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Adsorption and Photocatalysis of Spherical TiO_2 Particles Prepared by Hydrothermal Reaction

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Abstract : TiO_2 spherical particles were prepared using hydrothermal reaction at different temperatures of 110, 150 and 190℃ for 5 h. The TiO_2 samples were characterized by BET, XRD and SEM analysis. Specific surface areas and particle sizes are in the range of 148 ~ 240 m^2g^{-1} and 323 - 450 nm, composed of tiny nanoparticles with size of 5 ~ 7 nm. It was found that photocatalytic degradation of methylene blue is highly sensitive to particle sizes on the adsorption and photocatalysis.

Keyword : Nanoparticles; Spherical titanium dioxide; Photocatalysis; Methylene blue; Hydrothermal reaction

1. Introduction

The hydrothermal technique is becoming one of the most important tools for advanced materials processing, particularly owing to its advantages in processing nano-structural materials for a wide variety of technological applications such as electronics, optoelectronics, catalysis, ceramics, magnetic data storage, biomedical and biophotonics. The hydrothermal technique not only helps in processing monodispersed and highly homogeneous nanoparticles, but also acts as one of the most attractive techniques for processing nano-hybrid and nanocomposite materials [1].

Recently, the hydrothermal processing of TiO_2 has been carried out by many workers. It has been studied extensively in the last few years owing to its unique properties. TiO_2 shows maximum light scattering with virtually no absorption. It is non-toxic and chemically inert. It has been employed extensively in the studies of heterogeneous photocatalysis and has been accepted as one of the best photocatalysts for the degradation of environmental contaminants [1].

TiO_2 nanocrystallite is usually synthesized via hydrothermal reaction using titanium alkoxides as source materials [2,3], since such factors as the particle size, crystallographic phase and morphology of the nanocrystallites can be manipulated. Generally, there are three kinds of alkoxides of titanium that are often used, tetraethyl titanate (TTET), tetrabutyl titanate (TTBT) and titanium tetraisopropoxide (TTIP). Among these three alkoxides, TTIP is used mostly in dye-sensitized solar cells (DSSCs) partly due to the moderately hydrolysable rate compared to the other two alkoxides [2]. The hydrothermal synthesis of TiO_2 sols using TTIP as the starting material has been well studied by Barbé et al. [2]. In hydrothermal reactions, particle growth is affected more by temperature than by time according to Ostwald ripening [4].

In the present paper, the different sizes of TiO_2 spheres were systematically prepared via hydrothermal reaction, and the effects of synthesis conditions on their structure and morphology were analyzed. Experimental and theoretical analysis of the effect of adsorption and photoactivity on nano-TiO_2 spheres was conducted based on the photocatalytic degradation of methylene blue (MB).

2. Experimental

2.1 Preparation of TiO_2 spheres

First, 50 mL EtOH and 40 mL acetonitrile were mixed and added 1 mmol methylamine solution. Then, 6 mmol titanium(Ⅳ) isopropoxide was dripped into EtOH(10 mL) and dissolved in the above solution with

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continuous magnetic stirring. After that, 150 mL ethanol:H_2O=1:1 was dripped into the solution with stirring for 1 h. The mixture was transferred into a 100 mL Teflon-lined auto-clave and kept at 110℃ (named HTR (1)), 150℃ (named HTR (2)) and 190℃ (named HTR (3)) for 5 h. After cooling, the solution was centrifuged and washed by deionized water and absolute ethanol, respectively, and then dried at 100℃ for 12 h. All chemicals were analytical grade and used as purchased without further purification.

2.2. Characterization

The crystal structures of spherical TiO_2 particle prepared by the hydrothermal reaction were characterized using X-ray diffractometry (XRD, X'Pert PRO MPO, Philips) with Cu Kα radiation (λ=0.154 nm) at scanning rate of 2° min^{-1} from 10 to 80 in the 2θ range. The morphology and size of the particles in the samples were examined by FE-SEM (Hitach, S-4800). Specific surface areas were measured by nitrogen adsorption at 77K (Micromeritics Tristar ASAP 2020) using Brunauer–Emmett–Teller (BET) method. The concentration of MB was evaluated by UV spectrophotometer (UV-160A, Shimadzu).

2.3. Evaluation of adsorption equilibrium and photocatalytic activity

Adsorption equilibrium experiments were carried out by contacting a given amount of HTR(1) with MB of 5 ~ 50 mg/L in a shaking incubator at 30℃ until equilibrium is reached (2 h). A constant mass of adsorbent (1.0 mg) was weighed into 100 mL glass bottles and in contact with 40 mL of MB solution of different initial concentrations. Upon equilibration, the samples were analyzed to determine the residual equilibrium liquid phase MB concentration. The concentration of MB was analyzed by UV spectrophotometer at 660 nm.

The photocatalytic reactor consists of a cylindrical jacketed quartz tube with 5.0 cm in diameter and 50 cm in length. Four 8 W shortwave UV lamp 254 nm, Philips, USA) were placed inside the reactor. The light source assembly was placed concentrically inside the 1500 mL Pyrex glass container of 10.0 cm in diameter and 28.5 cm in height filled with 500 mL MB solution. The distance between the source and the bottom of the vessel was 1.5 cm to aid for better stirring using a magnetic stirrer. To maintain the same temperature of the solution during the reaction, water was circulated through the annulus of the jacket quartz tube. The MB concentration was 10 ppm with a catalyst loading of 50 mg. Before irradiation, the suspension aqueous solution was stirred continuously in darkness for 30 min to ensure adsorption/desorption equilibrium. The adsorption equilibrium concentration was used as the initial value for the further kinetic treatment of the photodecomposition processes. The samples were collected from the mixture solution at regular intervals and filtered to analyze by UV spectrophotometer apparatus to determine the concentration of MB.

3. Results and discussion

The Brunauer–Emmett–Teller (BET) surface areas of the porous TiO_2 microspheres are determined by N_2 adsorption using an ASAP-2020 surface area analyzer. The samples prepared at different temperatures showed higher specific surface areas in the range of 148 ~ 240 m^2g^{-1}, especially for the porous TiO_2 microspheres prepared at 190 ℃ for 5 h (148 m^2g^{-1}). The pore volumes of the porous TiO_2 microspheres (0.479 ~ 0.546 cm^3g^{-1}) are also significantly larger than that of P25 [6]. The N_2 adsorption–desorption isotherms and the pore size distribution (PSD) curves of the porous TiO_2 microspheres are illustrated in Figure 1. Type IV isotherms exist for the porous TiO_2 microspheres, indicating porous structures. PSD curves (Figure 1(B)) of the porous TiO_2 microspheres display very sharp and narrow peaks located in the range of 8.0 ~ 14.7 nm demonstrating that the porous TiO_2 microspheres have very narrow and uniform pore sizes distribution. Therefore, the TiO_2 microspheres porous were high surface areas and uniform porous nanostructures.

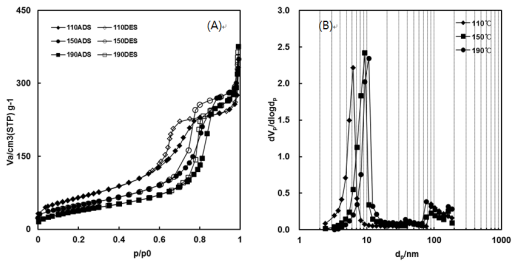


Figure 1. Nitrogen adsorption-desorption isotherms (A) and the corresponding pore size distribution curves (B) of the porous TiO_2 microspheres prepared at different temperatures for 5 h: 110, 150 and 190 ℃.

Figure 2 also shows the results of the XRD analysis on the reaction products obtained at different hydrothermal reaction temperatures for 5 h. All the sharp peaks observed in the XRD pattern belong the anatase phase of TiO_2. The diffraction peaks become stronger and sharper by increasing the hydrothermal temperature, indicating the formation of larger crystal size and higher crystal degree [4]. Average crystallite sizes of nanocrystallites was estimated based on the Scherrer's

equation [5]:

$$L = \frac{\alpha \lambda}{\beta \cos\theta} \quad (1)$$

where parameter α is taken to be 0.5 and wavelength λ taken to be 0.154056 nm. β is the 2θ-FWHM of peak anatase (101) in XRD patterns. Then after hydrothermal treatments, as temperature increased from 110 to 190 ℃, it was calculated the crystal sizes are about 5 ~ 7 nm.

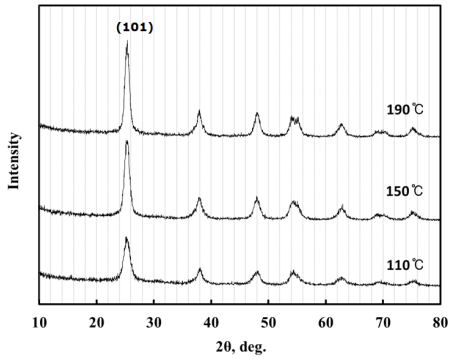


Figure 2. XRD pattern of different size TiO_2 spheres prepared by hydrothermal reaction at 110, 150 and 190℃ for 5 h.

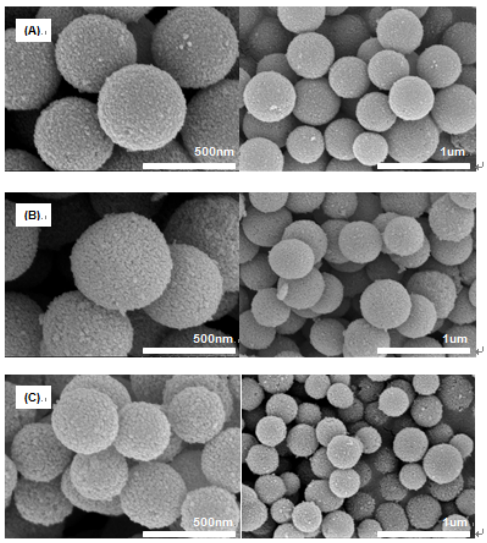
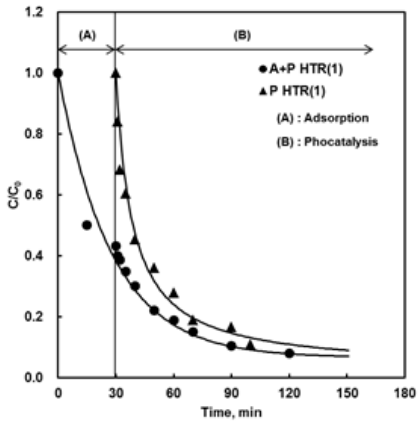


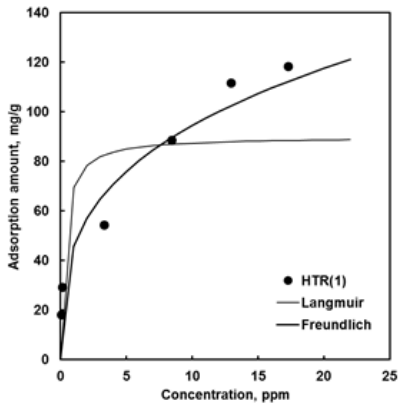
Figure 3. SEM micrographs of TiO_2 powder prepared by hydrothermal reaction methods at the different temperature (TTIP:H_2O ratio=1:6, 5 h) (A) 110℃, (B) 150℃ and (C) 190℃.

The morphology and structure of the samples were further investigated by FE-SEM. Figure 3 shows the typical FE-SEM images of the as-prepared uniform TiO_2 spheres. As the reaction temperature is increased, the diameter of the resulting TiO_2 sphere decreased. The average diameters of HTR (1), HTR (2) and HTR (3) are about 450, 440 and 323 nm, respectively.

The adsorption and photocatalytic decomposition kinetics of MB on HTR (1) is given in Figure 4(a). The two reaction systems, i.e., the adsorption followed by photodegradation, and the simultaneous adsorption and photodegradation were denoted as A+P and P, respectively. Figure 4(a) compares the variation of MB concentration as a function of time in A+P with the P systems mediated by HTR (1).



(a) Variation of MB concentration as a function of time in A+P and P systems over HTR(1)



(b) Adsorption isotherm

Figure 4. Adsorption isotherm and adsorption/ photocatalytic degradation of the methylene blue by TiO_2 spheres prepared by hydrothermal reaction (HTR (1))

Figure 4(b) shows the adsorption isotherms of MB. Adsorption equilibrium data of MB on HTR (1) were correlated with the Freundlich equation. The parameters were obtained by fitting the data using a modified

Levenberg–Marquart method (IMSL routine DUNSLF). The solid lines in Figure 4(a) are the results predicted by Freundlich parameters (K=46.6 mg/g and n=5.28, where K (mg/g) and n related the multilayer adsorption capacity and intensity of adsorption) [7].

The kinetic data were treated with the Lagergren first-order model [8],

$$\frac{dq}{dt} = k_1(q_e - q) \quad (2)$$

Integrating Eq. (2) with respect to integration conditions $q = q_0$ to $q = q_t$ at $t = 0$ to $t = t$, the kinetic rate expression becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

The first-order rate constant k_1 can be obtained from the slope of the plot of $\log(q_e - q_t)$ vs time. The A+P and P systems first-order rate constants were found to be 0.0829 min^{-1} and 0.0929 min^{-1} for initial MB concentration of 10 ppm, respectively.

Before photocatalytic reaction, 57% MB was adsorbed by the HTR(1). As shown in Figure 4(a), the concentration of MB is decreased to 0.9 ppm at 90 min on HTR (1).

4. Conclusions

In this work, we have prepared anatase TiO_2 spheres using hydrothermal synthesis. The specific surface areas and particle sizes are in the range of 148 ~ 240 m^2g^{-1} and 323 - 450 nm, and they are composed of tiny particles with size of 5 ~ 7 nm. The kinetics of adsorption/photodegradation and photodegradation obeys the first-order kinetic, whose rate constant was 0.0829 and 0.0929 min^{-1} of the MB onto hydrothermal synthesis TiO_2 sphere at 110 ℃ for 5 h. The uniform particle size, high specific surface area and high pore volume of the samples prepared by hydrothermal synthesis in this work are may not only be applied in photocatalysis, adsorption, dye-sensitized solar cell, separation, sensing, and as functional filling materials in textile, paints, paper, and cosmetics.

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