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Hydrothermal growth of novel radiolarian-like porous ZnO microspheres on compact TiO_2 substrate

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Abstract

Radiolarian-like porous ZnO microspheres, consisting of ZnO nanosheets about 500 nm in length, 100 nm in width and 50 nm in thickness, have been synthesized by a facile hydrothermal process on compact TiO_2 substrate. The products were characterized and analyzed by SEM, TEM and XRD. Selected Area Electron Diffraction (SAED) pattern reveals that the nanosheets in ZnO microspheres are single crystalline. The preference orientation along $(10\bar{1}0)$ plane was observed by the XRD and SAED results. A possible formation mechanism was preliminary proposed for the formation of the novel nanostructure.

Keywords: Zinc oxide; Nanostructure; Crystal growth; Hydrothermal growth

1. Introduction

Zinc oxide is an important low-cost basic II–VI semiconductor material with a wide band gap energy of 3.37 eV, which has been widely used in photonics devices, gas sensors and dye-sensitized solar cells for its optoelectronic, electrical and photoelectrochemical properties [1]. To achieve the better and optimized performances in the applications above, various morphologies of ZnO with specific large surface area and high porosity such as oriented nanorod ZnO arrays [2], tower-like, flower-like and tube-like ZnO arrays [3], mesoporous structured polyhedral drum and spherical cages and shells [4], single-crystal tubular ZnO whiskers [5] and controllable large-scale ZnO ordered pore arrays [6] have been synthesized.

Herein, a facile and effective wet chemical route was presented to obtain novel radiolarian-like porous ZnO microspheres (denoted as RPZM) on compact TiO_2 substrate, in which aqueous solutions of 5 mM zinc nitrate and methenamine were used to hydrothermally synthesize RPZMs. The formation mechanism is also preliminarily

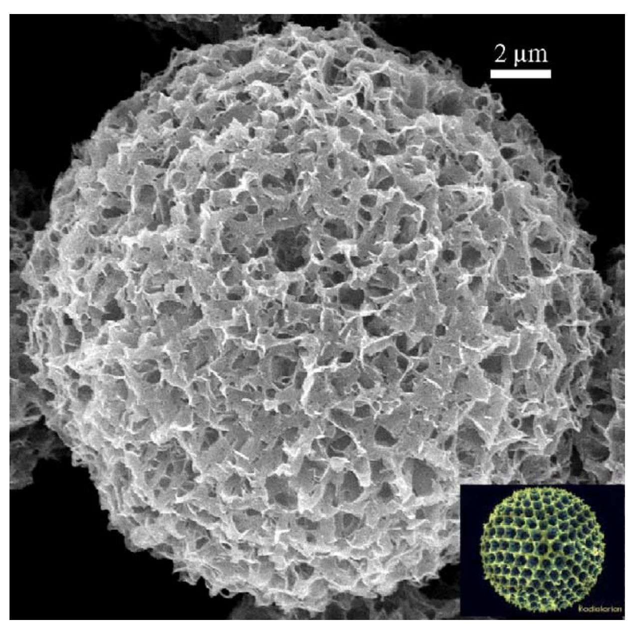

Fig. 1. SEM image of a RPZM at low-magnification, comparing with the skeleton of radiolarian in inset figure.

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discussed. Materials with this novel nanostructure are supposed to be of significant importance for extending the applications of ZnO.

2. Experimental

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification and treatment. The synthesis procedure involves four steps: (1) glass substrates were cleaned by ultrasonic in isopropyl solution containing NaOH, distilled water, ethanol and acetone in turn; (2) compact TiO_2films were fabricated on the glass substrates following the reported procedure [7]; (3) 32 ml 5 mM zinc nitrate and 32 ml 5 mM methenamine aqueous solutions were mixed in a Teflon-lined stainless steel autoclave to form the deposition solution; (4) RPZMs were obtained on substrates immersed in the mixture solution at 95 °C for 4 h. The sample was characterized and analyzed by X-ray diffraction (XRD) (Rigaku, D/max-RB, Cu Kα, 40 kV, 100 mA), field emission scanning electron microscope (FESEM) (JEOL, JSM-6301F, 15 kV), energy-dispersive X-ray spectroscopy (EDX) (Oxford, INCA 300) and transmission electron microscope (TEM) (JEOL, JEM-1200EX, 120 kV).

3. Results and discussion

The morphology of one RPZM was shown in Fig. 1, which demonstrated the similarity between RPZM and the skeleton of

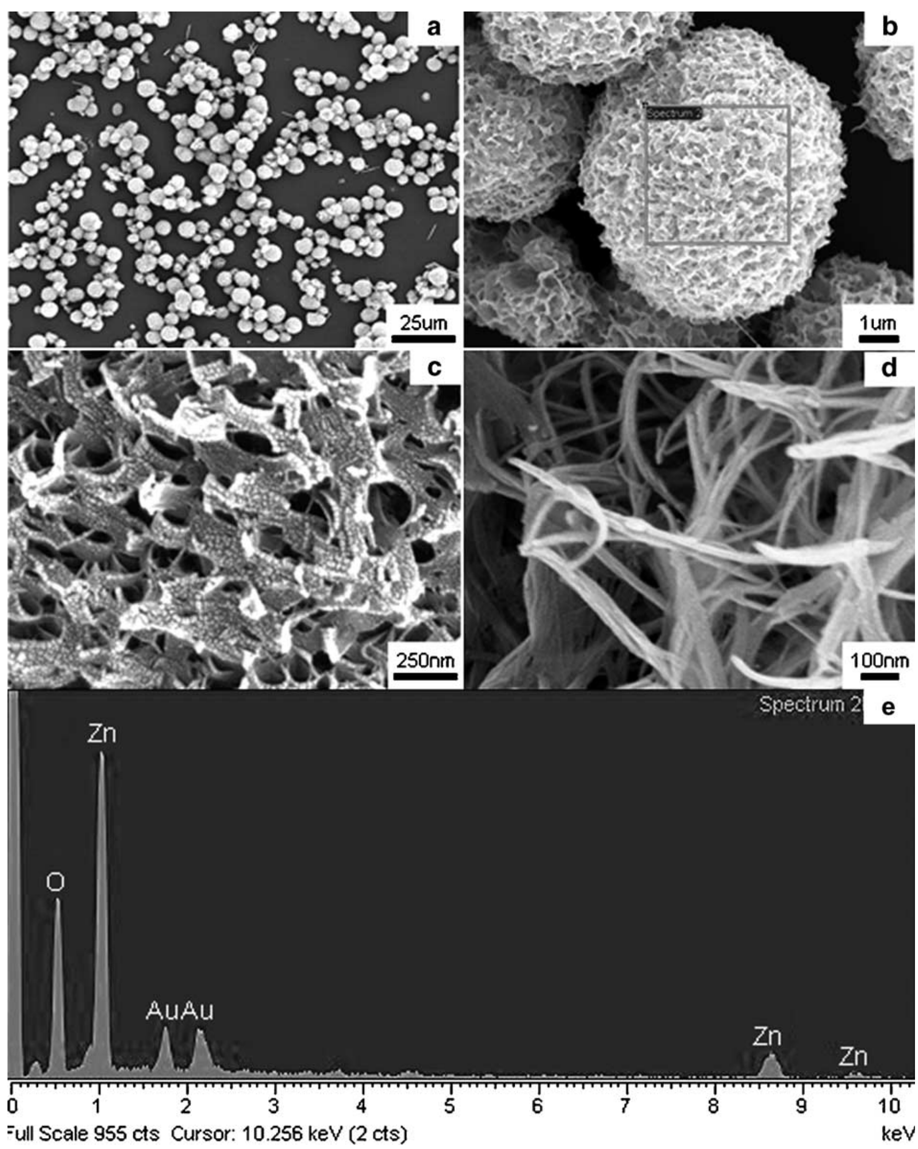

Fig. 2. SEM images of obtained RPZM: (a) space distribution of RPZMs on the surface of compact TiO_2 film, (b) the morphology of a whole RPZM, (c) the surface morphology of a RPZM, (d) nanowires observed around the RPZMs and (e) The EDX spectra measured on the marked area in b. The peak of Au was induced by the thin layer of Au sputtered on the surface of the sample to improve the conductance of it for SEM observation.