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Hierarchical ZnO "rod like" architecture synthesized via reverse micellar route for improved photocatalytic activity

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ABSTRACT

Hierarchical ZnO "rod like" architecture was successfully synthesized via reverse micellar route and characterized by various techniques. The FESEM studies show controlled decomposition of zinc oxalate into ZnO "rod like" architecture at 500 °C with slow heat rate at 1°/min. Interestingly, improved photocatalytic activity was observed for the degradation of Rhodamine B, due to the self assembly of hexagonal nanoparticles of zinc oxide forming hierarchical ZnO "rod like" architecture which can greatly enhance the light utilization rate due to its special architecture and enlarge the specific surface area, providing more reaction sites and promoting mass transfer. More importantly, the reusability studies of this architecture were most economical.

1. Introduction

ZnO is one of the most interesting semiconductor materials due to a wide band gap of 3.37 eV and extensively investigated in various applications including solar cells, sensors, nanogenerators and photocatalysis [1–4]. Recently, the photocatalytic degradation of organic pollutants in water bodies using semiconductors such as TiO_2 and ZnO has been found great attention of researchers due to their unique ability in the water treatment [5–6]. Although, TiO_2 has been extensively investigated and widely employed, ZnO appears to be a suitable alternative to TiO_2. Since, ZnO is relatively inexpensive, high photosensitivity, non-toxic nature, large band gap, excellent chemical and mechanical stability and its photodegradation mechanism is also similar to that of TiO_2 [7–8]. Furthermore, the quantum efficiency of ZnO is also significantly larger than that of TiO_2 [9]. Therefore, ZnO can be considered as highly efficient semiconductor material for photocatalytic degradation of organic pollutants.

However, the catalytic application of ZnO is considered to be highly dependent on morphology and size. In recent years, many efforts have been made to control the morphologies and size of ZnO via wet chemical methods including hydrothermal, sol–gel and reverse micellar methods [10–14]. But in most of these methods, the precursor along with the surfactant is heated using complex apparatus to get the oxide which probably leads to the decrease in selectivity and surface area. Reverse micelles have been used to synthesize a variety of materials with various shape and size where the surfactant aggregate acts as a removable nanostructure template for the formation of the anisotropic precursor and is completely washed off to obtain the product at room temperature. More importantly, the morphology and the particle size can be efficiently controlled by choosing proper surfactant and [water]/[surfactant] ratio (Wo) [14–15].

2. Experimental

Cetyltrimethylammonium bromide (CTAB) (Merck, 99.5%), 1-butanol (Merck, 99.5%), isooctane (Merck, 99.5%), ammonium oxalate (SISCO, 99.5%), zinc nitrate hexahydrate (Merck, 99.8%), and Rhodamine B (Merck, 99.7%) were used. All other reagents used in this work were analytically pure and used without further purification. The zinc oxide architecture was prepared by using a reverse micellar mediated route. The microemulsion was prepared using 39.64 g of CTAB, 40.4 mL of 1-butanol, and 200 mL of isooctane in a conical flask. Then 24 mL of 0.1 M Zinc nitrate solution was added drop wise while stirring to obtain a colorless solution. Another microemulsion was prepared using an aqueous solution of ammonium oxalate, keeping the other constituents identical. The two microemulsions were mixed while stirring and kept for 24 h. The solution became cloudy and a white precipitate was formed. The product was centrifuged and washed (thrice) with a mixture of chloroform and methanol (1:1). The oxalate precursor formed was dried for overnight at room temperature and heated at 500 °C for 12 h at heat rate of 1 °/min to obtain controlled ZnO "rod like" architecture.

X-ray diffraction studies (XRD) were carried out on a Bruker D_8 Advance diffractometer using Ni filtered Cu K_α radiation. FESEM studies

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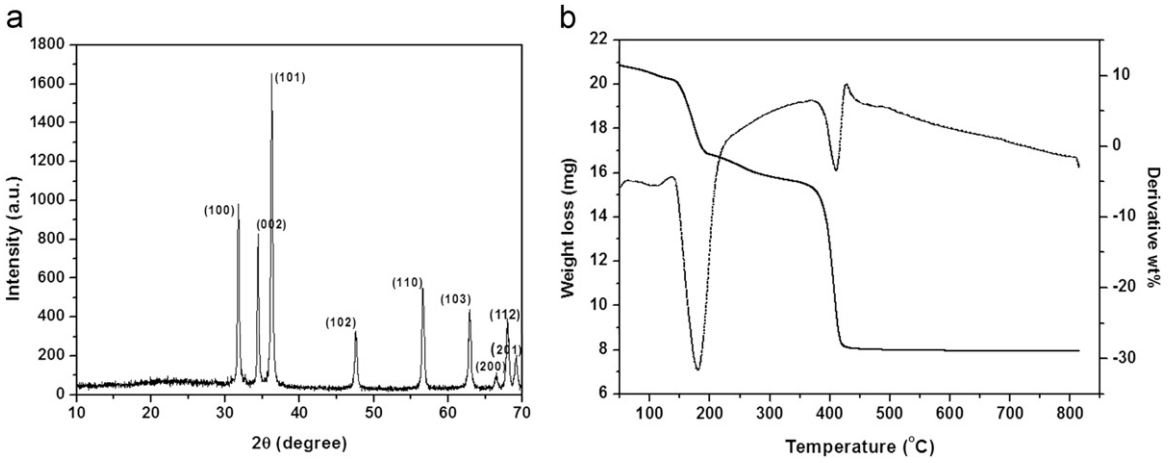

Fig. 1. (a) XRD pattern and (b) TGA of the synthesized ZnO "rod like" architecture.

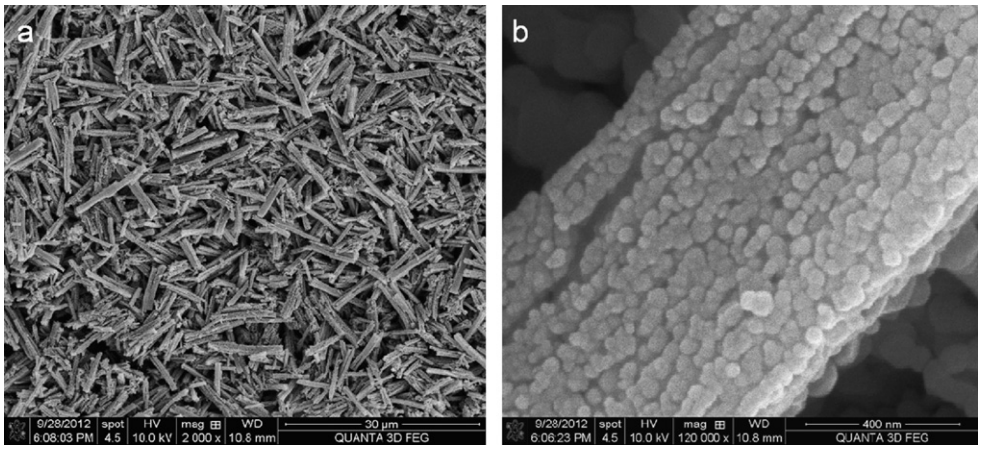

Fig. 2. FESEM images of the synthesized ZnO "rod like" architecture.

were carried out on a FEI quanta 3D FEG-FESEM instrument. UV–vis diffuse reflectance spectra were recorded on Lambda/20 Instruments. The nitrogen adsorption isotherms and the BET surface area were recorded by using Quanta chrome NOVA 1200e.

Photocatalytic activity of the synthesized ZnO "rod like" architecture (100 mg) was investigated for the degradation of Rhodamine B ($5\,mg\,l^{-1}$, 250 mL) in aqueous solution under UV irradiation (Hg Lamp, 125 W) at room temperature and compared with commercial ZnO powder under the same experimental conditions.

3. Result and discussion

Fig. 1a shows the XRD patterns of the synthesized hierarchical ZnO "rod like" architecture. The diffraction patterns for the sample show strong and sharp peaks, which confirm the wurtzite structure. The diffraction peaks can be indexed to cubic phase ZnO (JCPDS #891397), indicating the successful synthesis of pure phase ZnO "rod like" architecture. The estimated average crystallite size was 28.4 nm. The particle size was further supported by FESEM results. Thermal decomposition of zinc oxalate precursor was studied using TGA. Thermo gravimetric curve (Fig. 1b) clearly indicates that the removal of water molecules from a zinc oxalate precursor takes place in two steps. Initially the first decomposition around 200 °C and then the second decomposition of zinc oxalate to ZnO starts at 300 °C and is completed at 450 °C. Thus the pure nanocrystalline phase of ZnO was formed at 500 °C which

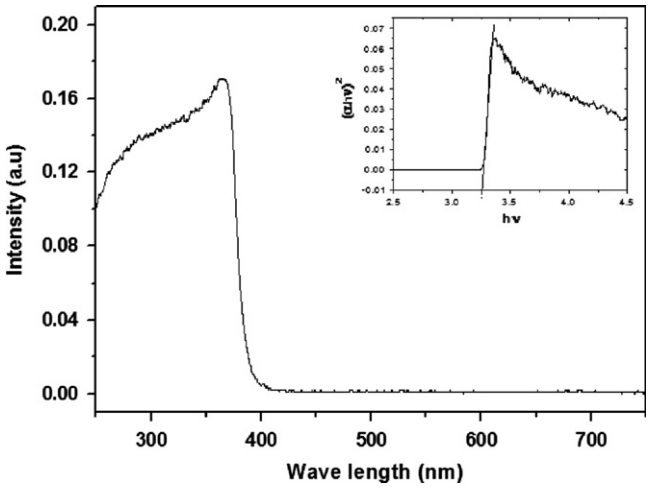

Fig. 3. Shows the UV–vis diffuse reflectance spectra of the synthesized ZnO "rod like" architecture (inset: the curves of $(\alpha h\nu)^2$ versus $h\nu$).

corroborates with the powder X-ray diffraction pattern. Fig. 2 shows the FESEM images of the synthesized ZnO "rod like" architecture. The FESEM results clearly indicate that the controlled decomposition of zinc oxalate into hierarchical ZnO "rod like" architecture with average diameter of 500 nm was successfully achieved with slow rate at 1°/min. The aligned hierarchical ZnO "rod like" architecture obtained due to the self assembled very fine

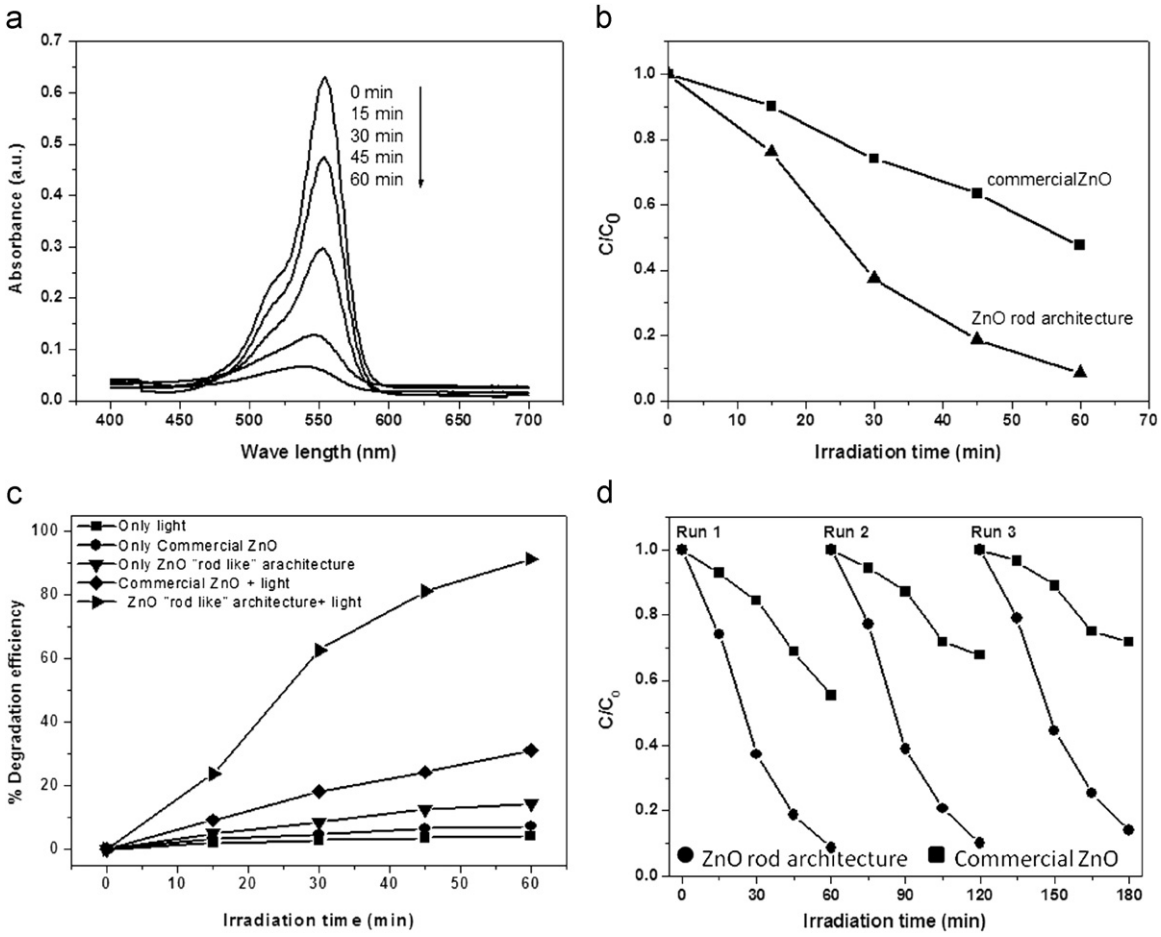

Fig. 4. (a) Photocatalytic degradation of Rhodamine B with ZnO "rod like" architecture: (b) a plot of C/C_0 as a function of irradiation time for an aqueous solution of Rhodamine B in presence of hierarchical ZnO "rod like" architecture and commercial ZnO, (c) a comparison of photocatalytic activity of different ZnO photocatalysts for degradation of Rhodamine B and d) reusability of hierarchical ZnO rod architecture.

hexagonal nanoparticles with average particle size 32 nm. Fig. 3 shows the UV–vis DRS spectra of ZnO "rod like" architecture. It was observed that the ZnO rod architecture showed absorption edge at 329 nm. This absorption was fairly sharp and in typical UV range, indicating relatively narrow particle size distribution. From the curves of $(\alpha h\nu)^2$ versus $h\nu$ shown in inset of fig. 3, it is found that the ZnO "rod like" architecture shows a band gap energy of about 3.25 eV. In general the surface area of the catalyst can play major role in influencing the catalytic or photocatalytic activity. The surface area of the synthesized ZnO architecture was determined using the nitrogen gas adsorption method. The BET surface area of ZnO "rod like" architecture (36.23 $m^2 g^{-1}$) is much higher than the surface area of commercial ZnO (4 $m^2 g^{-1}$). The relatively high specific surface area of this architecture is beneficial to its catalytic activity.

4. Photocatalytic activity

Photocatalytic activity of the synthesized ZnO "rod like" architecture was examined by degradation of Rhodamine B, as shown in Fig. 4. Fig. 4a shows the typical absorption spectra of the Rhodamine B during the process of photodegradation, which indicates the absorbance of the Rhodamine B decreases dramatically with the increment of the irradiation time. The photocatalytic activity of this ZnO "rod like" architecture was also compared with commercial ZnO powder, as shown in Fig. 4b. It was found that the photocatalytic activity of this architecture was much higher (almost three times) than that of commercial ZnO powder. Fig. 4c shows the degradation of Rhodamine B is about 4% in the presence of commercial ZnO powder and about 14% in the presence of ZnO "rod like" architecture under the dark condition whereas 7% degradation under light irradiation without ZnO photocatalyst. However, the degradation of Rhodamine B in the presence of ZnO "rod like" architecture with UV-light irradiation is about 91% under the similar reaction conditions, which clearly shows that it is much higher than that of commercial ZnO powder (35%). This result demonstrates that the degradation of Rhodamine B can be catalyzed by this hierarchical architecture dramatically due to higher adsorption capacity with large surface area. Importantly, the reusability of the synthesized ZnO architectures is much higher under similar condition. To study the stability of the synthesized ZnO "rod like" architecture, used samples were collected and further examined the reusability of this particular ZnO "rod like" architecture in three successive Rhodamine B degradation experiments and compared with commercial ZnO. As shown in Fig. 4d, the photocatalytic activity of ZnO architectures retain over 90% of its original activity after three successive experimental runs, which is also very important from a practical application point of view.

5. Conclusion

In summary, we have successfully synthesized hierarchical ZnO "rod like" architecture via reverse micellar mediated route. FESEM

observations showed the self assembly of hexagonal nanoparticles of ZnO forming hierarchical "rod like" architecture. Interestingly, the improved photocatalytic activity was observed due to the aligned hierarchical "rod like" architecture. Importantly, the reusability of the synthesized ZnO architecture was very high. Therefore, hierarchical ZnO "rod like" architecture could be very promising photocatalysts for degradation of organic pollutants and other applications.

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