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Synthesis of hollow core-shell $ZnCo_2O_4$ spheres and their formation mechanism

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Abstract

The general synthesis of hollow core-shell $ZnCo_2O_4$ spheres through a novel method of solvothermal carbon templating is newly demonstrated. The preparation of hollow core-shell structure involves the key strategy of loading precursor into the mesopores inside the colloidal carbon spheres driven by solvothermal treatment. In addition, the present method is also of high precursor adsorption efficiency owing to the completely conversion of metal source to precursor. It is revealed that the as-prepared products exhibit excellent textural properties of a large surface area and large pore volume. It is assumed that the present method can be extended to prepare a series of hollow core-shell materials for widespread applications.

Keywords: A. Powders: Chemical preparation; B. Porosity; C. Thermal properties; D. Transition metal oxides

1. Introduction

The hollow nanomaterials have proven to be promising in widespread applications, including drug delivery, catalysis, sensors, LIBs and waste removal, and the synthesis of hollow nanomaterials has stimulated great research interest due to the superior properties of low density, large specific area and surface permeability in the past few years [1–3]. A variety of strategies, including template-direct routes and template-free routes, have been adopted for the control synthesis of them [4–7].

Nanostructured metal oxides have been found to be potential candidates for versatile applications including catalysis, gas-sensing, and lithium-ions batteries (LIBs), and many other frontier areas of science in the past decades [8]. Take Co_3O_4 for example, it exhibits a pretty high theoretical capacity and the best cycling performance among the transition metal oxides [9]. However, cobalt oxides are limited because of their high cost and toxicity. As a consequence, many research groups have made extensive efforts to engineer new anode materials for LIBs through replacing Co_3O_4 partially by eco-friendly and cheaper alternative metals [10–12]. In recent, $ZnCo_2O_4$, as one of the ternary cobalt based metal oxides, has been developed owing to its improved reversible capacities, enhanced cycling stability and good environmental benignity [13]. Previously, Tian et al. have demonstrated the synthesis of hollow single-crystalline $ZnCo_2O_4$ nanocubes through the Kirkendall effect [14]. However, to the best of our knowledge, works focused on the preparation of hollow $ZnCo_2O_4$ particles are really few.

In the present study, we demonstrate the synthesis of $ZnCo_2O_4$ spheres with unique hollow core-shell structure through a general method of solvothermal carbon templating. Not only has the solvothermal treatment drove the completely conversion of metal source to precursor, it also played a key role in driving the loading of precursor into the mesopores inside carbon spheres templates, leading to the extremely high precursor adsorption efficiency. The resultant hollow core-shell $ZnCo_2O_4$ spheres exhibit excellent textural properties of a large surface area and large pore volume, which may promise them potential applications in catalysis, gas-sensing, LIBs, and so on.

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2. Methods and materials

2.1. Materials

Glucose was purchased from Tianjin Co., Ltd (Tianjin). $CoAc_2 \bullet 4H_2O$ and $ZnAc_2 \bullet 2H_2O$ were purchased from Lide Co., Ltd (Tianjin). Ethylene glycol (EG) was purchased from Tianli Co., Ltd (Tianjin). All chemicals are of analytical grade reagents and used as received without further purification.

2.2. Synthesis

Carbon spheres with an average particle size of approximate to 500 nm were fabricated according to the presented method and were used as templates [15]. A typical synthesis of hollow core-shell $ZnCo_2O_4$ spheres was conducted as follows: a black suspension was resulted in after dissolving 0.11 g $ZnAc_2 \bullet 2H_2O$ and 0.50 g $CoAc_2 \bullet 4H_2O$ in 30.0 ml EG 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 (precursor absorbed composites) were separated from the mixture and dried at 100 °C. To remove the templates and create the hollow core-shell structure of products, the as-synthesized precursor absorbed composites were heated to 600 °C with a temperature ramp of 5 °C min^{-1} and kept at the same temperature for 3 h in air.

2.3. Characterizations and measurements

Powder X-ray diffraction (XRD) pattern of products was recorded on a Japan D/max-rB X-ray diffractometer. The morphologies and structures of samples were conducted on a Hitachi Japan Hitachi S-4800 field emission scanning electron microscopy (FESEM) and a Japan JEOL JEM-1400 transmission electron microscopy (TEM), respectively. The thermogravimetric (TG) and differential thermalanalysis (DTA) curves of precursor absorbed composites were recorded on a China ZCT-2000 thermo-gravimetric analysis carried out with a temperature ramp of 10 °C min^{-1} under air flow. The surface area and pore size distribution of products were determined through nitrogen (N_2) adsorption–desorption carried out on a USA Micromeritic ASAP 2020 nitrogen adsorption apparatus.

3. Results and discussions

The composition and phase purity of resultant hollow core-shell $ZnCo_2O_4$ spheres were examined by XRD, and the results are shown in Fig. 1 (Fig. 1). All the diffraction peaks can be readily indexed to the cubic phase $ZnCo_2O_4$ (space group Fd-3m(227) with a lattice constant $a = 8.095$ Å, JCPDS card no. 23-1390). The diffraction peaks, which can be filed to (111), (220), (311), (222), (400), (422), (511), (440), and (533) planes, are labeled in Fig. 1. No other peaks are found, revealing the high purity of sample.

Fig. 2 show the TEM images of carbon spheres (a), precursor absorbed composites (b), and the resultant hollow core-shell $ZnCo_2O_4$ spheres (c and d), respectively. One can conclude from Fig. 2a that the uniform spherical carbon spheres exhibit an average particle size of approximately 500 nm. Fig. 2b illustrates the TEM image of precursor absorbed composites, from which the uniform spherical morphology of particles is also inferred. The spheres presented in both Fig. 2a and b possess smooth surface. According to the TG-DTA results, as shown in Fig. 4, the loading of precursor onto or into the templates is suggested. However, the typical core-shell structure, which generally refers to the coating of nanocrystals upon the outer surface layer of templates, is not observed in Fig. 2b. As a consequence, it is assumed that the precursor must has been loaded into the templates because of their large amount of mesopores. In general, these mesopores are functionalized by a large number of –OH and –COOH groups, making the adsorption of metal ions and nucleates into them very easy [16,17]. Moreover, during the solvothermal treatment, driven by the vigorous internal thermal motion of molecules, the precursor can be deeply loaded into the mesopores, leading to a certain precursor loading depth which is required for the creation of hollow core-shell structure. As presented, if the precursor loading depth is too short, all the precursor distributes in the narrow region near the outer surface, and a single shell is likely to be obtained owing to the shorter diffusion length. Sequentially, hollow spheres with merely a single shell form as there is not enough precursor to sustain the inner cores or more inner hollow shells [18].

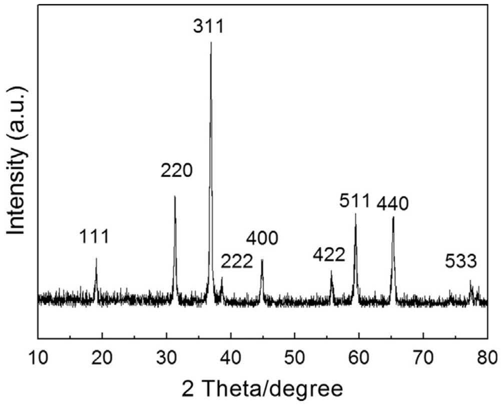


Fig. 1. XRD pattern of resultant hollow core-shell $ZnCo_2O_4$ spheres.

Fig. 2c and d further exhibit the TEM observations of resultant hollow core-shell $ZnCo_2O_4$ spheres. It is inferred that the particles are hollow structured according to the strong contrast between the dark edges and pale centers. Further, as shown at the arrows, inner cores inside the hollow shells are also confirmed. The average particle size of hollow core-shell spheres is approximately 300 nm, which is much smaller than that of templates and precursor absorbed composites. The shrinkage should be attributed to the dense of precursor co-occurring with the removal of carbon templates during calcination [16]. In addition, it is illustrated that the hollow shells consist of a large number of small nanocrystals, suggesting the porous region deriving from particle aggregates with slit-shaped pores.

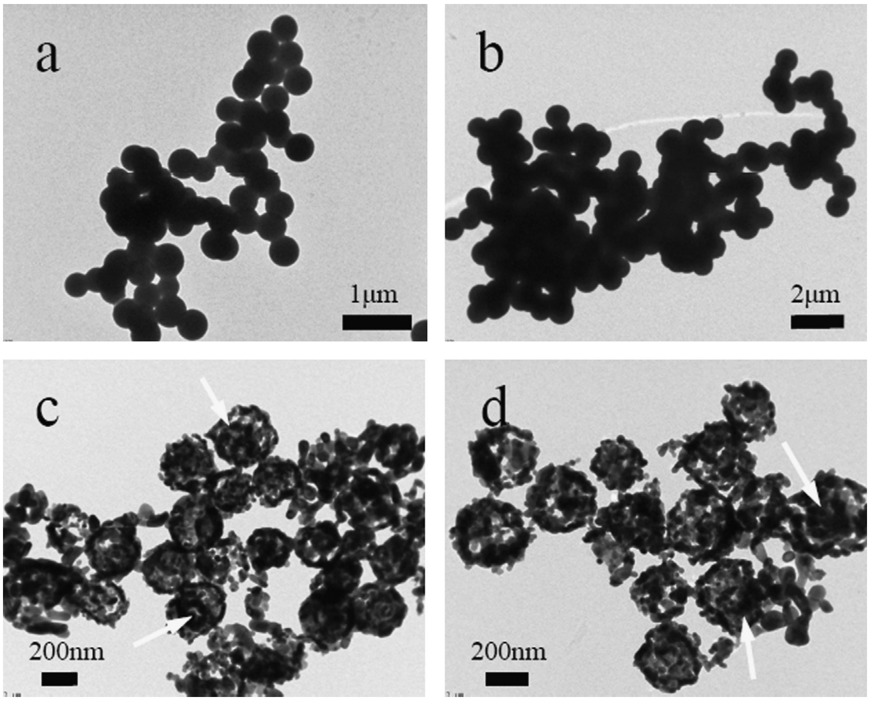


Fig. 2. TEM images of as-prepared carbon spheres (a), precursor absorbed composites (b), and resultant hollow core-shell $ZnCo_2O_4$ spheres (c and d), respectively.

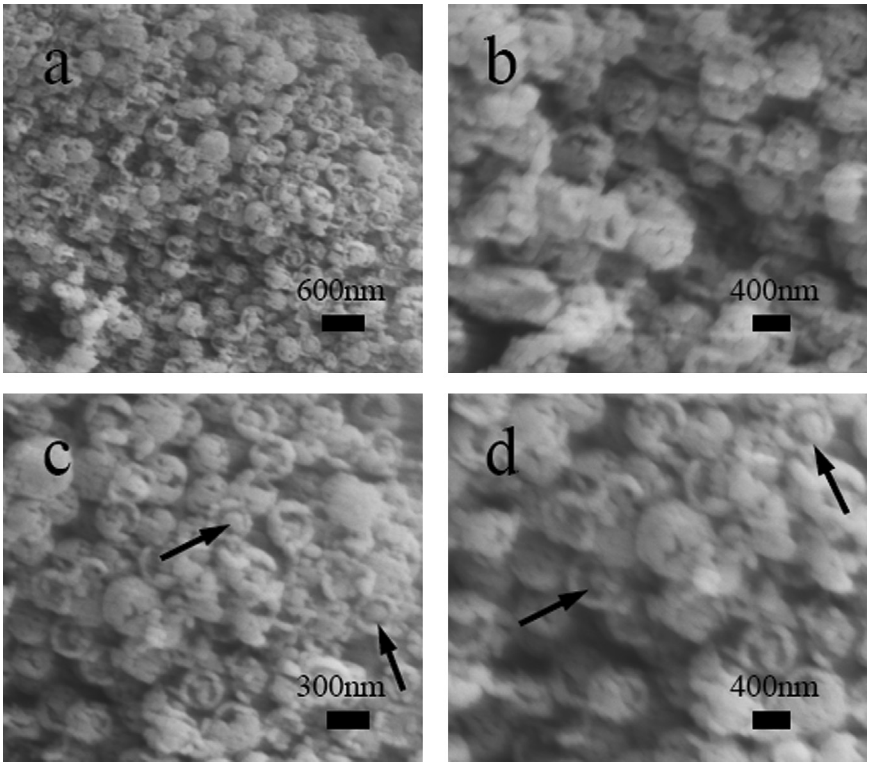
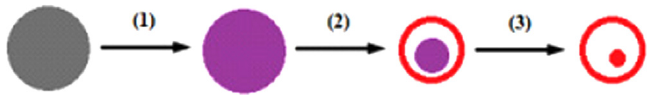


Fig. 3. FESEM images of resultant hollow core-shell $ZnCo_2O_4$ spheres.

FESEM further provide insights into the morphology and detailed structure of the resultant products, as presented in Fig. 3a–d. The crashed hollow shells, which consist of a large amount of small particles, and the contained inner cores inside the hollow shells provide evidence for the hollow core-shell feature of sample. The average particle size of resultant hollow core-shell $ZnCo_2O_4$ spheres is calculated to be approximately 300 nm, which is well identical with TEM results.

A general schematic illustration of the formation process of hollow core-shell $ZnCo_2O_4$ spheres is proposed in Scheme 1.



Scheme1. Formation mechanism of hollow core-shell $ZnCo_2O_4$ spheres.

Briefly, three key strategies are involved: (i) the complete conversion of metal source to precursor and the loading of it into carbon spheres templates;(ii) part removal of templates and the separation of oxide shell and composite core during calcination; and (iii) complete removal of template and the final preparation of hollow core-shell structure. The completely conversion of metal source to precursor and the loading of it into mesoporous templates is the key strategy, which is achieved during the solvothermal treatment. As is well known, the carbon spheres are porous and the surface layers of which are generally functionalized by groups such as –OH and –COOH [16]. As a consequence, metal ions can be easily absorbed by them from the solution. Assisted with the solvothermal treatment, hydroxides and oxides are generally prepared because of the hydrolysis of metal ions at high temperature [19–21]. Therefore, in the preparation of hollow core-shell $ZnCo_2O_4$ spheres, the mesopores inside carbon spheres afford the places for the hydrolysis of metal ions to occur at, and in this case, the self-nucleation that may lead to solid particles can be well avoided [22].

The separation of oxide shell and composite core, as described at step two, is required for the creation of hollow core-shell $ZnCo_2O_4$ spheres. The occurring of separation is similar to the formation of multiple shell hollow spheres in a previous work [18]. As the forming of oxide shell is not match with the removal of carbon templates, the separation of outer shell and inner core is resulted in. Detailed information see to TG-DTA results, as shown in Fig. 4. As the oxide shell and composite core separated from each other, the resultant $ZnCo_2O_4$ spheres with hollow core-shell structure are finally fabricated after the completely removal of templates during further calcination.

Fig. 4 show the thermogravimetric (TG) and differential thermalanalysis (DTA) cruves of precursor absorbed composites. Generally, the weight loss occurring from 50 °C to 200 °C is assigned to the evaporation of free water. However, the main weight loss occurring from 200 °C to 360 °C, corresponding to the major exothermic peak, should be attributed to the removal of carbon spheres templates. It can be inferred that the loss of templates may include two steps because the exothermic peak clearly shows the different combustion kinetics of template [13]. In detail, during the calcination over 200 °C and 260 °C, the outer part of templates can be easily removed owing to the exposing of them in air. However, as the oxide shell formed, the combustion kinetic of templates greatly decreased, resulting in the platform from 260 °C to 360 °C at the exothermic peak. Any weight losses and exothermic peaks over 360 °C are not found, illustrating that the templates must have been removed completely. The weight of precursor-absorbed sphere is measured to be high as 47.5%. Such a result should be attributed to the completely conversion of metal source to precursor driven by solvothermal treatment. In this case, very few of metal source was left in the solution so that the potential wasting of materials and pollution can be well avoided.

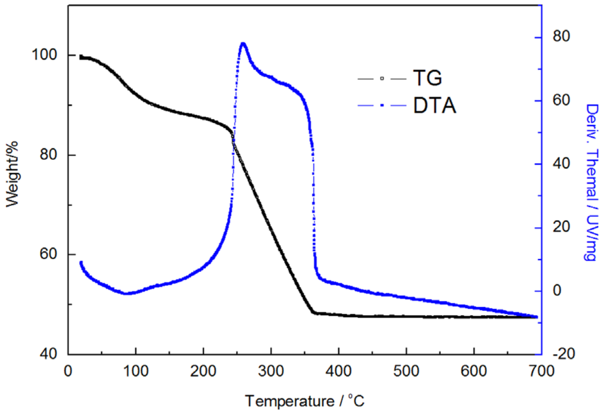


Fig. 4. The TG and DTA curves of precursor absorbed composites.

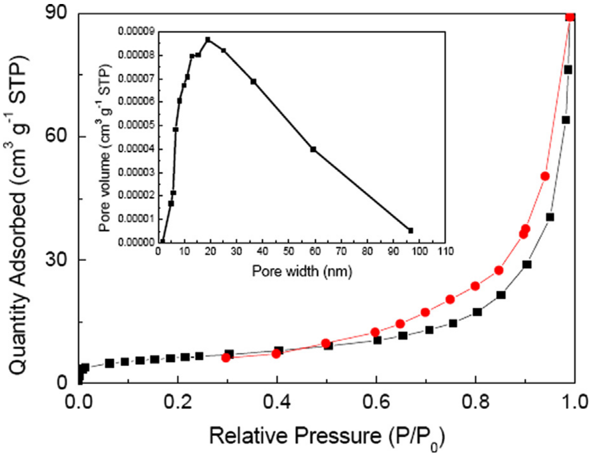


Fig. 5. Nitrogen adsorption–desorption isotherm and BJH desorption pore width distribution (inset) of hollow core-shell $ZnCo_2O_4$ spheres.

The surface area and Barrett–Joyner–Halenda (BJH) desorption pore size distribution of hollow core-shell $ZnCo_2O_4$ spheres are determined through nitrogen adsorption–desorption isotherm, as shown in Fig. 5. It can be inferred that the hysteresis loop is of type Ⅱ (BDDT classification) with bimodal pore size distribution in the mesoporous and macroporous regions [23]. It is found that the hollow core-shell $ZnCo_2O_4$ spheres exhibit a large surface area of 15.968 $m^2 g^{-1}$. The pore size distribution is calculated from the desorption branch of the nitrogen isotherm by the BJH method, as shown in Fig. 5 inset. The results show that the average pore width of resultant hollow core-shell $ZnCo_2O_4$ spheres is approximately 30.1 nm. The total pore volume of resultant hollow core-shell $ZnCo_2O_4$ spheres has also been calculated to be 0.063 $cm^3 g^{-1}$. The results may reveal that these porous hollow core-shell $ZnCo_2O_4$ sphere can provide sufficient space to buffer the volume change during of anodes based on the conversion reaction during the repeated Li^+ insertion/extration, and therefore they are suggested as a cycleable anodic material for lithium ion batteries [24].

4. Conclusions

In summary, through a general method of solvothermal carbon templating which involves the loading of precursor into mesoporous templates, $ZnCo_2O_4$ spheres with unique hollow core-shell structure have been prepared. The present method is of high precursor adsorption efficiency that can prevent it from the potential wasting of materials and pollution. The present method can be further extended to synthesize a vast mass of metal oxides with unique hollow structures and excellent properties for great potential applications.

Acknowledgments

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