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One-step template-free synthesis of $ZnWO_4$ hollow clusters

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Abstract $ZnWO_4$ hollow clusters made up of nanorods were successfully prepared through a tripotassiumcitrate assisted hydrothermal process at 180 °C. The hollow clusters' diameter was about400 nm, and these clusters were made up of nanorods with a diameter of about 10 nm and a length ofabout 50 nm. X-ray power diffraction (XRD), scanning electron microscopy (SEM), transmissionelectron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were usedto characterize the structure and morphology of the synthesized products. Based on experiments, thegrowth of these hollow clusters followed an aggregation-Ostwald ripening process. The photocatalyticactivities for aqueous Rhodamine B of samples were investigated, and it was seen that $ZnWO_4$ hollowclusters exhibited a strong photocatalytic activity.

Introduction

The unique physicochemical properties displayed by hollow structures have received increasing attention because they are ideal candidates for applications ranging from targeting drug delivery to catalysis carriers and isolated chemical reactors [1–3]. There have been two main methods for the synthesis of hollow structures: the template-directed synthesis [4, 5] and the emulsion synthesis [6, 7]. Apart from these methods, recent development in this field is also directed to template-free processes. In particular, various known physical phenomena, such as oriented attachment, Ostwald ripening, and Kirkendall effect, have been employed in many wet fabrications in hollow inorganic nanostructures [8]. Among them, mass transport via Ostwald ripening has been proven to be a facial approach to obtain inorganic hollow structures. For example, Zhang et al. reported the synthesis of TiO_2 hollow spheres [9], and Gao et al. synthesized Fe_3O_4 core–shell hollow structures through Ostwald ripening process [10].

$ZnWO_4$, as a possible new material for scintillators [11], laser hosts [12], and optical fibers [13], has been the subject of interests in recent years. In addition, zinc tungstate also exhibited relatively high photocatalytic and photoelectrocatalytic activities for the mineralization of organic compounds [14]. $ZnWO_4$ nanorods and nanowires have been obtained through a hydrothermal process [15, 16], and the photocatalytic activities of nanorods have been reported. [17]. However, there has been only one report, about hollow $ZnWO_4$ structures using alcohol solvothermal process [18], so far to the best of our knowledge.

Here, we report a simple hydrothermal process to obtain $ZnWO_4$ hollow clusters which were made up of nanorods through an aggregation—Ostwald ripening process. In contrast to the previously reported study [18], no organic solvents were used, and the samples showed higher purity and better morphology. Besides, the photocatalytic activity of the hollow clusters was investigated. According to our experiments, the $ZnWO_4$ hollow clusters showed a stronger photocatalytic activity than previously reported.

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Experimental section

Synthesis

All the chemical reagents used in this experiment were of analytical grade. In a typical experiment, 0.001 mol of $Zn(CH_3COO)_2 \cdot 2H_2O$ was first dissolved in 10 mL of distilled water, after which 0.100 g tri-potassium citrate was added into the solution under constant stirring. After 10 min, 10 mL of 1.0 M Na_2WO_4 solution was introduced into the solution under constant stirring. After being stirred at room temperature for 10 min, the mixture was transferred into a 25-mL Teflon-lined autoclave, and maintained at 180 °C for 12 h. The products were collected by filtration, washed several times with distilled water and absolute alcohol, and finally dried in vacuum at 50 °C for 6-8 h.

Characterization

The samples were characterized by XRD on a Japan Rigaku D/Max-γA 200 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.541\ 78$ Å). The morphologies of the samples were examined by scanning electron microscopy (SEM, JEOL JSM-6700F), and the TEM was carried out on a JEM-100CXII at an accelerating voltage of 100 kV. The structure of the samples was examined by high-resolution transmission electron microscopy (HRTEM, JEM-2010) with an accelerating voltage of 200 kV.

Measurements of photocatalytic activity

The photocatalytic activities were evaluated by the decomposition of RhB, tested under UV irradiation ($\lambda = 254$ nm). The average UV light intensity was 125 μW cm^{-2} on the solution surface, and the irradiation area was ~40 cm^2. The aqueous suspension of RhB (200 mL, 1×10^{-5} M) containing 100 mg photocatalyst was dispersed in a vessel. Before photodegradation, an adsorption–desorption equilibrium state was established by ultrasonic and mechanical stirring for 30 min. The samples were taken from the suspension at an interval of about 10 min and centrifugated to remove the suspended particulates. Then, the concentration of RhB in solution was analyzed with a UV–vis spectrophotometer at 550 nm.

Results and discussion

Characterizations of the final products

Figure 1 shows the XRD pattern of the as-prepared $ZnWO_4$ sample. All the diffraction peaks in the patterns are indexed to the known structure of $ZnWO_4$ (JCPDS card 89-0447). The sharp diffraction peaks indicate that the products should be well crystallized, and no peaks attributable to other impurities are observed.

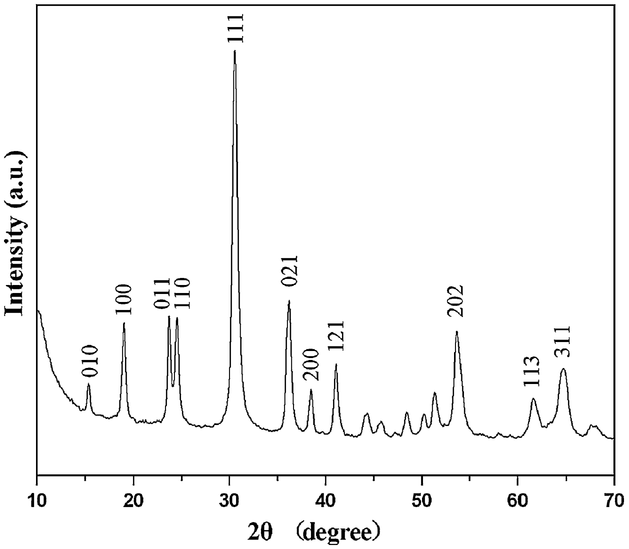

Fig. 1 XRD pattern of as-prepared $ZnWO_4$ hollow clusters

The morphologies and nanostructures of the as-prepared samples were investigated by SEM. A mid-magnification SEM image is shown in Fig. 2a, clearly exhibiting that the nanoclusters with the diameter of about 400 nm have been synthesized on a large scale. It is clearly seen that some clusters are broken, and the broken clusters appear to have hollow interiors. Figure 2b is a high-magnification SEM image of two clusters, from which we can see that the outer surfaces of the nanoclusters are rough, revealing that the spherical shell comprises loosely packed nanorods with widths of about 10 nm, which is further confirmed by the corresponding TEM image (Fig. 2c, d). A strong contrast difference between the edges (dark) and centers (bright) indicates hollow interiors with a wall thickness of about 100 nm. The HRTEM images provide further insight of the hollow structures. Figure 2e is an image recorded on the shell of hollow clusters, indicating that small crystallites are actually aggregates composed of small nanoparticles. HRTEM image obtained on the tip of a hollow cluster (Fig. 2f) shows clear, interplanar spacing of 0.47–0.57 nm, corresponding to the (100) and (010) crystal faces, respectively. These results show that the hollow clusters are made up of high-quality single crystal nanorods.

Effect of citrate concentration

It was found that the tri-potassium citrate concentration has a remarkable effect on the morphology of $ZnWO_4$ nanostructures. Figure 3 shows the TEM images of $ZnWO_4$ nanostructures as a function of tri-potassium citrate

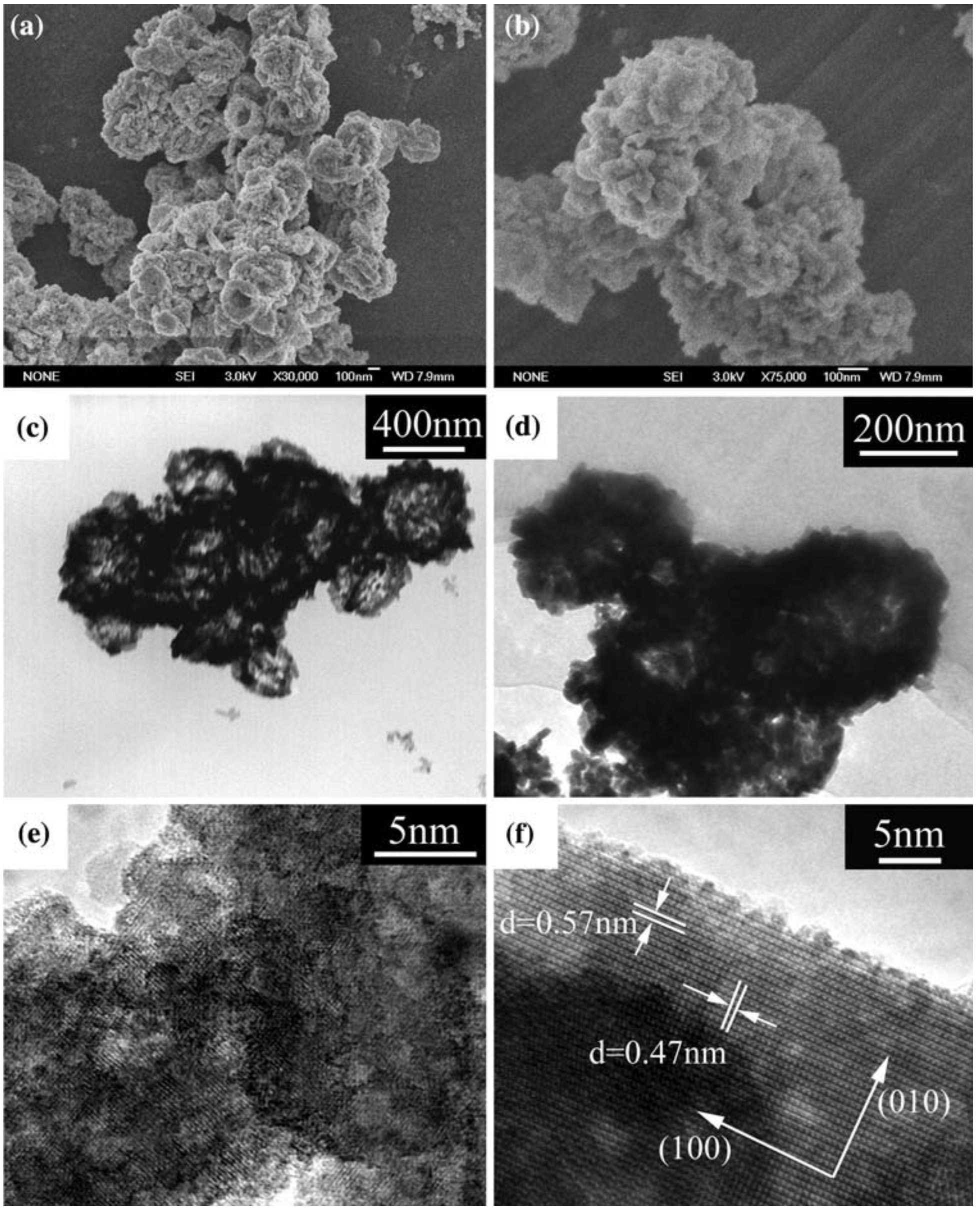

Fig. 2 **a** Medium magnification SEM image of the as-prepared $ZnWO_4$ samples; **b** high magnification SEM image of the products; **c** a typical TEM image of $ZnWO_4$ hollow cluster; **d** TEM image of several $ZnWO_4$ hollow clusters; **e** HRTEM image recorded on the shell of a hollow cluster; **f** HRTEM image recorded on the tip of a hollow cluster

concentration. During the experiments, the amount of citrate was varied from 0 to 0.300 g, but other conditions were kept constant. With no tri-potassium citrate employed, the morphology of the product was nanorods with a length of about 50 nm (Fig. 3a). When 0.040 g tri-potassium citrate was employed, shuttle-like structures were obtained, seen in Fig. 3b. As the amount of tri-potassium citrate increased to 0.080 g, some of the nanorods aggregated into clusters while most of the nanorods remained separate (Fig. 3c). Figure 3d showed that hollow clusters were obtained when the amount of tri-potassium citrate increased to 0.100 g. However, when the amount of tri-potassium citrate was increased to 0.150 g, rarely were hollow clusters found, as shown in Fig. 3e. $ZnWO_4$ solid clusters were obtained when 0.300 g tri-potassium citrate was introduced (Fig. 3f).

It is well known that citrate is an important biological ligand for metal ions and can form strong complex with many metal ions. Lin et al. had successfully synthesized LnF nanostructures using citrate as additive and investigated its effects [19, 20]. On the basis of our experiments, we believe that citrate has two major effects on the growth of the $ZnWO_4$ hollow clusters, just the same as in Lin's experiments. First, citrate can coordinate with zinc ions and control the precipitation process, resulting in good morphology. Second, it acts as inducing materials for aggregation of nanoparticles in the entire preparation procedure.

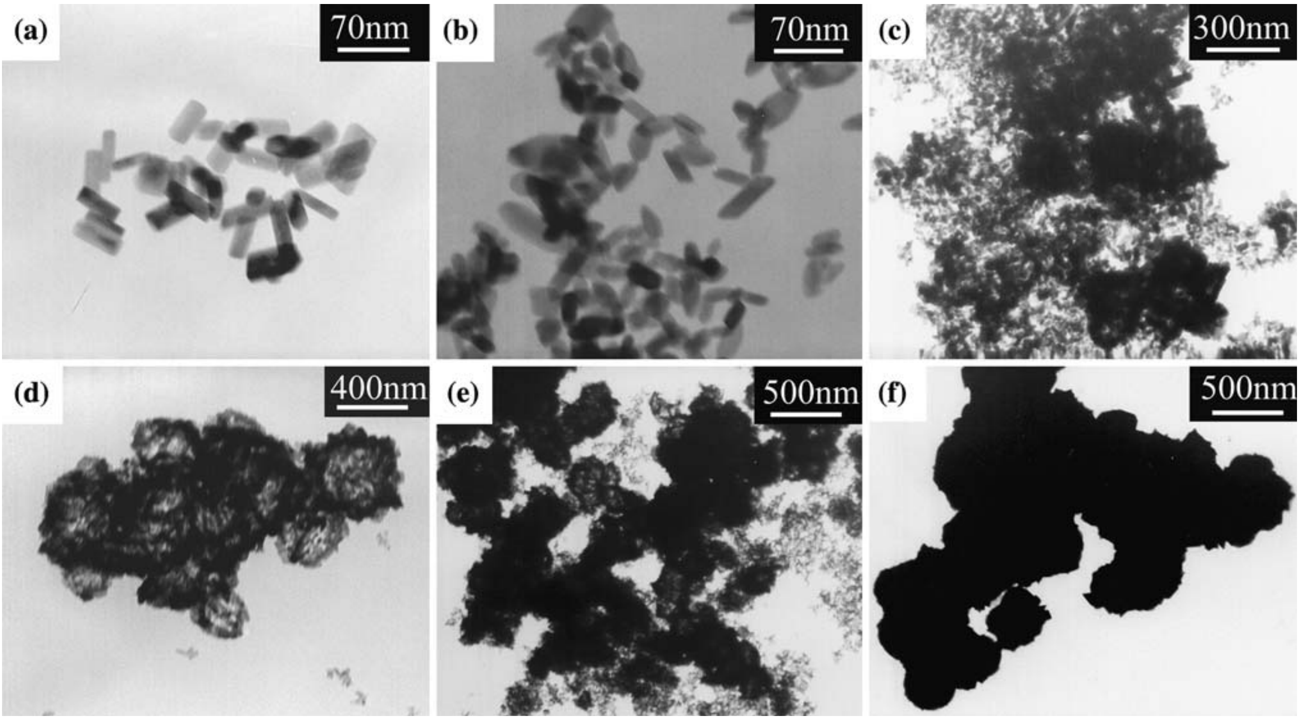

Fig. 3 TEM images of $ZnWO_4$ obtained with different amounts of citrate: **a** 0; **b** 0.040 g; **c** 0.080 g; **d** 0.100 g; **e** 0.150 g; **f** 0.300 g

Growth process of $ZnWO_4$ hollow clusters

To investigate the growth process of the $ZnWO_4$ hollow clusters, a series of time-dependent experiments were conducted to obtain intermediates. TEM images in Fig. 4 show the shape evolution of samples obtained from 0 to 8 h. Amorphous precursors with sizes of 5–10 nm were formed before hydrothermal process (Fig. 4a). At the early reaction stage (2 h), large scale of nanorods was formed, some of which had aggregated into kind of spherelike morphology, as presented in Fig. 4b. When reacted for 6 h, more and more aggregates were obtained, and some of them had already had the hollow-cluster morphology (Fig. 4c). Hollow clusters with better morphology were obtained when the hydrothermal treatment was 8 h, as clearly seen in Fig. 4d. On reaching the reaction time of 12 h, $ZnWO_4$ hollow clusters were finally obtained, shown in Fig. 2. We also found that during the hollowing process, the size of these nanoclusters did not change much.

Based on the above results, the growth of $ZnWO_4$ hollow clusters followed the aggregation via Ostwald ripening process. Because $ZnWO_4$ belongs to the monoclinic structure, it is easily growth into the 1D structure [21]. First, a number of small nanorods nucleate from solution under hydrothermal condition, and quickly congregate into spherical aggregates in order to decrease their surface energies. This initial phase might not be well crystallized owing to rapid spontaneous nucleation, and thus, Ostwald ripening dictates growth and recrystallization happened next. The original driving force for this ripening. could be attributed to the existence of intrinsic density variations inside the starting aggregates. The less dense particles in the center of the aggregates dissolved gradually, while denser particles (the shell parts) in the same aggregate grew [22, 23]. During this process, the inner crystallites dissolved and transferred out, resulting in the final hollow structures [24].

Photocatalytic activities of $ZnWO_4$ hollow clusters

The photodegradation of RhB was used to evaluate photocatalytic activities of $ZnWO_4$ hollow clusters and the results are shown in Fig. 5. It is clearly seen that the intensity of the absorption band of RhB at 550 nm decreases rapidly, which indicates that concentration of RhB decreases during the photocatalytic process. It is impressive that over 90% of RhB is degraded after 60-min irradiation. It is obvious that $ZnWO_4$ hollow clusters exhibited superior photocatalytic activities than reported before [17]. It is generally accepted that the catalytic process is mainly related to the adsorption and desorption of molecules on the surface of the catalyst [25]. The high specific surface area of the nanocatalysts results in more

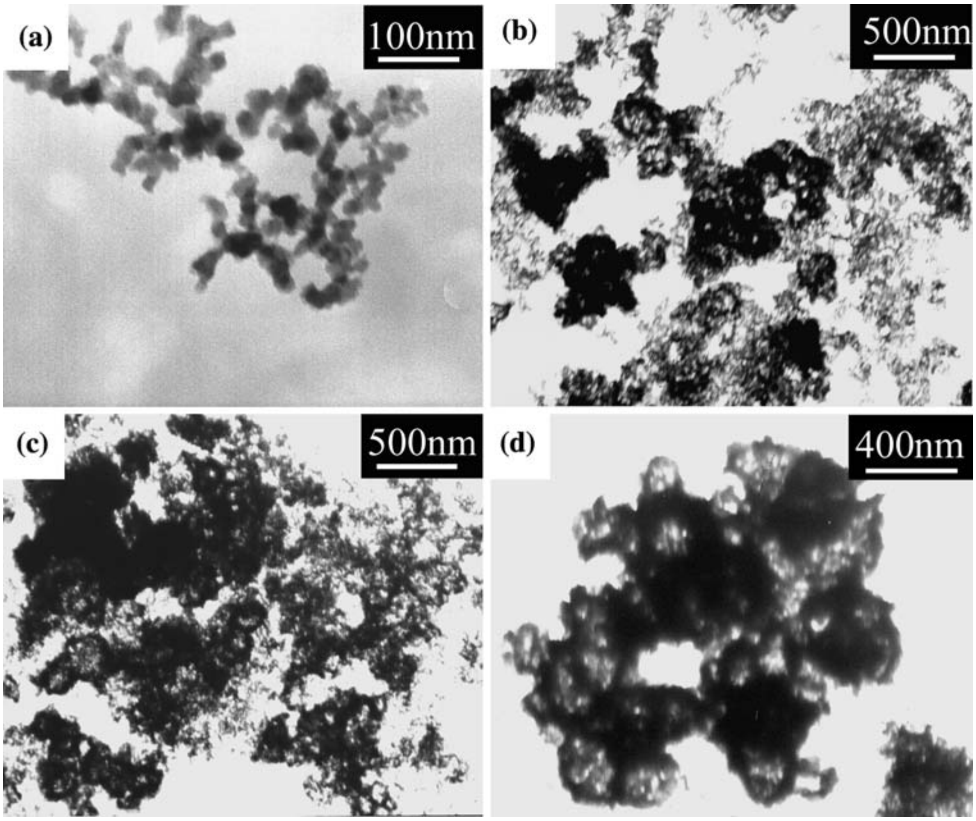

Fig. 4 TEM images of $ZnWO_4$ obtained with different hydrothermal reaction time: **a** 0 h; **b** 2 h; **c** 6 h; **d** 8 h

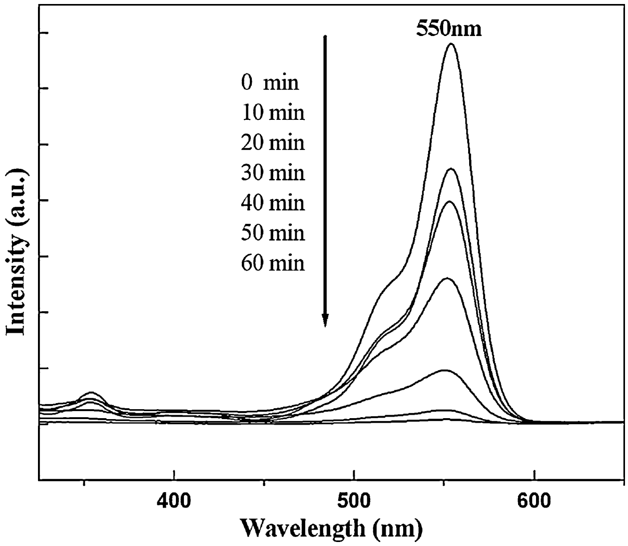

Fig. 5 Temporal evolution of the UV–vis spectral changes during the photodegradation of PhB over ZnWO4 hollow clusters

unsaturated surface coordination sites exposed to the solution. In addition, the interconnected hollow pores in the catalyst enable storage of more molecules [26]. Therefore, the enhancement of catalytic activity by high specific surface area and hollow structure is reasonable.

Conclusions

$ZnWO_4$ hollow clusters made up of nanorods have been synthesized through a hydrothermal process, and the presence of citrate played an important role in the formation of hollow clusters. It was confirmed that the formation of these hollow clusters followed the aggregation via Ostwald ripening process. Experimental results indicated the $ZnWO_4$ hollow clusters showed strong photocatalytic activities, which may have potential applications in future.

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