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Generalized synthesis of yolk–shell metal oxide spheres

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Abstracts

Varieties of yolk–shell metal oxide spheres, including SnO_2, CeO_2 and Tb_4O_7, with high yield have been successfully prepared *via* a general solvothermal method by using carbon spheres as sacrificial templates. The creation of yolk–shell structure is achieved after the removal of carbon templates by annealing. The results show that the typical products of yolk–shell SnO_2 spheres exhibit excellent textural properties, which makes them good candidates for use in gas-sensing, energy storage, and so on. Many more metal oxides with such a unique yolk–shell structure can be easily prepared through the present approach, and they may show great application potentials.

Keywords: A. Calcination; B. Porosity; C. Thermal properties; D. Sensors; Powders: chemical preparation

1. Introduction

The creation of microscopic materials has experienced a great structural evolution from simple to complex with the development of modern synthesis technology and analytical instruments because materials always show a strong correlation between their geometry and their functions [1–3]. For instance, in addition to general solid materials, the creation of hollow materials has become a critical issue in recent years owing to their great advantages of large void space area fraction, low density and special shape, which generally results in enhanced properties and novel application potentials compared to solid particles [4–10]. For the sake of further enhancing the properties and extending the applications of materials, their preparation with novel structures has attracted significant attention [11–16]. For instance, compared to the general hollow spheres, metal oxides with unique yolk–shell (hollow core–shell) and multiple shell hollow structure exhibit greatly enhanced gas-sensing properties [17].

Owing to the potential of their emerging applications spanning from catalyst, sensors, and microelectronic devices, to energy conversion devices including solar and fuel cells, nanoscale metal oxides are of tremendous current interest to scientists and engineers [18,19]. For example, Tin oxide (SnO_2) with an n-type wide bandgap equal to 3.6 eV is a functional material widely applied in gas-sensing and energy storage [20–23]. Cerium(IV) oxide (CeO_2), as one of the most important catalysts, has also attracted much research interest because of its effective technological applications [24,25]. Terbium(III,IV) oxide (Tb_4O_7), a typical rare earth oxide, may also show great application potentials in drug delivery systems and so on [26].

Previously, by using a solvothermal carbon template method, we have prepared yolk–shell $ZnCo_2O_4$ spheres. Herein, we further present the general synthesis of a series of metal oxides, including SnO_2, CeO_2, and Tb_4O_7, with unique yolk–shell structure through a similar approach. The results show that the typical products of yolk–shell SnO_2 spheres exhibit excellent properties, which promise great potential in technical applications.

2. Methods and materials

2.1. Materials

Glucose was purchased from Tianjin Co., Ltd. (Tianjin). Tb_2O_3, $Ce(NO_3)_3 \cdot 6H_2O$ and $NH_4Ac \cdot 2H_2O$ were purchased from Yuanli Co., Ltd. (Tianjin). $SnCl_2 \cdot 2H_2O$ was purchased from Kermel Co., Ltd. (Tianjin). N,N-Dimethylformamide (DMF) was purchased

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from Tianli Co., Ltd. (Tianjin). Concentrated HCl and HNO_3 were purchased from Tianda Co., Ltd. (Tianjin). All chemical materials were used as received.

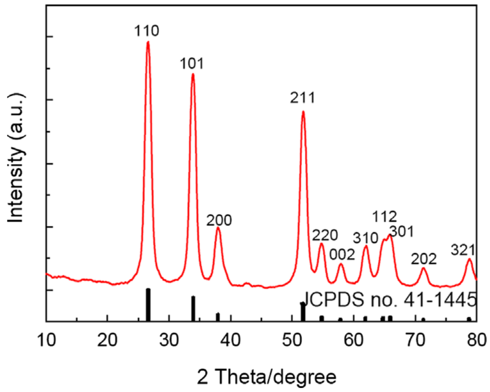

Fig. 1. XRD pattern of resultant yolk–shell SnO_2 spheres.

2.2. Synthesis

2.2.1. Preparation of yolk–shell SnO_2 spheres

Carbon spheres with an average particle size of 500 nm were prepared according to a present method and used as templates to direct the synthesis of yolk–shell metal oxide spheres [27]. For the synthesis of yolk–shell SnO_2 spheres, a suspension was made after dissolving 0.1 g $SnCl_2 \cdot 2H_2O$ in a mixture containing 25.0 mL DMF, 5.0 mL H_2O and 0.5 mL concentrated HCl (37%) followed by the dispersion of 0.3 g as-prepared carbon spheres. The suspension was transferred into a 50 mL Teflon-linked autoclave, and it was maintained at 180 °C for 12 h. Black precipitates were separated from the mixture and were dried at 100 °C. The black precipitate was further heated to 600 °C with a temperature ramp of 5 °C min^{-1} and kept at the same temperature for 3 h in air, and the yolk–shell SnO_2 spheres were formed.

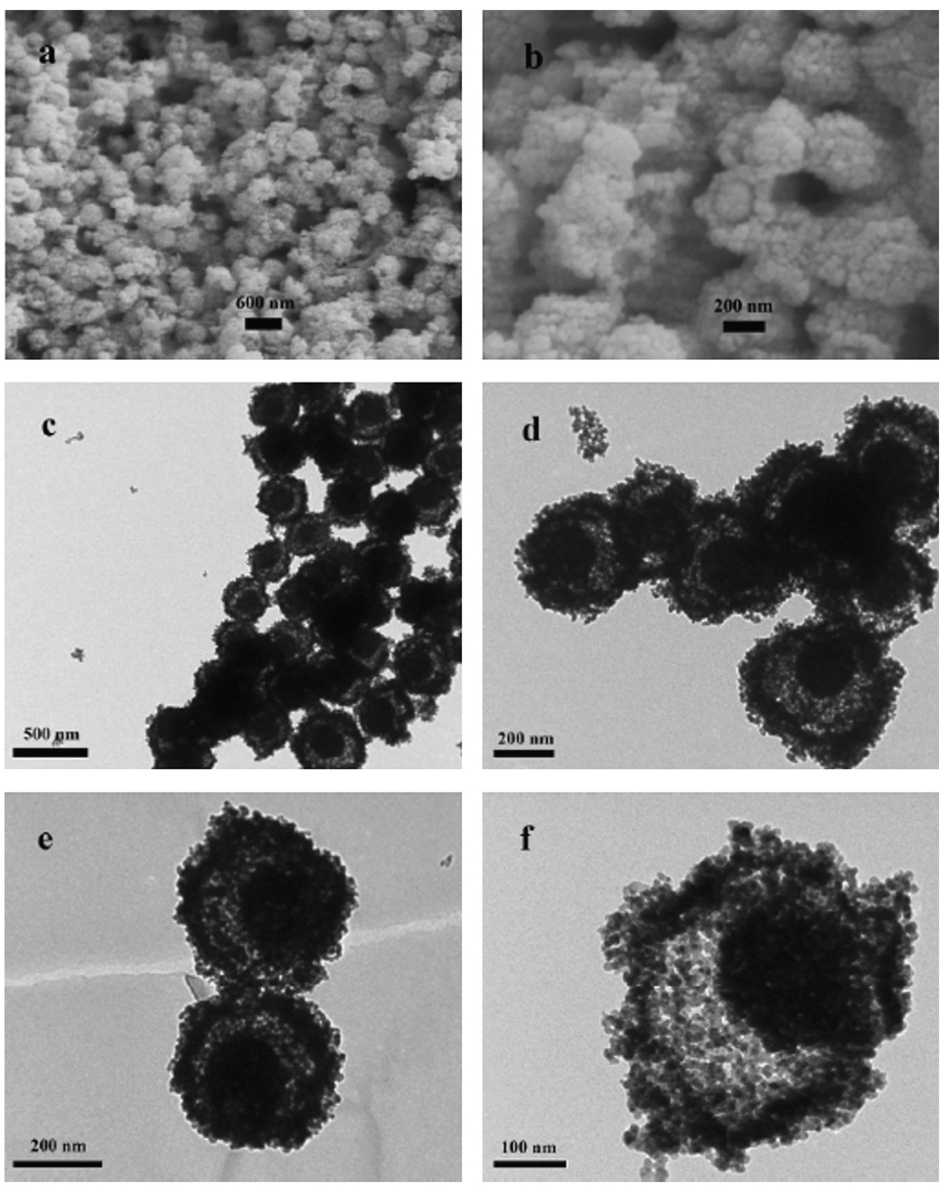

Fig. 2. FESEM (a, b) and TEM (c)–(f) images of yolk–shell SnO_2 spheres.