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Synthesis and Characterization of Hollow Anatase TiO_2 Spheres and its Application in the Photodegradation of γ-Lindane under Ultraviolet Light

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Abstract. Hollow anatase titania spheres have been synthesized using hydrothermally–prepared carbon spheres as the template. Here, the combination of hydrothermal process with sol–gel followed by calcination in air was done in order to obtain hollow anatase TiO_2 spheres by utilizing fructose and tetrabutyl titanate (TBT) as the precursors. The structure and morphology of the products were characterized using various techniques, including Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermal gravimetric and differential thermal analysis (TG–DTA), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). XRD showed that all peaks of TiO_2 correspond to anatase crystalline phase. The BET surface area of the hollow spheres was about 22 m^2g^{-1}. The photocatalytic activity of the hollow anatase TiO_2 was measured under UV light using γ-lindane as the target pollutant and was compared to commercially available TiO_2.

Introduction

Inorganic materials with hollow spherical structures with nanometer to micrometer dimensions have attracted enormous attention. This is due to their low density, large specific area, mechanical and thermal stability, surface permeability and wide range of potential applications [1-6]. In recent years, considerable efforts have been made in the fabrication of hollow titania structures due to their potential applications in photocatalysis [7], drug delivery, catalyst support and so on. Several different methods, such as templating method [8], polymer-induced method [9], sol–gel method [10] and hydrothermal method [11], have been reported for the production of hollow TiO_2 spheres. Ren *et al.* [12] reported the fabrication of hollow microspheres of mesoporous TiO_2 using the surfactant assisted method. Collins *et al.* [13] prepared hollow titania microspheres by non-aqueous emulsion. Mesoporous core-shell structured titania microspheres could also be obtained via a hydrothermal precipitation process by Guo *et al* [14]. The template method has been proven as a successful preparation procedure for the synthesis of hollow spheres. Templates can be divided into hard and soft templates. When hard templates are used to fabricate inorganic hollow spheres, the structure of the hollow product is similar to the template. While for soft templates the morphology of the hollow products is usually poor because of the soft template's deformabilities. Various materials, such as polymers, inorganic non-metallic and metal particles, can be used as hard templates. Carbon spheres are effective templates to prepare metallic and metallic oxide hollow spheres because carbon is hydrophilic and is functioned with ─OH and other groups on its surface, which make surface modification unnecessary. This study reports the preparation of hollow TiO_2 particles by hydrothermally prepared carbon spheres as the hard template. The carbon template was obtained by employing fructose as the precursor. The prepared samples were characterized by SEM, FESEM, TEM, FTIR, TG–DTA and XRD. To reveal the potential application of hollow TiO_2 in analytical chemistry, the photocatalytic degradation of organochlorine pesticide, γ-lindane, (γ-HCH) using hollow TiO_2 spheres was compared with commercial TiO_2 particles. The photocatalytic results revealed that the hollow TiO_2 exhibited a good degree of photocatalytic activity and could be

separated easily. To our knowledge, this is the first report in which photocatalytic activity of hollow titania spheres is examined for photodegradation γ-HCH.

Experimental

Materials. All chemicals used are of analytical grade or highest synthetic purity and purchased from Sigma-Aldrich. The water used was deionized water.

Synthesis of Carbon Spheres. Colloidal carbon spheres were prepared by hydrothermal treatment of 0.5 M fructose aqueous solution in a teflon-lined autoclave at 160 °C for 5 h. The products were collected by centrifugation and then rinsed with deionized water and alcohol, three times each. The final product was dried at 80 °C for 5 h.

Synthesis of Hollow TiO_2 Spheres. The starting solution was prepared by mixing 0.3 g of the carbon spheres prepared and 60 mL of ethanol. Then 3 mL of tetrabutyl titanate ($Ti(OBu)_4$) was added into the solution. The mixture was vigorously stirred at room temperature for 24 h. The products were obtained after washing, drying and calcination at 600 °C for 3 h in the air.

Characterization. The crystalline phase and crystallite size of the hollow TiO_2 powder were determined by an X-ray diffractometer (Bruker AXS D8 Automatic Powder Diffractometer) using the Cu-Kα radiation with λ = 0.154 nm at 40 kV and 40 mA, over the 2θ range of 10°–90°. The morphological observations were performed by using a JOEL JSM-6701F field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) analysis was recorded on a JEOL JEM-2100 at an acceleration voltage of 200 kV. The FTIR spectra of the samples were taken using Perkin–Elmer Spectrum spectrometer over the range of 400–4000 cm^{-1}. Thermogravimetric analysis of carbon and hollow TiO_2 spheres were carried out in a TGA-SDTA 851e METTLER instrument. The reaction environment was maintained with nitrogen flow and the heating rate was set at 10 °C min^{-1}. The result for surface area of the sample was obtained on a BET Micromeritics ASAP 2010 with the gas composition of 30% N_2 and 70% He.

Photocatalytic Degradation of γ-Lindane. Exactly 0.05 g of hollow titania spheres was dispersed into 100 mL of an lindane aqueous solution (200 ppb) and then irradiated with a 6 W ultraviolet lamp (365 nm, Spectroline® ENF-260 C/FE) under continuous stirring. Before the irradiation, the suspension was maintained in the dark for 24 h to reach complete adsorption–desorption equilibrium. At a defined time interval, 1mL of suspension was removed and then the concentration of γ-HCH was analyzed by gas chromatography with a micro electron capture detector (GC–μECD). For comparison, the same procedure was also done using commercial titania (BET surface area 132 m^2 g^{-1}). An Agilent 19091S-433 gas chromatograph (GC) equipped with a μECD system and a HP–5MS column (30 m × 0.25 mm × 0.25 μm) was used. The temperature program of the GC–μECD selected was as follows: 160 °C (1 min), 160–230 °C at 40 °C min^{-1}, 230–270 °C at 30 °C min^{-1}, 270 °C (1 min). The temperature of μECD and injector was held at 300 and 280 °C, respectively. 1μL of each sample was injected for three times and the data collected was averaged.

Results & Discussion

SEM image of the carbon spheres heat treated at 160 °C is shown in Fig. 1(a). It can be seen from the figure that the as-prepared carbon spheres are regular spheres in shape with an average diameter of 1.1 μm. Fig. 1(b) illustrates the FESEM image of the morphology of the hollow TiO_2 spheres obtained after the removal of the carbon sphere template. It can be seen that the obtained product is hollow spheres with an average diameter of 990 nm.

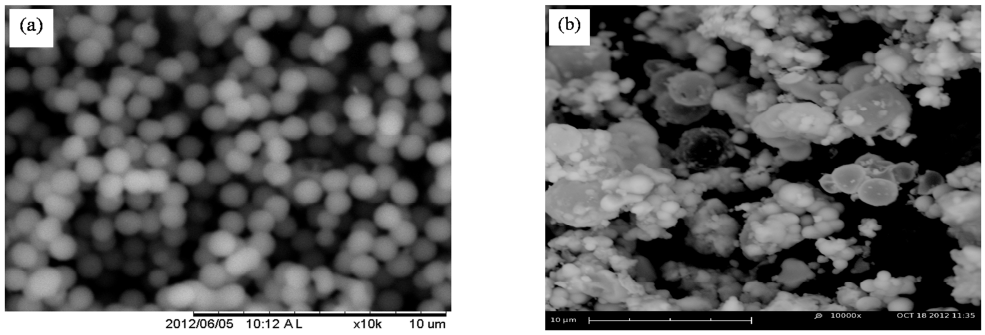

Fig. 1 SEM image of (a) carbon spheres formed by heating at 160 °C for 5 h and FESEM image of (b) hollow TiO_2 spheres

Fig. 2(a) shows the TEM image of a titania hollow particle. The strong contrast between the dark edge and bright center indicates the hollow structure of the titania sphere. The TEM image also reveals that the utilization of carbon spheres as the template resulted in the successful formation of spherical shell. It can also be seen that the size of the hollow sphere is about 950 nm, which smaller than the original size of the carbon spheres template. A high–resolution transmission electron microcopy (HRTEM) image in Fig. 2(b) shows that the space of fringe image was 0.308 nm, corresponding to the distance between (1 0 1) crystal plane of anatase TiO_2.

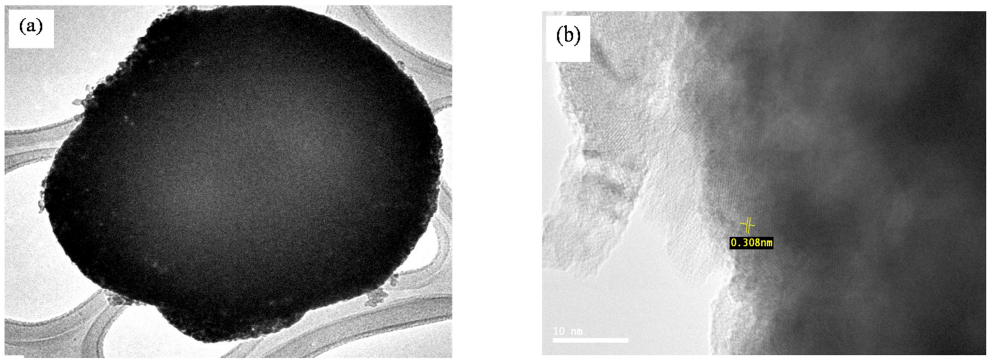

Fig. 2 (a) TEM image of hollow anatase TiO_2 spheres prepared by template method and (b) HRTEM image of the selected particle.

The FTIR spectrum of the carbon spheres is shown in Fig. 3(a). The peaks at 3000–3700, 1605 and 1000–1460 cm^{-1} originated from the stretching vibrations of -OH, C=C and -C-O, respectively. The presence of water is supported by the appearance of the OH stretching mode at 3000–3700 cm^{-1}. Fig. 3(b) shows the FTIR spectrum for hollow TiO_2 spheres, confirming the formation of the inorganic shells and the successful removal of organic components. The bands in the range of 500–900 cm^{-1} originated from the titanium dioxide. It can also be seen that the OH stretching mode exists in the sample after calcination.

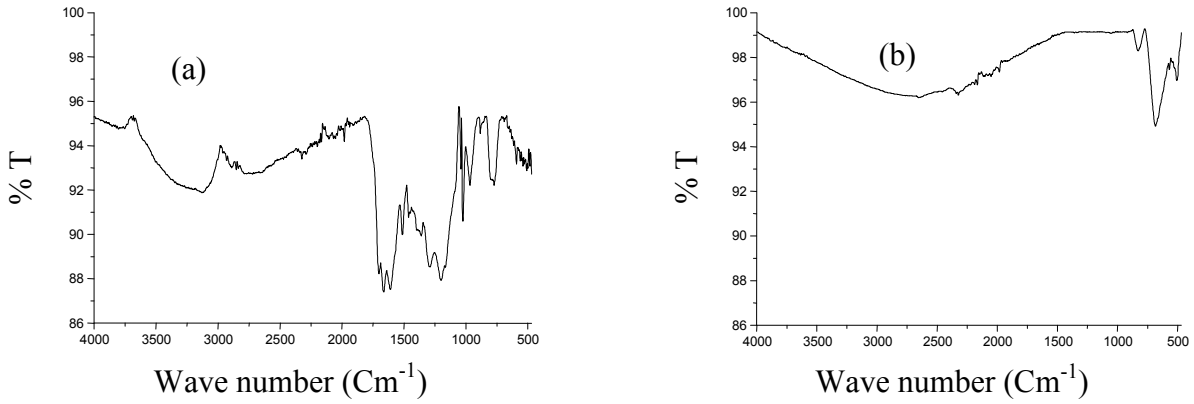

Fig. 3 FTIR spectra of (a) carbon spheres prepared by hydrothermal method and (b) hollow TiO_2 spheres.

X-ray powder diffraction (XRD) analysis was applied to examine the crystal structure of the TiO_2 particles. Fig. 4 shows that the diffraction peaks of TiO_2, at 2θ = 25.3, 37.8, 48.0, 53.9, 55.1 and 62.7°, are agreeable with (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1) and (2 0 4) crystal planes of anatase TiO_2 (JCPDS file No. 21-1272). Furthermore, no impurity peaks were detected in this figure, which clearly illustrates the high purity of the as-prepared sample.

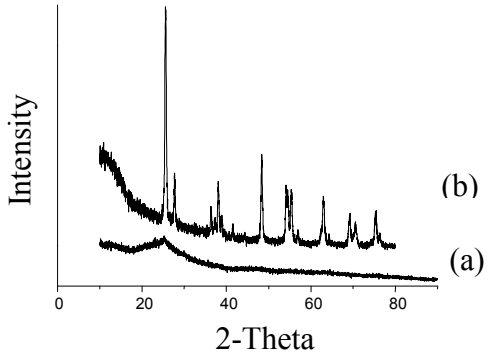

Fig. 4 XRD patterns of (a) carbon and (b) hollw anatase TiO_2 spheres.

Fig. 5 (a) and (b) shows the TG–DTA curves of the carbon spheres and hollow titania spheres, respectively. The first weight loss in the range of 25–100 °C can be attributed to the release of water, whereas the second weight loss corresponds to the removal of strongly bonded water or surface hydroxyl groups and organic components in the range of 150–740 °C. Thus the calcinations at 600 °C in air were employed to remove the carbon core particles in the present experiment.

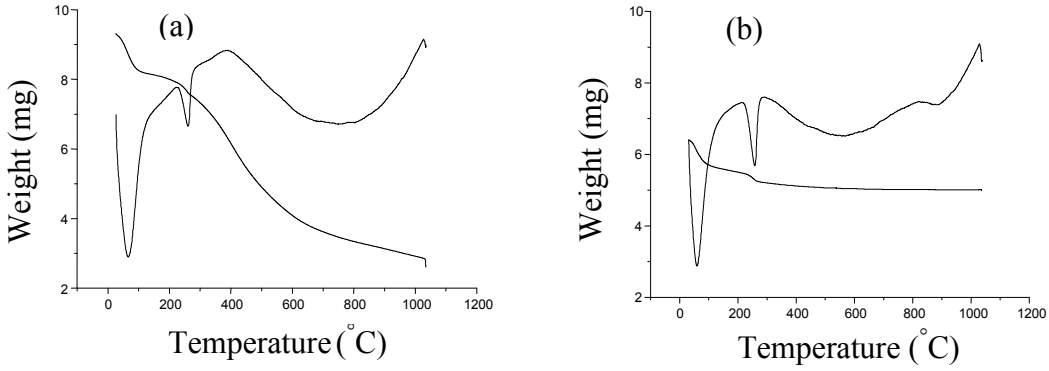

Fig. 5 TG–DTA curves of (a) carbon spheres and (b) hollow TiO_2 spheres.

The structural properties of TiO_2 were further investigated by the Brunauer-Emmett Teller (BET) method which provides the information on surface area of the sample. The BET surface area of the prepared TiO_2 measured by adsorption at 130 °C was 22 m^2g^{-1}. For comparison, the same experimental conditions were also done for commercial TiO_2 particles. The specific surface area of the commercial TiO_2 was found to be 132 m^2 g^{-1}, which is much higher than that of the TiO_2 sample (22 m^2 g^{-1}). The lower BET surface area of TiO_2 hollow spheres could be due to the aggregation of the particles after heat treatment at 600 °C for 3 h.

Evaluation of Photocatalytic Activity

In order to investigate the analytical potential of TiO_2 hollow spheres in the environment, the photodegradation of γ-HCH was taken as the example and its γ-HCH photodegradation efficiency was compared with that of commercial TiO_2. The degradation efficiency can be calculated using Eq. (1):

$$\text{Degradation efficiency (\%)} = (1-C/C_0) \times 100 \quad (1)$$

Here, C_0 is the initial concentration of γ-HCH before UV irradiation and C is the concentration of γ-HCH remaining in the solution after irradiation. The temperature used was in the range of 25–30 °C in all of the experiments. The change in pH during the degradation of the pesticide was monitored with a digital pH meter. After 6 h of irradiation, the degradation efficiency (Eq. (1)) of γ-HCH was 98.6 % and 98.5 % for TiO_2 hollow spheres and commercial TiO_2 respectively. It can be seen that the photocatalytic activity of commercial TiO_2 is slightly lower than that of hollow TiO_2 spheres, even with a much larger BET specific surface area of 132 m^2 g^{-1}. The higher photocatalytic activity of the TiO_2 hollow spheres can be ascribed to its better light scattering ability. The hollow spherical structure could absorb more incident light through multiple–reflection of UV light within the sphere's interior void, allowing them to enhance light–harvesting and thus resulting in higher photocatalytic activity [15]. Moreover, hollow TiO_2 spheres have an important advantage over the commercial TiO_2 since it can be readily separated from the slurry system by simple filtration and sedimentation after the photocatalytic reaction. Fig. 6 depicts the photocatalytic degradation results of γ-HCH by hollow TiO_2 and commercial TiO_2.

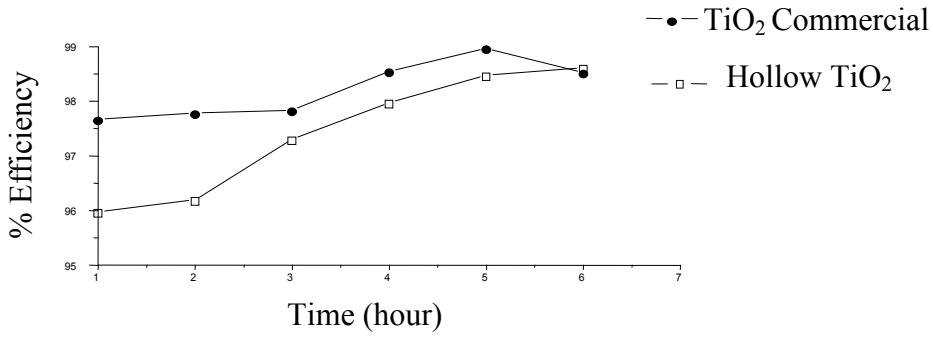

Fig. 6 Plots of the efficiency of hollow TiO_2 and commercial TiO_2 against irradiation time of UV.

Summary

Hollow titania spheres have been successfully fabricated by coating TiO_2 with hydrothermally prepared carbon spheres and then by removal of the carbonaceous component via calcinations. Fructose was used as precursor for the carbon spheres. The structure and morphology of the product were characterized by using various techniques, including FESEM, TEM, TG–DTA, XRD and FTIR. The BET surface area of hollow spheres was about 22 m^2g^{-1}. The photocatalytic activity of hollow titania spheres was evaluated by the degradation of γ-HCH under UV light irradiation and compared to commercial titania. Results show that the photocatalytic activity of hollow structured

titania is higher than that of the commercial titania in the decomposition of γ-HCH due to its better light scattering.

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