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Synthesis of ZnO hollow spheres through a bacterial template method and their gas sensing properties

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ABSTRACT

In this report, ZnO hollow spheres were synthesized by an economic and environment-friendly bacterial template method. The hollow spheres resembled the morphology of the bacterial templates with multilayered porous shells. Their sensing properties were investigated with Co_3O_4 incorporation. The response of the spheres was enhanced from 8–11 to 38–49 to 100 ppm acetone with Co_3O_4 incorporation, and the response and recovery time were shortened from 10–12 s and 61–79 s to 1.2–1.9 s and 27–48 s, respectively.

1. Introduction

Hollow mesostructures have attracted much attention due to their potential applications in catalysis, drug delivery, photonic devices, chemical sensors, lithium ion batteries and biotechnology [1–7]. To date, a series of hollow structures have been synthesized using hard templates such as PS, silica and carbon sphere [8–11]. However, it usually requires multiple steps to fabricate hollow mesostructures with traditional template methods. For example, carbon microsphere templates are usually synthesized in a Teflon-sealed autoclave at 160–180 °C for 3–6 h [11], which is of high cost, environment unfriendly and time consuming. On the contrary, biological templates are of low cost, environment-friendly, and can be easily obtained from bacteria, virus, etc. [1,2,12–14].

ZnO, a well-known n-type semiconductor, has been widely used in gas sensors. Two main methods can be used to enhance the performance (e.g. response and selectivity) of the gas sensors. One method is to enlarge the specific surface area using unique structures such as hollow spheres [15] and nanowires [16]. For example, Zhang et al. prepared ZnO hollow spheres to detect NO_2 and the high sensitivity was ascribed to the enlarged available surface area arising from the hollow structures [15]. The other is to add some metal oxides such as CuO, In_2O_3, Co_3O_4 [17–20]. For example, Lee et al. prepared Co_3O_4-decorated ZnO nanowires to selectively detect NO_2 and C_2H_5OH [20]. The gas selectivity mechanism was explained in terms of catalytic effect of Co_3O_4 and the extension of electron depletion layer due to the formation of p (Co_3O_4)–n (ZnO) junctions. However, rare reports concern gas sensing properties of Co_3O_4-decorated ZnO hollow spheres.

Herein, we report a simple bacterial template method to synthesize Co_3O_4-decorated ZnO hollow spheres with porous shell at low temperature. The porous hollow structures favor to enhance the performances of gas sensors by accelerating gas diffusion as well as offering a fully activated surface. To evaluate the performance of sensors with Co_3O_4 incorporation, we compared their responses to 100 ppm acetone. The response of the spheres was enhanced from 8–11 to 38–49 with Co_3O_4 incorporation, and the response and recovery time were shortened from 10–12 s and 61–79 s to 1.2–1.9 s and 27–48 s, respectively. The excellent sensing performance makes such a Co_3O_4-decorated ZnO nanostructure to be promising for sensor devices.

2. Experimental

All chemicals were of analytical grade and used without further purification. The *Microzyme* cells were suspended in distilled water with optical density (OD 600 nm) adjusted to 1.0. The ZnO hollow spheres were prepared from these cell templates. In a typical procedure, 0.4 g zinc acetate and 8 ml triethanolamine were added to 40 ml bacterial suspension simultaneously. After magnetically stirring at 60 °C for 3 h, the resulting product was centrifuged and washed with distilled water and ethanol for several times. To

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prepare Co_3O_4-decorated ZnO hollow spheres, 0.1 g as-prepared ZnO and 0.02 g cobalt nitrate were dissolved in 50 ml distilled water followed by ultrasonication at room temperature. Then the mixture was dried in air at 60 °C. Finally, both pure and Co_3O_4-decorated ZnO powders were calcined at 400 °C and cooled naturally in air. The hollow spheres were characterized by scanning electron microscopy (SEM) [Hitachi S-4800] equipped with an energy-dispersive X-ray spectrometer (EDX) and the crystal structure of the samples was determined by X-ray diffraction (XRD) [Siemens D-5000 with Cu Kα1 radiation, λ = 0.15406 nm].

The sensors were prepared as described previously [21–23]. The hollow spheres were dispersed into an adhesive terpineol to form a paste and then coated on the outside surface of an alumina tube. A Ni–Cr alloy coil crossing through the tube was employed as a heater. To improve their stability, the gas sensors were sintered at 300 °C for 7 days in air. The sensing properties were characterized by NS-4003 (China Zhong-Ke Micro-nano IOT Ltd). The working temperature and relative humidity were 300 °C and 57%, respectively. The response (S) was defined as $S = R_a/R_g$, where R_a is the sensor resistance in air and R_g the resistance in target gas. The response and recovery time of the sensor was defined as the time required for a change in the sensor resistance to reach 90% of the equilibrium value after injecting and removing the detected gas, respectively. The data in Figs. 3 and 4 were derived from ZnO-Co_3O_4 (1) and ZnO (1) (Table 1).

Table 1
Resistance and response/recovery time of pure and ZnO–Co_3O_4 sensors to 100 ppm acetone at 300 °C.

	R_a (MΩ)	R_g (KΩ)	Response time (s)	Recovery time (s)	Response R_a/R_g
ZnO–Co_3O_4 (1)	43	870	1.5	32	49
ZnO–Co_3O_4 (2)	48	970	1.2	29	49
ZnO–Co_3O_4 (3)	45	1000	1.9	43	45
ZnO–Co_3O_4 (4)	51	1300	1.7	27	39
ZnO–Co_3O_4 (5)	35	930	1.7	48	38
ZnO (1)	4.2	460	11	79	9
ZnO (2)	4.8	440	10	61	11
ZnO (3)	3.1	380	12	63	8

3. Results and discussion

Fig. 1a shows the SEM image of the original bacteria. The size of most coccoid bacteria is around 1 μm, and some smaller cocci (about 400 nm in diameter) can also be observed. Fig. 1b and c displays the morphology of the as-prepared Co_3O_4-decorated ZnO hollow spheres after grinding. The hollow spheres resembled the morphology of the bacteria templates with multilayered porous shells. The size of the sphere was larger than that of the original template, about 500 nm–1.5 μm. Many broken spheres (marked by black squares) can be clearly observed, and the spheres display hollow structure. The wall of the spheres was porous and mainly piled up with ZnO grains about 20 nm (Fig. 1c). Here, it should be noted that the morphology of ZnO does not completely resembled from that of bacteria in our experiments. This is due to antibacterial activity of ZnO, which can disrupt of the bacteria cell membrane and change the shape of spiral bacteria to coccoid shape [24]. When *Bacillus subtilis* replaced *Microzyme* while other parameters kept the same, the morphologies of ZnO also could not resemble well from that *B. subtilis* (Fig. S1a and b). Fig. 1d shows the XRD patterns of as-prepared Co_3O_4-decorated ZnO hollow spheres. All the diffraction peaks are indexed to the wurtzite hexagonal ZnO (JCPDS card # 36-1451). No obvious peaks of Co_3O_4 are observed, presumably due to the low atomic ratio and similar ionic radius of Zn^{2+}, Co^{2+} and Co^{3+} ions [25]. EDX data (Fig. S2) shows that the Co_3O_4-decorated ZnO sample was composed of C, O, P, Zn, and Co. The remaining C and P may be originated from the ash of the cells.

A possible growth mechanism of Co_3O_4-decorated ZnO spheres is illustrated in Fig. 2. It generally composes of three steps, including: (1) formation of $Zn(OH)_2$ layer on the cell surface; (2) decoration of Co; (3) annealing process to remove the inner bacteria

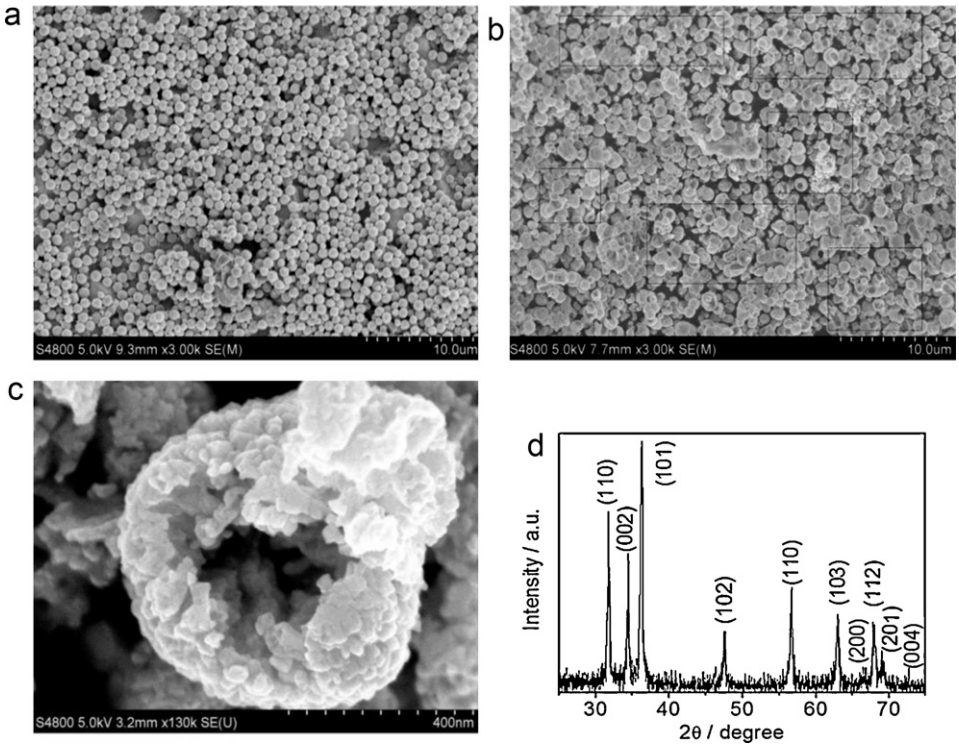

Fig. 1. (a) SEM image of original bacterial template. (b and c) SEM images of Co_3O_4-decorated ZnO hollow spheres with different magnifications. (d) XRD pattern of Co_3O_4-decorated ZnO hollow spheres.