SnO_2 and ZnO Nanostructured Spheres Self-assembled by Nanocrystals: Microwave-assisted Preparation and Enhancement of Photocatalytic Activity

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We have developed a simple microwave-assisted solvothermal method for the preparation of SnO_2 and ZnO hierarchically nanostructured spheres self-assembled by nanocrystals. The photocatalytic activity is significantly enhanced by simply mixing SnO_2 and ZnO nanostructured spheres without any treatment or processing.

In the past three decades, the photocatalytic properties of semiconductor-based catalysts for the degradation of organic pollutants and production of clean hydrogen fuel from water have received considerable attention owing to energy and environmental concerns. In order to enhance the photocatalytic properties, a number of strategies have been developed, for example, doping, surface modification, and using composites. Doping with anions[1] or cations[2–4] in the semiconductor can change the energy states and narrow the band gap which enhances the absorption in the visible light region or change the crystalline structure and retard the recombination of the photoexcited charge carriers. Surface modification with inorganic or organic species, using composites, core/shell structures and heterostructures can also increase the surface active sites or trap the electrons and holes to prevent their recombination by the interaction of different components in the composites, leading to the improvement of photocatalytic properties.[5,6] Another way to increase the photocatalytic property is to control the crystal size, crystallinity, crystalline phase, and morphology of the semiconductors. Controlling the size of the semiconductor allows for the tuning of the band gap, which determines the absorption edge of the semiconductor. In addition, the semiconductor nanocrystals have a higher specific surface area and provide more surface sites where free radicals can be generated by the reaction between the photogenerated charge carriers and adsorbed molecules, leading to a superior photocatalytic activity.

The complex hierarchical nanostructures with large surface areas are promising for new kinds of photocatalysts.[7–9] The hierarchical nanostructures are constructed by the assembly of nanocrystal building blocks (such as nanosheets, nanorods, and nanoparticles). Recently, we reported the preparation of homogeneous nanocomposite ZnO–SnO_2 hollow spheres and hierarchical nanosheets using ZnO rods, $SnCl_4 \cdot 5H_2O$, NaOH, and CTAB in aqueous solution by the hydrothermal method standing for 12 h, and the ZnO–SnO_2 nanocomposites showed a high photocatalytic activity.[5] Herein, we report the preparation of single-phase SnO_2 or ZnO hierarchically nanostructured spheres self-assembled by nanoparticles or nanorods by the microwave-assisted solvothermal method using mixed solvents of water and methanol at 160 °C for a short period of time (30 min). By simply mixing ZnO and SnO_2 hierarchically nanostructured spheres without any further treatment, we obtained the photocatalyst with much higher photocatalytic activity compared with singe-phase ZnO or SnO_2.

In a typical procedure, 0.351 g of $SnCl_4 \cdot 5H_2O$ or 0.219 g of $Zn(CH_3COO)_2 \cdot 2H_2O$, 0.5 g of cetyltrimethylammonium bromide (CTAB), and 1.2 g of NaOH were dissolved in a mixture of 20 mL of deionized water and 10 mL of methanol. Then, 2.75 mL of ethyl acetate was added into the mixture under magnetic stirring for 10 min. The resultant mixture was heated at 160 °C by microwave–solvothermal process (MDS-6, Sineo, Shanghai) for 30 min. For the photocatalytic activity measurement, 20 mg of the catalyst (for the mixture, the total amount was still 20 mg, and ZnO and SnO_2 were added into the solution, respectively) was suspended in 40 mL of aqueous Methyl Orange (MO) solution (20 mg/L), and then the suspension was shaken for 30 min in the absence of light. UV irradiation was carried out using a 300-W high-pressure Hg lamp (maximum 365 nm). MO concentrations were analyzed using a UV–vis spectrophotometer (UV-2300, Techcomp) at its maximum adsorption wavelength of 464 nm.

The XRD patterns show that the product was a single phase of SnO_2 or a single phase of ZnO. Figure 1 shows the TEM (JEOL JEM 2100F) micrographs of the SnO_2 and ZnO samples. From Figure 1a, one can see that the SnO_2 sample consisted of spheres with diameters of about 200–400 nm. The high-magnification TEM micrograph (inset of Figure 1a) shows that the SnO_2 spheres were constructed by the self-assembly of small nanoparticles with diameters of several nanometers. SEM (JSM-6700F) micrograph (Figure 1b) shows that the ZnO sample consisted of spheres with diameters of about 1–2 μm which were constructed by self-assembled nanorods.

The microwave–solvothermal method has been rapidly developed owing to rapid heating, faster kinetics, homogeneity, higher yield, better reproducibility, and energy saving compared with conventional solvothermal method. Moreover, the microwave–solvothermal method also enables chemical reactions to occur in an elevated-temperature and pressurized closed system similar to a solvothermal condition in a short preparation time of

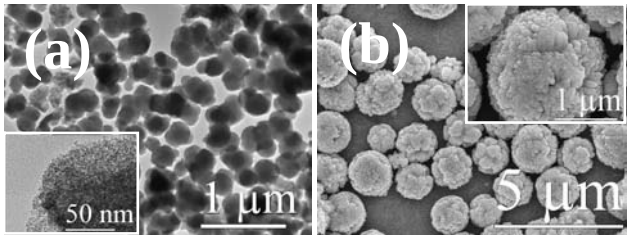

Figure 1. (a) TEM micrograph of as-prepared SnO_2 nanostructured spheres self-assembled by nanocrystals, (b) SEM micrograph of as-prepared ZnO nanostructured spheres self-assembled by nanorods.

minutes rather than days. Here, we prepared single-phase SnO_2 or ZnO hierarchically nanostructured spheres self-assembled by nanoparticles or nanorods by the microwave-assisted solvothermal method at 160 °C for a short period of time (30 min).

The photocatalytic degradation of MO was investigated. Figure 2a shows the degradation of MO in the presence of SnO_2, ZnO nanostructured spheres and the mixture of both at a mass ratio of 15:5. About 56% of MO was degraded in 60 min in the presence of ZnO or SnO_2 nanostructured spheres. ZnO nanostructured spheres showed a better photocatalytic activity than SnO_2, while the difference in the photocatalytic activity narrowed with increasing time; the degradation rate of MO was almost the same over both samples when the time reached 60 min.

A significant enhancement in the degradation rate of MO was observed by just simple mixing of ZnO and SnO_2 nanostructured spheres (15 mg SnO_2/5 mg ZnO) at room temperature without any processing or treatment. Figure 2a shows the photocatalytic activity for the photodegradation of MO over the mixture of SnO_2 and ZnO nanostructured spheres, from which one can see that about 50% MO was degraded in 20 min, 90% in 30 min and almost 100% in 40 min, implying that the degradation rate of MO over the mixture of ZnO and SnO_2 nanostructured spheres was much higher than that of single-phase ZnO or SnO_2 nanostructured spheres. The photocatalytic activity can be greatly enhanced by simple mixing of the two components of ZnO and SnO_2 nanostructured spheres at room temperature without any processing. Our experiments showed that the photocatalytic activity of the mixture increased with increasing quantity of SnO_2 and that the optimal mass ratio of SnO_2 to ZnO was 15:5.

The photocatalytic activities of the commercial ZnO, SnO_2, and their mixture were also investigated for comparison. The commercial ZnO sample consisted of irregularly shaped crystals with sizes of about 0.5–2 μm, and the commercial SnO_2 sample consisted of irregularly shaped nanocrystals with an average diameter of about 100 nm. As shown in Figure 2b, the two commercial samples showed lower photocatalytic activity in the degradation of MO compared with the nanostructured samples. In the presence of the commercial SnO_2, there was only 18% of MO degraded after 60 min UV irradiation, while 56% of MO degraded in the presence of SnO_2 nanostructured spheres. The commercial ZnO also showed lower photocatalytic activity compared with ZnO nanostructured spheres. The photocatalytic activity of the mixture of the commercial SnO_2 and ZnO was slightly higher than single-phase commercial ZnO and much higher than single-phase commercial SnO_2. The enhancement effect for the photocatalytic activity of the mixture of the commercial SnO_2 and ZnO was much weaker than that for the mixture of the ZnO and SnO_2 nanostructured spheres.

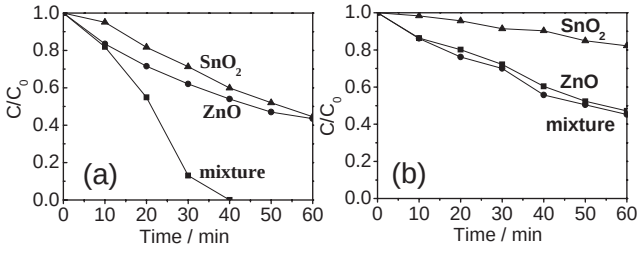

Figure 2. The degradation of MO over different photocatalysts: (a) as-prepared SnO_2, ZnO nanostructured spheres, and the mixture of both at a mass ratio of 15:5, (b) commercial SnO_2 and ZnO, and the mixture of both at a mass ratio of 15:5.

Previous work reported that SnO_2/ZnO composite exhibits a superior photocatalytic activity compared with single-phase SnO_2 or ZnO.[5,10,11] The reason for the increase in the photocatalytic activity was ascribed to the enhanced charge separation derived from the coupling of ZnO with SnO_2.[5,10,11] It is known that three factors contribute to the enhancement of the photocatalytic activity: modifying the band of the semiconductor, increasing the surface active sites and hindering the recombination of photogenerated electrons and holes. The room-temperature UV–vis diffuse reflectance spectra showed that the band gap of the mixture was very similar to that of the single-phase ZnO. Moreover, the surface active sites of the catalyst were not changed by the simple mixing of the two components. So the enhancement of photocatalytic activity of the mixture may mainly be attributed to the effective separation of the photoinduced electrons and holes. It has been reported that SnO_2 is a good electron-trapping agent.[9] We propose that the photogenarated electrons on the conduction band of ZnO can be transferred to the conduction band of SnO_2 when they are in contact with each other in the solution, hindering the recombination of photogenerated electrons and holes. In addition, SnO_2 and ZnO nanostructured spheres are favorable for the transfer of electrons or holes generated inside of the crystal to the surface and facilitate the degradation of MO.

In summary, we have developed a simple microwave-assisted solvothermal method for the preparation of SnO_2 or ZnO nanostructured spheres self-assembled by nanocrystals. The photocatalytic activity is significantly enhanced by simply mixing SnO_2 and ZnO nanostructured spheres self-assembled by nanocrystals compared with the single-phase ZnO or SnO_2. This result provides a new promising route for the design and preparation of new kinds of photocatalysts with high photocatalytic activities, thus expanding their applications in the field of photocatalysis.

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