Preparation of Anatase Hollow TiO$_2$ Spheres and Their Photocatalytic Activity in the Photodegradation of Chlorpyrifos

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Hollow anatase titania (TiO$_2$) spheres were synthesized using fructose and tetrabutyl titanate (Ti(OC$_4$H$_9$)$_4$, TBT) as the precursors via the conventional hard template method. The morphological, structural and thermal properties of the products were characterized using scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric and differential thermal analysis (TG-DTA), Brunauer–Emmett–Teller (BET) surface area analysis and diffuse reflectance ultraviolet visible (DR UV–Vis) spectroscopy. XRD revealed that the hollow TiO$_2$ prepared was in the anatase phase and the BET surface area measured was about 22 m$^2$ g$^{-1}$. The photocatalytic activity of the synthesized hollow anatase TiO$_2$ in the photodecomposition of chlorpyrifos was 18.67% which was higher that that obtained using commercial TiO$_2$.

**Keywords:** Hollow anatase titania; Photodegradation; Fructose; Chlorpyrifos.

INTRODUCTION

For years, inorganic materials that possess hollow spherical structures, with dimensions of nanometer to micrometer, have attracted many researchers. This is because of their immense potential, owing to the favorable characteristics of having low density, large specific area, good mechanical and thermal stability, surface permeability. In recent times, considerable efforts have been made to fabricate hollow titania (TiO$_2$) structures due to their potential applications in photocatalysis, drug delivery, catalyst support and so on. Methods such as templating, polymer-induced, sol–gel and hydrothermal have been used for the production of hollow TiO$_2$ spheres. The fabrication of hollow mesoporous TiO$_2$ microspheres using the surfactant assisted method has been reported by Ren *et al.* The preparation hollow TiO$_2$ microspheres by non-aqueous emulsion has also been carried out by other researchers. Mesoporous core-shell structure titania microspheres have also been fabricated through the hydrothermal precipitation process. Among all, the template method has invariably been proven as a successful preparation procedure for the synthesis of hollow spheres. The templates can be divided into hard and soft templates. The fabrication of inorganic hollow spheres using the hard template results in hollow products with structures similar to that of the template. For the soft templates, the morphology of the hollow products is usually poor because of the soft template’s deformability. Various materials, such as polymers, inorganic non-metallic and metal particles, can be used as hard templates. Carbon spheres are effective templates for the preparation of metallic and metallic oxide hollow spheres as carbons are hydrophilic and the surface are functionalized with –OH and other groups. Due to the available functional groups, modifications of carbons are not required. This study focuses on the preparation of hollow TiO$_2$ particles using hydrothermally prepared carbon spheres as the hard template and fructose as the precursor. Various techniques were employed to characterize the prepared samples. The results revealed that the hollow TiO$_2$ showed better photocatalytic activity in the photodegradation of organophosphorous pesticide, chlorpyrifos, as compared with commercial TiO$_2$ particles.

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RESULTS AND DISCUSSION

Materials characterization

The SEM image of the carbon spheres which underwent heat treatment at 160 °C is shown in Fig. 1(a). The image shows that the carbon spheres are regular in shape, with an average diameter of 1.2 µm. Fig. 1(b) shows the morphology of the hollow TiO₂ spheres obtained after the removal of the carbon spheres template. The TiO₂ obtained are hollow spheres with diameters of 170–1100 nm. The inset micrograph in Fig. 1(b) shows a partly broken sphere thus confirming that the spheres are hollow inside. The FESEM images revealed that only a small percentage of the hollow spheres were fractured. Most of the spheres were still intact.

Fig. 2(a) shows the TEM image of the hollow TiO₂ particles. The strong contrast between the dark edges and the bright centre indicates the hollowness of the TiO₂ sphere. The TEM image also reveals that the utilization of carbon spheres as the template resulted in the formation of TiO₂ with spherical shells. The high-resolution transmission electron microscopy (HRTEM) image in Fig. 2(b) shows that the space of fringe image is 0.352 nm, which corresponds to the distance between (101) crystal plane of anatase TiO₂.

The FTIR spectrum of the carbon spheres is shown in Fig. 3(a). The peaks at 1669 and 1612 cm⁻¹ are attributed to the stretching vibrations of C=O and C=C groups, respectively. The absorbances observed at 1000–1460 cm⁻¹ are attributed to the C–O stretching and –OH bending vibrations, thereby indicating the existence of residual hydroxyl groups in large numbers. Similar observations have also been reported by other researchers. The presence of water is supported by the peak appearance of OH stretching mode at 3000–3700 cm⁻¹.

Fig. 3(b) shows the FTIR spectrum for hollow TiO₂ spheres. The broad peak around 450–890 cm⁻¹ corresponds to the stretching vibrations of C=O and C=C groups, respectively. The absorbances observed at 1000–1460 cm⁻¹ are attributed to the C–O stretching and –OH bending vibrations, thereby indicating the existence of residual hydroxyl groups in large numbers. Similar observations have also been reported by other researchers. The presence of water is supported by the peak appearance of OH stretching mode at 3000–3700 cm⁻¹.
to the Ti–O bond. The peak at 686 cm⁻¹ is assigned to the symmetric O–Ti–O stretching, while the peak at 505 cm⁻¹ is due to the vibration of Ti–O bond. This confirms the formation of the inorganic shells and the removal of organic components. It can also be observed that the intensity of the peak for OH stretching mode increased after calcination. These surface hydroxides are of great advantage for the photocatalytic activity of anatase TiO₂ as they provide higher capacity for oxygen adsorption.

X-ray powder diffraction (XRD) analysis was employed to examine the crystal structure of TiO₂ particles. Fig. 4(b) shows the presence of diffraction peaks of TiO₂ at 2θ = 25.3, 37.8, 48.0, 53.9, 55.1 and 62.7°, which correspond to the (101), (004), (200), (105), (211) and (204) crystal planes of anatase TiO₂ (ICDD file No. 01-086-1157) (Fig. 4(a)). The sharpness of the peaks implies high crystallinity of the TiO₂. No other peaks were detected in the diffractogram, which confirms the high purity of the as-prepared sample. The crystal size of anatase was determined using the Scherrer’s equation:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

where \( D \) is the crystal size of the catalyst, \( \lambda \) is the X-ray wavelength (1.54056 Å), \( \beta \) is the full width at half maximum (FWHM) of the diffraction peak (radian), \( K \) is a coefficient (0.89) and \( \theta \) is the diffraction angle at the maximum peak. The crystal size of hollow TiO₂ calculated was 23.82 nm. This value is similar to the one determined by TEM. Fig. 4(b) shows that the carbon spheres used as the template are amorphous in nature.

Fig. 5 (a) and (b) shows the TG–DTA curves of the carbon spheres and hollow TiO₂ spheres, respectively. From the TG curves, the first weight loss in the range of 25–100 °C is attributed to the release of water. The second weight loss at 150–740 °C for carbon and at 100–400 °C for hollow TiO₂ corresponds to the removal of the strongly bonded water or surface hydroxyl groups and organic components. Calcination in air at 600 °C was employed to remove the carbon core particles in the present experiment.

The structural properties of TiO₂ were further investigated by the Brunauer-Emmett Teller (BET) surface area analysis. The BET surface area of the TiO₂ obtained measured by the adsorption branch at 130 °C was 22 m² g⁻¹. Comparatively, the specific surface area for the commercial TiO₂ particles was 132 m² g⁻¹, which was much higher than the prepared TiO₂ spheres. The low BET surface area of the prepared hollow TiO₂ spheres was attributed to the aggregation of the particles after the heat treatment at 600 °C for 3 h.
The DR UV–Vis spectra of the hollow TiO$_2$ spheres and commercial TiO$_2$ are shown in Fig. 6 (a). The figure shows that the absorption of the commercial TiO$_2$ and hollow TiO$_2$ are in the UV region. The absorption band edges of commercial TiO$_2$ and the hollow TiO$_2$ are estimated to be around 371 and 385 nm, respectively. The energy band gap of crystalline semiconductors can be calculated using the following equation:

$$\alpha = A (h \nu - E_g)^n$$  \hspace{1cm} (2)

where $\alpha$ is the absorption coefficient, $h$ is Planck constant, $\nu$ is the incident light frequency, $A$ is a constant, $E_g$ is the band gap and $n$ depends on the nature of the transitions. The transitions may have values of 1/2, 2, 3/2 and 3, which correspond to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively.\(^{21}\) In TiO$_2$, $n = 2$ is usually considered. Experimental diffuse reflectance data cannot be used directly to measure the absorption coefficients ($\alpha$) because of scattering contributions to the reflectance spectra. Scattering coefficient depends weakly on the energy and Kubelka-Munk function ($F(R_s)$), ($R_s$ is the diffuse reflectance) can be considered to be proportional to the absorption coefficient within the narrow range of energy containing the absorption edge features. In such way, the determination of the absorption edge energy can be estimated from the ($F(R_s) · h \nu$)$^{1/n}$ versus $h \nu$ plot. In particular, the experimental band gap value can be obtained from the x-intercept of the straight tangent line to this plot. The indirect band gap energies ($E_g$) of the hollow titania and commercial TiO$_2$ are estimated to be 3.18 and 3.3 ev, respectively (Fig. 6 (b)). The band gap energy for the hollow titania is similar to the band gap energy of the commercial TiO$_2$. The small difference between these values might be due to experimental errors during measurement.

**Evaluation of photocatalytic activity**

The photocatalytic activity of hollow TiO$_2$ spheres in the environment was tested out in the photodegradation of chlorpyrifos and its chlorpyrifos photodegradation efficiency was compared with that of commercial TiO$_2$. The photocatalytic degradation efficiency was calculated using Eq. (3) below:

$$\text{Degradation efficiency (\%)} = (1 - C/C_0) \times 100$$  \hspace{1cm} (3)

where $C_0$ is the initial concentration of chlorpyrifos before UV irradiation and $C$ is the concentration of chlorpyrifos that remained in the solution after UV irradiation. After 3 h of irradiation, the degradation efficiency of chlorpyrifos was 75.21% for hollow TiO$_2$ spheres and 56.54% for the commercial TiO$_2$. This shows that the photocatalytic activity of commercial TiO$_2$ is lower than that of hollow TiO$_2$ spheres, despite its larger BET specific surface area. The higher photocatalytic activity of the TiO$_2$ hollow spheres is ascribed to its higher ability in light scattering. The hollow spherical structure enhanced the absorption of incident light through multiple–reflection of the UV light within the interior void of the spheres. Due to that, more light was harvested therefore enhancing the photocatalytic activity of the TiO$_2$. Similar observations have also been reported by other researchers.\(^{22}\) The hollow TiO$_2$ spheres also have another advantage over the commercial TiO$_2$ as they can be readily separated from the slurry system by simple filtration and sedimentation after the photocatalytic reaction.
Fig. 7 shows the photocatalytic activity of hollow TiO$_2$ spheres and commercial TiO$_2$ in the photodegradation of chlorpyrifos.

**EXPERIMENTAL**

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

**Synthesis of carbon spheres:** Colloidal carbon spheres were prepared in a teflon-lined autoclave by hydrothermally treating 0.5 M aqueous solution of fructose at 160 °C for 5 h. The products were collected by centrifugation, followed by rinsing three times with deionized water and alcohol. The resulting 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 prepared carbon spheres with ethanol (60 mL), followed by the addition of titanium tetrabutoxide (Ti(OBu)$_4$) (3 mL). The mixture was vigorous stirred at room temperature for 24 h. hollow TiO$_2$ spheres were obtained after washing, drying and calcination at 600 °C for 3 h in air.

**Characterization:** The morphological characterizations were performed using FESEM (JOEL JSM-6701F) and TEM (JEOL JEM-2100) at an accelerated voltage of 200 kV. The FTIR spectra of the samples were obtained using a Perkin–Elmer spectrometer at the range of 400–4000 cm$^{-1}$. For the DR UV–Vis spectra, a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer was used. The spectra was recorded at room temperature in air at the wavelength range of 200 to 600 nm. The BET Micromeritics ASAP 2010 with gas composition of 30% N$_2$ and 70% He was used to obtain information on the surface area of the sample.

**X-ray diffraction (XRD):** The phase and crystallite size of the hollow TiO$_2$ were determined using X-ray diffractometer (Bruker AXS D8 Automatic Powder Diffractometer) operating at 40 kV, 40 mA and Cu-K$_\alpha$ radiation ($\lambda = 1.5406$ nm) at $2\theta = 10^\circ$–$80^\circ$.

**Thermogravimetry and differential thermal analysis (TGA–DTA):** Thermogravimetric analysis of the carbon and hollow TiO$_2$ spheres were carried out using TGA-DTA 851e METTLER instrument. Determinations were carried out at temperatures ranging between 50 °C to 1200 °C at heating rates of 10 °C min$^{-1}$ under nitrogen gas flow.

**Photocatalytic degradation of chlorpyrifos:** About 0.05 g of the hollow titania spheres were dispersed into 100 mL of 10 ppm aqueous chlorpyrifos solution and then irradiated with 6 W ultraviolet lamp (365 nm, Spectroline$^{\text{TM}}$ ENF-260 C/FE) under continuous stirring. Before irradiation, the suspension was maintained in the dark for 24 h to reach complete adsorption–desorption equilibrium. Every, 1 mL of suspension was removed and the concentration of the chlorpyrifos was analyzed using gas chromatography with a micro electron capture detector (equipped with a µECD system and a HP–5MS column (30 m × 0.25 mm × 0.25 µm). For comparison purpose, the procedure was repeated using commercial titania (BET surface area of 132 m$^2$ g$^{-1}$). The temperature program of the GC–µECD selected is as follows: 160 °C (1 min), 160–230 °C at 40 °C min$^{-1}$, 230–270 °C at 30 °C min$^{-1}$ and 270 °C (1 min). The temperature of the µECD and injector was held at 300 and 280 °C, respectively. Each sample was injected three times with the mount of 1 µL each time and the average value was used.

**CONCLUSIONS**

Anatase hollow TiO$_2$ spheres were successfully prepared by using hydrothermally prepared carbon spheres as the template. Various techniques were used to study the structure and morphology of the prepared TiO$_2$. The BET surface area of the obtained hollow TiO$_2$ spheres was very much lower than that of the commercial TiO$_2$. The photocatalytic activity of the hollow TiO$_2$ spheres was evaluated in the photodegradation of chlorpyrifos under UV light irradiation. Despite the low surface area, the photocatalytic activity of the hollow TiO$_2$ spheres was 18.67% higher than that by the commercial TiO$_2$, which is might be due to the better light scattering in the hollow TiO$_2$ spheres.

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