



Fabrication of positively and negatively charged, double-shelled, nanostructured hollow spheres for photodegradation of cationic and anionic aromatic pollutants under sunlight irradiation[☆]

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ABSTRACT

A novel approach to prepare double-shelled, nanostructured hollow spheres with positively and negatively charged was proposed. If the difference in isoelectric points between M_xO and N_yO was large enough, at a certain pH range, the inner and outer shell of double-shelled $M_xO@N_yO$ hollow spheres were positively and negatively charged, respectively. A proof-of-concept was shown, using WO_3 and TiO_2 as anionic and cationic building subunits, respectively. The nanoparticles of WO_3 and TiO_2 were coated successively onto the functionalized polystyrene (PS) template beads, the resulted $PS@WO_3@TiO_2$ nanocomposites were calcined at elevated temperature, and then double-shelled $WO_3@TiO_2$ hollow spheres were obtained. The dispersity, morphology, size, and lattice of these hollow spheres were tested by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The presence and purity of both WO_3 and TiO_2 phases were confirmed by electron energy loss mapping analysis and X-ray diffraction analysis (XRD). The specific surface area and the average pore diameter of these hollow spheres were $53.04\text{ m}^2/\text{g}$ and 8.042 nm , respectively. The photocatalytic activity for the degradation of cationic and anionic aromatic pollutants was in the order of double-shell hollow spheres $WO_3@TiO_2 >$ single-shell $WO_3-TiO_2 >$ P25, i.e., the synergistic effect of coupling TiO_2 with WO_3 on photocatalytic performance was proved by us.

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1. Introduction

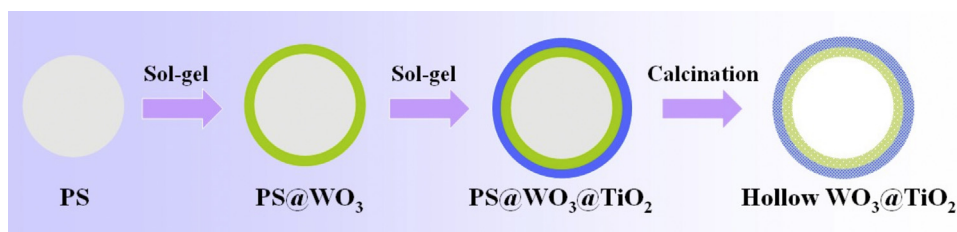
In recent years, sunlight driven photocatalysis plays an important role in dealing with organic pollutants [1–3]. Both anionic and cationic organic pollutants are coexisted in the wastewater. In the development of nanostructured photocatalysts, three key obstacles should be overcome, including the separation of photoexcited electrons and holes [4], the residence time of the light on/in the photocatalyst [5,6], and the simultaneous degradation of anionic and cationic organic pollutants. Such challenges can be unlocked

by structural and morphological innovations [7–9], e.g., the structure of hollow spheres has been used to solve the first two obstacles [10,11]. If the inner and outer surface charges of hollow spheres are positive and negative, respectively, the affinity between anionic and cationic pollutants and the photocatalyst will be enhanced, and then the major obstacle of heterogeneous photocatalysis (i.e., the poor surface coverage of pollutants on the photocatalyst) can be resolved. Therefore, it is necessary to develop double-shelled hollow spheres with positively and negatively charged for the photodegradation of anionic and cationic organic pollutants.

Herein, we present a novel, simple, and general method for preparing such photocatalysts. Using polystyrene spheres (PS) with negatively charged as sacrificial templates, metal ions with positively charged could be adsorbed onto PS. After oxidation and hydrolysis, metal oxide (denoted as M_xO) were formed and coated onto PS. The surface hydroxyl from M_xO could be used for the coordination of the other metal (denoted as N). After calcination at high temperature, double-shelled $M_xO@N_yO$ hollow spheres could be obtained. If the difference of the isoelectric point between M_xO and

[☆] Electronic supplementary information (ESI) available: SEM and TEM images, XRD pattern, EDX data, TG data, FTIR spectra, nitrogen adsorption–desorption isotherm, surface area, and porosity measurements of $WO_3@TiO_2$ hollow spheres, correlation coefficient R^2 , and isoelectric point of nanometer semiconductors.

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Scheme 1. Scheme of fabrication of the monodisperse double-shelled $\text{WO}_3@TiO_2$ hollow spheres using the “template + sol-gel + calcination” method.

N_yO was large enough, the inner and outer shell of $M_xO@N_yO$ hollow spheres would carry a net positively and negatively charged, respectively, at a certain pH range (Scheme 1). A proof-of-concept was shown, using tungsten trioxide (WO_3) and titanium dioxide (TiO_2) as cationic and anionic building subunits, respectively, because the isoelectric point is 0.4 for WO_3 and 6.2 for TiO_2 [12]. With a band gap of 2.7 eV, WO_3 is a promising visible-light-responsive photocatalyst for the degradation of organic pollutants [13,14]. As well, TiO_2 has been widely used as a photocatalyst for its relatively high photocatalytic activity, wide band gap (3.2 eV), low cost, low toxicity, and high chemical stability [15–17]. Therefore, some studies have reported on the core-shell $\text{WO}_3\text{-TiO}_2$ spheroids [18,19], $\text{WO}_3\text{-TiO}_2$ films [20,21], $\text{TiO}_2\text{-WO}_3$ nanotubes [22–24], $\text{WO}_3\text{-TiO}_2$ nanorod arrays [25,26], and $\text{WO}_3\text{-TiO}_2$ nanowires [27], and single-shelled $\text{WO}_3\text{-TiO}_2$ hollow spheres [28]. Despite intense efforts in $\text{WO}_3\text{-TiO}_2$ nanocomposites, $\text{WO}_3@TiO_2$ hollow spheres with new structural characteristics of double-shelled and surface positively and negatively charged have not been proposed yet.

2. Experimental

2.1. Reagents and chemicals

Tetrabutyl titanate (TBOT, J&K, 99%), tungsten hexachloride (WCl_6 , Aladdin), sodium persulfate (Xilong, 98%), and ethanol (Xilong, 99.7%) were purchased in China and used without additional purification. Methyl acrylate (Sinopharm, 98%) and styrene (Sinopharm, 99%) were used after passing through the inhibitor removal column and vacuum distillation. Distilled water was employed as the polymerization medium.

2.2. Synthesis of PS spheres

According to a modified method [29], PS spheres were prepared by the interpolymer interactions between styrene and methyl acrylate. A double-neck and round-bottom flask equipped with reflux condenser, mechanical agitation, temperature controller, and N_2 agitation was used as reactor. The air in the reactor was replaced by a steam of N_2 and then the reaction system was kept under N_2 until the polymerization was finished. After adding 85 mL of distilled water, 10.47 mL of styrene, and 0.52 mL of methyl acrylate, the reactor was heated and maintained at 70 °C, the solution of sodium persulfate (0.15 g in 5 mL of water) was added to start the polymerization process for 24 h, and then PS as latex with ca. 10% solid content were collected.

2.3. Synthesis of $PS@WO_3$, $PS@TiO_2$, and $PS@WO_3\text{-TiO}_2$ particles

WCl_6 (0.2 mmol) was dissolved in 20 mL of ethanol, forming a 0.01 mol/L solution. As core template, 0.25 g of PS was uniformly dispersed by ultrasonication in 50 mL of ethanol. The WCl_6 solution was added at a speed of 10 s per drop under vigorous stirring, and then kept for 20 h. After removing the solvent by the centrifugation, the resulting $PS@WO_3$ was washed three times with ethanol and

dried in vacuum at 60 °C for 6 h. Using TBOT (0.6 mmol), both WCl_6 (0.06 mmol) and TBOT (0.6 mmol) as the precursors, respectively, $PS@TiO_2$ and $PS@WO_3\text{-TiO}_2$ sample were also prepared by same method.

2.4. Synthesis of $PS@WO_3@TiO_2$ particles

In 10 mL of ethanol, TBOT (0.15 mL) was dissolved and then $PS@WO_3$ (0.03 g) dispersed in the mixture of 0.65 mL of water and 10 mL of ethanol was added. After refluxing at 70 °C for 10 h, obtained $PS@WO_3@TiO_2$ particles was washed with ethanol by three cycles of centrifugation/redispersion and then dried in vacuum at 60 °C for 6 h.

2.5. Fabrication of single-shelled of WO_3 , single-shelled of TiO_2 , single-shelled of $WO_3\text{-TiO}_2$, and double-shelled $WO_3@TiO_2$ hollow spheres

In a conventional muffle furnace, the obtained $PS@WO_3@TiO_2$ or $PS@WO_3$ or $PS@TiO_2$ or $PS@WO_3\text{-TiO}_2$ particles were heated with a rate of 5 °C/min from room temperature to 550 °C and calcinated at 550 °C for 3 h. The PS were removed and then single-shelled of WO_3 , single-shelled of $WO_3\text{-TiO}_2$, and double-shelled $WO_3@TiO_2$ hollow spheres were finally obtained.

2.6. Characterization

Scanning electron microscopy (SEM) images were carried out on a Gemini microscope (Hitachi, S-4800, Japan) at an accelerating voltage of 10 kV. Prior to analysis, samples were coated with thin Au layer to increase the contrast and quality of the images. Transmission electron microscopy (TEM) images were recorded on FEI America Tecnai G2 F20 U-TWIN microscope operated at 200 kV acceleration voltages. Samples were prepared by drying a drop of the dilute solutions of the particles on a carbon grid. In order to prove the independent presence of WO_3 shell and TiO_2 shell, i.e., double-shelled $WO_3@TiO_2$ hollow spheres, samples were analyzed by elemental mapping image and EDX analysis on same TEM. In this analysis, when electron beam was incident into a specimen, a part of the electrons was inelastically scattered and lost a fraction of the energy. The distribution of element in a specimen was clarified by selecting and imaging the electrons with a specific energy loss. X-ray scattering patterns (XRD, D/MAX-TTRIII(CBO), Rigaku corporation, Japan) were scanned by analyzing the samples using Cu-K α monochromatic beam at 40 kV and 30 mA over 20 min rang 20–80. Fourier-transform infrared (FTIR) spectra were recorded with a Perkin Elmer Instruments Co. Ltd. FTIR spectrometer prepared by mixing the samples with KBr. Thermo-gravimetric analysis (TG) was performed on a TG 2009F1 analyzer (NETZSCH, Germany). Before measurements, samples were dried in vacuum for ca. 12 h and then heated with a rate of 15 K/min in porcelain crucibles from 25 °C to 900 °C with nitrogen as carrier gas. The UV–vis absorption spectra were measured using a UV–vis 2550 spectrophotometer (Shimadzu corporation). The system was referenced to a BaSO_4 powder

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