Electronic Supplementary Information (ESI)

Template-free synthesis and gas sensing properties of hierarchical hollow ZnO microspheres

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Experimental

All reagents in the experiment were analytic grade (Beijing Chemicals Co. Ltd.) and used as received without further purification. Hierarchical hollow ZnO microspheres were synthesized via a one-pot template-free hydrothermal process. In a typical procedure, zincacetate·dihydrate ($ZnAc_2 \cdot 2H_2O$, 0.05 M, 0.1 M, 0.2 M), tripotassium citrate monohydrate ($K_3C_6H_5O_7 \cdot H_2O$, 0.1 M) and sodium hydroxide (NaOH, 0.25 M) were dissolved into 40 mL of deionised water at the same time, under vigorous stirring for about 20 min. Then, the mixed solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave and kept at 180 °C for 12 h. After the autoclave cooled naturally down to room temperature, the precipitates were collected by centrifugation, washed several times with distilled water and absolute ethanol respectively, and dried in air at 80 °C for 12 h.

Characterisations

The X-ray diffraction (XRD) patterns were recorded by a Rigaku D/max-2500 diffractometer with Cu Kα radiation (λ=1.54 Å). Field-emission scanning electron microscopy (FESEM) observations were carried out using a JEOL JSM-7500F microscope with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) measurements were obtained on a JEOL JEM-2100 microscope at an acceleration voltage of 200 kV.

Measurement of sensing properties

A schematic diagram of the as-fabricated sensor and a photograph of the sensor on the socket are

shown in Fig. S1. In order to fabricate a gas sensor, the product was mixed with deionized water to form a paste. The sensor was made by coating the paste on an alumina tube. A pair of gold electrodes was formed at each end of the alumina tube before it was coated with the paste, and each electrode was connected with a Pt wire. Then, the devices were heated at 400 °C for 2 h in muffle. A heater of Ni–Cr coil was inserted into the alumina tube to supply the operating temperature. The sensing properties of the sensors were determined using a RQ-2 gas-sensing characterization system under laboratory conditions (30±10% RH, 23±1 °C). The measurement was processed by a static process in a test chamber (50 L in volume). Environmental air was used as both a reference gas and a diluting gas to obtain desired concentrations of target gases. A typical testing procedure was as follows. The sensor was put into the chamber at the beginning. Then the calculated amount of the target gas or liquid was injected into the chamber by a microsyringe. When the response reached a constant value, the upper cover of the test chamber was removed and the sensor began to recover in air. For the target gases obtained from liquid, the concentration of target gas was calculated by the following formula,

$$C = \frac{22.4 \times \rho \times V_1}{M \times V_2} \times 1000$$

where C (ppm) is the target gas concentration, ρ (g/mL) is the density of the liquid, V_1 (μL) is the volume of liquid, V_2 (L) is the volume of the chamber, and M (g/mol) is the molecular weight of the liquid. The gas response S was defined as the ratio R_g/R_a oxidizing gas or R_a/R_g for reductive gas, where R_a and R_g are the resistances measured in air and the tested gas atmosphere. The time taken by the sensor to achieve 90% of the total resistance change was defined as the response time (τ_{res}) and recovery time (τ_{recov}), respectively.

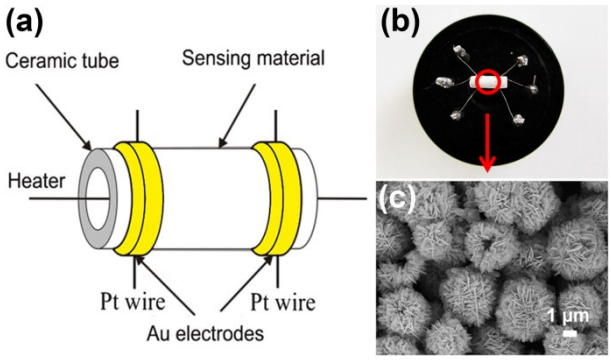

Fig. S1 *(a) Schematic diagram of the sensor; (b) Photograph of the completed sensor; (c) FESEM image of the hierarchical-hollow ZnO microspheres.*

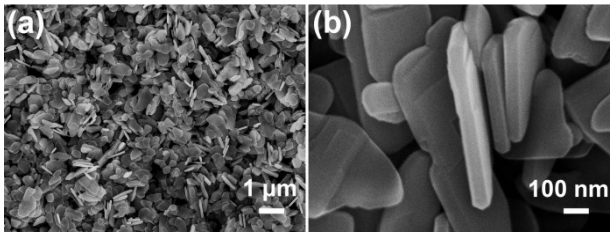

Fig. S2 *(a) Low magnification and (b) high magnification FESEM images of the product prepared without tripotassium citrate monohydrate.*

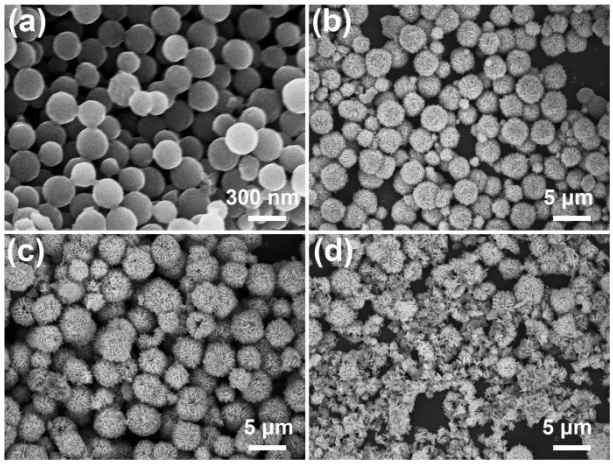

Fig. S3 *The low magnification FESEM images of morphology evolution at different reaction times: (a) 0.5 h, (b) 3 h, (c) 12 h and (d) 24 h.*

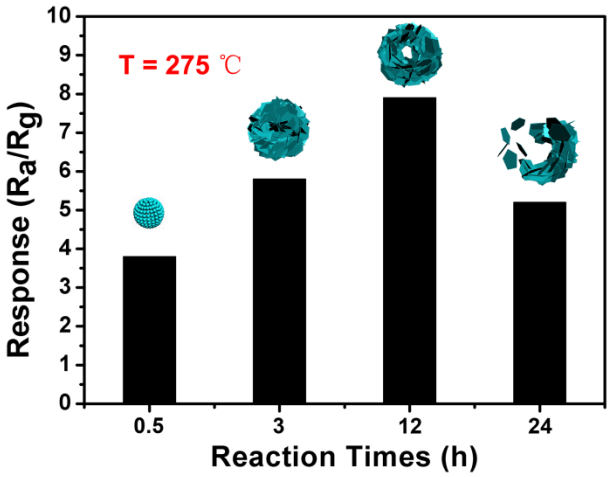

Fig. S4 *Response versus different morphologies (for samples grown at different reaction times: (a) 0.5 h, (b) 3 h, (c) 12 h and (d) 24 h) to 100 ppm ethanol at 275 ℃.*