Research Paper

Fabrication of WO₃ Nanowrinkles on Silica Bead for Photocatalysis under Visible Light

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Abstract

WO₃ nanowrinkles were successfully synthesized on SiO₂ beads via a hydrothermal reaction. The as-prepared WO₃-SiO₂ core shell composites were characterized by X-ray diffraction, ultraviolet-visible spectroscopy, Brunauer-Emmett-Teller measurements, and scanning electron microscopy. The photocatalytic activity of nanowrinkled WO₃-SiO₂ core shell composites toward O₂ evolution was two times higher than that of commercial WO₃ nanoparticles. The Rhodamine-6G degradation efficiency of nanowrinkled WO₃-SiO₂ composites was two times higher than that of commercial WO₃ nanoparticles. The fabrication method used in this study can be used for developing novel photocatalytically active WO₃ composites for the photodissociation of water under visible light.

Keywords: Tungsten oxide, Silica bead, Core-shell structure, Photocatalyst, Dye degradation, O₂ evolution

I. Introduction

Photocatalysts utilize solar energy to photodissociate water and purify environmental organic pollutants. Titanium dioxide (TiO₂) is the most commonly used photocatalyst and has been studied extensively [1]. However, the wide bandgap (3.2 eV) of TiO₂ photocatalysts limits their practical applications, especially those requiring visible light [2-4]. Another promising metal oxide photocatalyst, tungsten trioxide (WO₃), has been used extensively in catalytically active materials and electrochromic devices owing to its wide bandgap range of 2.4-2.8 eV. This wide bandgap range makes WO₃ highly active photocatalytically under visible light [5-7].

Recently, core-shell nanostructured materials have gained immense attention owing to their fascinating properties and wide range of catalytic applications. Various efforts have been made to improve the photocatalytic activity of WO₃, one of which is by fabricating different types of substrate-supported WO₃ cores. To improve the photocatalytic efficiency of WO₃, different types of functional metal oxide substrates are used as core materials [8,9]. These functional materials

not only act as robust supporters for effective separation after the reaction, but also increase the surface area of the photocatalyst. In this study, core-shell structured WO₃ nanowrinkles were fabricated on silicon dioxide (SiO₂) beads, which acted as the support. The as-prepared WO₃-SiO₂ core-shell composites showed higher photocatalytic efficiency for Rhodamine-6G degradation under visible light illumination than that of WO₃ nanoparticles. In addition, the photocatalytic oxygen evolution properties of the resulting nanowrinkled WO₃@SiO₂ core-shell beads were evaluated by measuring the amount of oxygen evolved, which is a result of water splitting, and then compared them with those of WO₃ nanoparticles.

II. Experiments

Preparation of SiO₂ beads: According to the previous reports [10], silica beads with the size of 300-1000 nm were prepared by carrying out the hydrolysis of tetraethylorthosilicate (TEOS, 10 mL) in ethanol (150 mL) in the presence of 35 % ammonium hydroxide solution (NH₄OH, 35 mL) at room temperature. The size of the beads was controlled by changing the concentrations of TEOS and NH₄OH. For instance, in the case of 500-nm silica beads, 20 mL of TEOS was

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added to a solution containing 350 mL of ethanol and 75 mL of 35 % NH₄OH, and then the mixture was stirred for 3 h at room temperature. To increase the size of the silica beads from 500 to 700 nm, 16 mL of TEOS and 8 mL of NH₄OH were simultaneously added drop-wise into the solution containing 500-nm silica beads. Small silica beads were obtained by decreasing the amounts of TEOS and NH₄OH.

Surface functionalization of SiO₂ bead with amine group: The prepared SiO₂ beads (1.0 g) were introduced into a two necks round bottom flask (250 mL). The flask was then evacuated under vacuum below 10⁻² torr for 2 h and was charged with high purity argon. Dry toluene (50 mL) was added to the flask and was sonicated for 5 min to disperse the SiO₂ beads in the toluene. 3-aminopropyl trimethoxysilane (1 mL), which is a surface-silylating agent, was added and refluxed for 6 h with continuous stirring. After reaction, the reactor was cooled down to the room temperature and was washed with fresh toluene to remove extra surface-silylating agent completely. After washing, surfaced modified SiO₂ beads were dried by evacuation for 20 min.

Preparation of flake wall type-shell beads: Silica beads (0.06 g) were added to vials containing dimethylformamide (DMF) (5 mL) and were dispersed ultrasonically for 3 min. Then, 1,4-phenylenediamine (0.06 mol, 0.06 g) was dissolved in these vials containing DMF (5 mL). Tungsten hexachloride (WCl₆) (0.06 mol, 0.24 g) was then added to a 25 mL-round bottom flask containing 10 mL of DMF. The resulting solution was heated at 140 °C for 10 min with continuous stirring. The solution of amine-functionalized silica beads was added to the WCl₆ solution with continuous stirring for 10 min. The resultant powders were calcined at 500 °C for 3 h in air at a heating rate of 5 °C/min to remove the organic components and to obtain the WO₃@SiO₂ beads.

Photocatalytic dye degradation: The photocatalytic activity of the WO₃@SiO₂ core-shell beads in aqueous solution was evaluated by carrying out Rhodamine-6G (5 mg/L) degradation under visible-light irradiation (300 W Xe lamp) by using a cut-off filter (> 420 nm). Prior to the irradiation, the suspensions of the WO₃@SiO₂ photocatalyst (30 mg) in Rhodamine-6G (50 mL) were stirred for 5 min in the dark. Subsequently, the sus-

pension (approximately 2 mL) was extracted after every 20 min and the change in the concentration of the solution was monitored by gauging the maximum absorbance of Rhodamine-6G at 550 nm by using a UV-vis spectrophotometer. The degradation efficiency of the photocatalyst was calculated using the equation:

$$D = \ln (C_0/C_t) \times 100 \%, \quad (1)$$

where C₀ is the initial concentration and C_t is the concentration after a certain time according to the Beer-Lambert law [11,12].

Oxygen evolution analysis: The photocatalytic reaction was carried out in an inner irradiation quartz cell (5 mL). The reaction cell was connected to a closed gas circulation system and the gases evolved were analyzed by using an on-line thermal conductivity detector (TCD) gas chromatograph (model: Agilent5890 seriesII, helium carrier) [6]. Similar to a typical photocatalytic reaction, 10 mg of the WO₃ powder, loaded with 0.3 wt% Pt nanoparticles, was suspended in 5 mL of an aqueous KIO₃ solution (5 mmol dm⁻³) under magnetic stirring. The reaction vessel was evacuated several times to remove the air completely. The mixture was then irradiated with light using a 200 W high-pressure mercury lamp. The temperature of the reaction medium was maintained at 298 K by circulating cooling water during the reaction.

III. Results and Discussion

Uniform-sized (~500 nm) SiO₂ beads were prepared using the Stober method, as shown in Figs. 1(a) and

Figure 1. (Color online) SEM images: (a), (b) silica beads as core material with different magnifications and (c), (d) wrinkled WO₃@SiO₂ bead composites.

Scheme 1. (Color online) Schematic of fabrication procedure of wrinkled $\text{WO}_3@\text{SiO}_2$ bead composites.

Figure 2. XRD pattern of wrinkled $\text{WO}_3@\text{SiO}_2$ bead composites, WO_3 nanoparticles and SiO_2 beads as indicated.

1(b). The procedure for the fabrication of WO_3 nanowrinkles on the surface of the silica beads is illustrated in Scheme 1. The morphology of the pristine core-shell $\text{WO}_3@\text{SiO}_2$ beads was examined using scanning electron microscopy and transmission electron microscopy [Figs. 1(c) and 1(d)]. The $\text{WO}_3@\text{SiO}_2$ bead microspheres produced after calcination at 773 K remained intact and maintained the fine nanowrinkled structure of the WO_3 shell with an average diameter of ca. 3 μm . The crystal structure of the $\text{WO}_3@\text{SiO}_2$ beads was examined using X-ray diffraction (XRD), as shown in Fig. 2. Because the silica beads (core) were amorphous, all the exhibited peaks can be attributed to the shell material, WO_3 . Calcined samples exhibit broad diffraction patterns characteristic of the monoclinic structure (JCPDS card 43-1035). In addition, the XRD peaks of the $\text{WO}_3@\text{SiO}_2$ bead microspheres could be indexed to those of the commercial WO_3 nanoparticles. This indicates that the WO_3 shells on the silica beads did not contain any impurity.

The surface areas of $\text{WO}_3@\text{SiO}_2$ beads and WO_3 nanoparticles were 411.2 and 314.2 m^2/g , respectively (Fig. 3), as revealed by their N_2 adsorption isotherms at 77 K and Brunauer–Emmett–Teller analysis. The

Figure 3. (Color online) Surface area from BET analysis of (a) wrinkled $\text{WO}_3@\text{SiO}_2$ bead composites and (b) WO_3 nanoparticles as indicated.

surface area of the $\text{WO}_3@\text{SiO}_2$ beads was larger than that of the WO_3 nanoparticles because of their nanowrinkled structure. This unique nanostructure of the $\text{WO}_3@\text{SiO}_2$ beads contributed to their improved catalyst performance.

The corresponding absorption spectra (represented by the Kubelka–Munk function) are displayed in Fig. 4. This indicates that at approximately 400 nm, $\text{WO}_3@\text{SiO}_2$ beads and WO_3 nanoparticles absorb the entire light.

The photocatalytic activities of the $\text{WO}_3@\text{SiO}_2$ beads and nanocrystalline WO_3 were evaluated by carrying out dye degradation. Figure 5(a) shows the C/C_0 vs. exposure time (to visible light irradiation) of the samples. Here, C represents the dye concentration at

Figure 4. (Color online) UV-vis absorption spectra of wrinkled WO₃@SiO₂ bead composites and WO₃ nanoparticles as indicated.

Figure 5. (a) Comparison of Rhodamine-6G degradation under visible light (>400 nm) (b) the amount of photocatalytic O₂ evolution on wrinkled WO₃@SiO₂ bead composites and WO₃ nanoparticles as indicated.

each time interval and C_0 represents the initial concentration. From the photolysis curves, it is evident that the dye degradation occurs only in the presence of the catalyst (WO₃@SiO₂ bead and nanocrystalline WO₃). The WO₃@SiO₂ beads degraded 80 % of the dye over a total test time of 3 h, while the nanocrystalline WO₃ degraded 62 % of the dye. This indicates that the WO₃@SiO₂ beads were approximately 1.3 times more efficient than the WO₃ nanoparticles.

Photocatalytic water oxidation reactions were carried

out using the WO₃@SiO₂ beads and nanocrystalline WO₃. Figure 5(b) shows the amount of O₂ evolved from an aqueous solution containing KIO₃ as the electron acceptor in the presence of each of the photocatalysts (WO₃@SiO₂ beads and nanocrystalline WO₃) by visible-light irradiation. The amount of O₂ evolved from the aqueous solution after 2 h for the WO₃@SiO₂ beads were 7.9 mL/g, which is more than 6 times of that evolved for nanocrystalline WO₃.

IV. Summary

Nanowrinkled WO₃ was fabricated on the surface of the uniform-sized SiO₂ beads (WO₃@SiO₂ beads). Owing to their unique morphology, the WO₃@SiO₂ beads showed higher dye degradation efficiency and O₂ evolution (from water splitting) than those of the nanocrystalline WO₃. Therefore, this fabrication method for WO₃ nanostructures offers a new pathway for developing photocatalytically active WO₃ composites for the photodissociation of water under visible light.

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