (MO) on the synthesized TiO_2 NPs.

2 Materials and Methods

2.1 Materials

Tetrabutyl titanate (TBOT, ≥98%) was used as a source of Ti^{4+} and procured from Tianjin Beilian Fine Chemical Reagents Company. Nitric acid (68%) and absolute ethanol (≥99%) were purchased from Beijing Chemical Reagents Company and used as a catalyst and solvent, respectively. Different dyes (99%) used in this study were purchased from China Medicine Company.

2.2 Synthesis of TiO2 NPs

TiO_2 NPs were synthesized by a combination of hydrolysis and hydrothermal reactions of TBOT. 3.0 mL of TBOT was mixed with 5.0 mL of ethanol and certain amount (1.0–9.0 mL) of 2.0 M HNO_3 to form a transparent solution. Subsequently, 24.0 mL of deionized water was added dropwise to the TBOT–C_2H_5OH–HNO_3 solution under constant stirring for 1 h to obtain homogeneity. The solution thus obtained was transferred to a Teflon-lined stainless autoclave of capacity 50-mL, followed by heating in a conventional oven at 110°C for 3 h. The resultant precipitate was washed several times in ethanol to remove any unreacted reactants and separated from the solution by high-speed centrifugation. Finally, the precipitate was dried in an oven at 80°C, resulting in the formation of a white powder with low density. In this study, we varied the amount of HNO_3 to analyze the effect of concentration of acid on the properties of resulting TiO_2 NPs. The samples obtained with 0, 1, 3, 5, 7, and 9 mL 2.0 M HNO_3 are hereafter designated as T-acid-0, T-acid-1, T-acid-3, T-acid-5, T-acid-7, and T-acid-9, respectively.

2.3 Characterization

TiO_2 NPs synthesized as discussed above were characterized by several techniques. X-ray diffraction patterns (XRD) of the TiO_2 NPs were obtained by a Rigaku D/Max-Ultima IV diffractometer using CuKα radiation. The specific surface area of the resultant TiO_2 NPs was measured with a Micrometrics ASAP2020 Analyzer (Brunauer-Emmett-Teller, BET

method). Transmission electron micrographs (TEM) and selected area electron diffraction (SAED) were recorded using a FEI TECNAI G2F20 transmission electron microscope. Thermogravimetric analysis (TGA) was carried out in air, at a heating rate of 5°C min^{-1} from room temperature to 800°C, using a Shimadzu DTG-60H apparatus.

2.4 Azo dyes adsorption

For adsorption experiments, the sample T-acid-1 was used as adsorbent since it possessed the highest specific surface area among the all synthesized samples; and, each adsorption experiment was conducted by adding fixed amount of TiO_2 NPs (30 mg) to 20 mL of dye solution. All adsorption experiments were carried out at room temperature (20°C). The mixture was agitated in a shaking water bath at a constant speed of 300 rpm at room temperature for a certain time. After the adsorption processes, solution and TiO_2 NPs were separated by high-speed centrifugation and the concentration of dye in the supernatant was immediately determined using a Shimadzu UV-Vis 2550 spectrophotometer at their respective absorbance maxima.

3 Results and Discussion

The XRD patterns depict the formation of TiO_2 with main diffraction peaks at $2\theta = 25.1$, 37.8, 48.0, 54.6, and 63.4, corresponding to the crystal planes of (101), (004), (200), (105), and (204), respectively (Fig. 1). These peaks are consistent with the JCPDS file (e.g., No.71-1167) of anatase. The average crystallite sizes (A.C.S) of all samples calculated from the half-width of the diffraction lines using the Scherrer's equation were in the range 3.1–3.7 nm, showing that relatively small anatase NPs could be obtained by this method. We found that the amount of HNO_3 has no significant influence on TiO_2 NPs crystallite sizes (Table 1). Fig. 2a shows the photographs of TiO_2 NP aqueous solutions with different concentration prepared from the sample T-acid-1. The synthesized TiO_2 NPs could be readily dispersed in water, with the solution remaining stable after more than several months, due mainly to the small size and hydrophilic properties of the NPs. As can be seen in TEM image (Fig. 2b), the as-synthesized TiO_2 NPs are highly crystalline and their average crystallite size is less than 5 nm, approximately consistent with the result obtained by XRD. The specific surface area of the final products was studied by nitrogen adsorption-desorption measurements. The synthesized TiO_2 NPs exhibit very large BET specific surface area (S_{BET}), i.e., up to 417 m^2 g^{-1} (Table 1). This value is significantly larger than those (200 – 256 m^2 g^{-1}) [8-10] of water-dispersible TiO_2 NPs synthesized via various methods, which is most likely due to the strategy using a mild synthesis optimized to produce small particles. From the BET analysis of synthesized samples, the amount of HNO_3 used in the synthesis reaction was found to have a strong influence on the S_{BET} of resultant TiO_2 NPs. The S_{BET} of samples T-acid-1, T-acid-3, T-acid-5, T-acid-7, and T-acid-9 were 417, 337, 315, 307, and 261 m^2 g^{-1}, respectively, indicating that the S_{BET} decreased with the increase of HNO_3 amount. This phenomenon has also been reported by other researchers [11, 12], and it can be attributed to a decrease in the cross-linking level. Owing to its large surface large specific surface area and high dispersibility, the present TiO_2 NPs are expected to be useful in water treatment; therefore, they were further used to remove azo dyes from simulated wastewater in this study. Fig. 3 shows the adsorption rate curves of CR, O II, and MO on the TiO_2 NPs. The adsorption rates of these dyes were so fast that no data point could be measured in the period from 0 to 5 min, and more than 80% of these dyes could be removed within 30 min. The highly water-dispersible properties of TiO_2 NPs can greatly increase the contact area and contact

opportunity between TiO_2 NPs and dye molecules, leading to the high adsorption rate of dyes. The adsorption of different dyes on TiO_2 NPs could reach equilibrium within 40 min.

Table 1.Textural Properties Of Synthesized Samples

Sample	S_{BET} (m^2g^{-1})	A.C.S (nm)
T-acid-0	263	3.7
T-acid-1	417	3.1
T-acid-3	337	3.2
T-acid-5	315	3.2
T-acid-7	307	3.5
T-acid-9	261	4.7

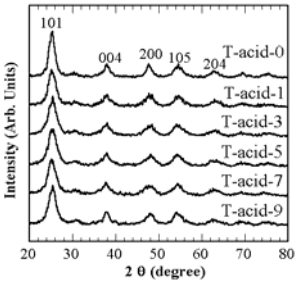

Figure 1. XRD patterns of the synthesed samples.

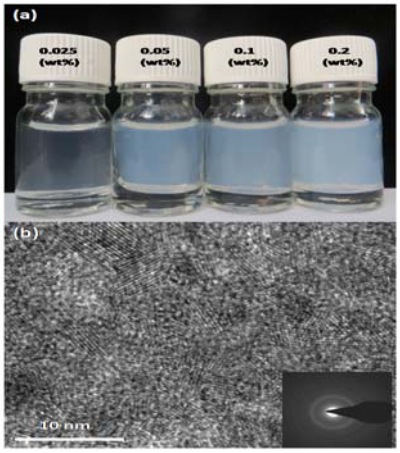

Figure 2. (a) Photographs of the TiO_2 NPs aqueous dispersions with different concentrations prepared from the sample T-acid-1; (b) TEM image and SAED pattern (inset) of the sample T-acid-1.

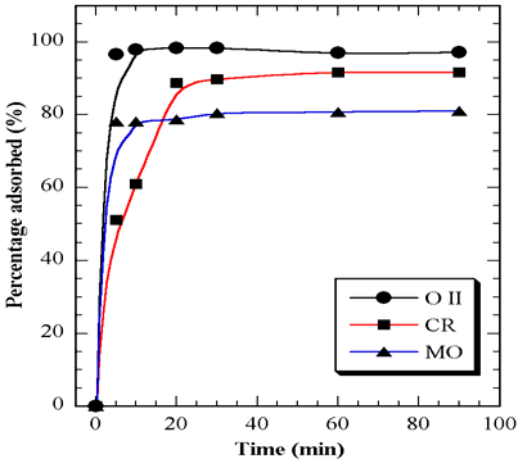

Figure 3. Adsorption rate curves for CR, O II and MO.

4 Summary

Highly water-dispersible TiO_2 NPs are successfully synthesized using a combination of hydrolysis and hydrothermal reactions of titanium butoxide (TBOT). The obtained TiO_2 NPs are composed of anatase with average size of ~3 nm and possess a high surface area (>400 m^2 g^{-1}). Owing to these excellent properties, the TiO_2 NPs show high adsorptive removal abilities for O II, CR, and MO. The adsorption of the three dyes on TiO_2 NPs could reach equilibrium within 40 min.

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