Research Article

A General Synthesis Strategy for Hierarchical Porous Metal Oxide Hollow Spheres

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The hierarchical porous TiO_2 hollow spheres were successfully prepared by using the hydrothermally synthesized colloidal carbon spheres as templates and tetrabutyl titanate as inorganic precursors. The diameter and wall thickness of hollow TiO_2 spheres were determined by the hard templates and concentration of tetrabutyl titanate. The particle size, dispersity, homogeneity, and surface state of the carbon spheres can be easily controlled by adjusting the hydrothermal conditions and adding certain amount of the surfactants. The prepared hollow spheres possessed the perfect spherical shape, monodispersity, and hierarchically pore structures, and the further experiment verified that the present approach can be used to prepare other metal oxide hollow spheres, which could be used as catalysis, fuel cells, lithium-air battery, gas sensor, and so on.

1. Introduction

Compared to the solid particles, hollow spheres have attracted much attention in recent years due to its outstanding properties, such as the controlled pore structure, low density, high specific surface area, high pore volume, and superior thermal and mechanical stability, in which widespread potential applications in catalysts, gas sensors, coatings, energy storage, conversion, and so forth can be found [1–4]. For example, the Co_3O_4 spheres with hollow structure could be used as an excellent catalyst for many key applications [5–9]; due to their large specific surface area and hierarchical pore structures, TiO_2 hollow spheres exhibit excellent photocatalytic performance [10–14], while SnO_2 hollow spheres could be used as an anode material for lithium ion batteries with high efficiency [15–18].

Recently, the design strategies and preparation methods of the hollow nano- or microspheres have been reported by many researchers, and the templates assisted synthesized method was commonly used as an effective approach to prepare hierarchical hollow spheres. The hard templates such as polymethyl methacrylate microspheres, polymer latex particles, polystyrene microspheres, and silica spheres and soft templates such as emulsion droplets, twelve sodium dodecyl sulfate (SDS), micelles, and gas bubbles were usually used [19–22]. The synthesis and pore structure regulation of hollow spheres with size and shape controlled morphologies may obtain other excellent performances and broaden its applications. Among the above templates, the monodispersed carbonaceous microspheres synthesized by hydrothermally treating of aqueous solutions of glucose and sugar were thought to be an ideal hard template for preparation of the hollow spheres [23]. Due to the existence of the functional groups which were located at the surface of the colloidal carbon spheres, the templates were suited for the absorption of cationic metal ions and precipitation of metal precursors. Therefore, in the present work, we aimed to report a general synthesis approach applicable to prepare metal oxide hollow spheres with tunable structure by using the hydrothermally synthesized colloidal carbon spheres as the hard templates.

2. Experimental Procedure

2.1. Synthesis of Carbon Spheres. The colloidal carbon spheres used in the present study were prepared by hydrothermally treating of aqueous solutions of glucose. Typically, 9 grams of
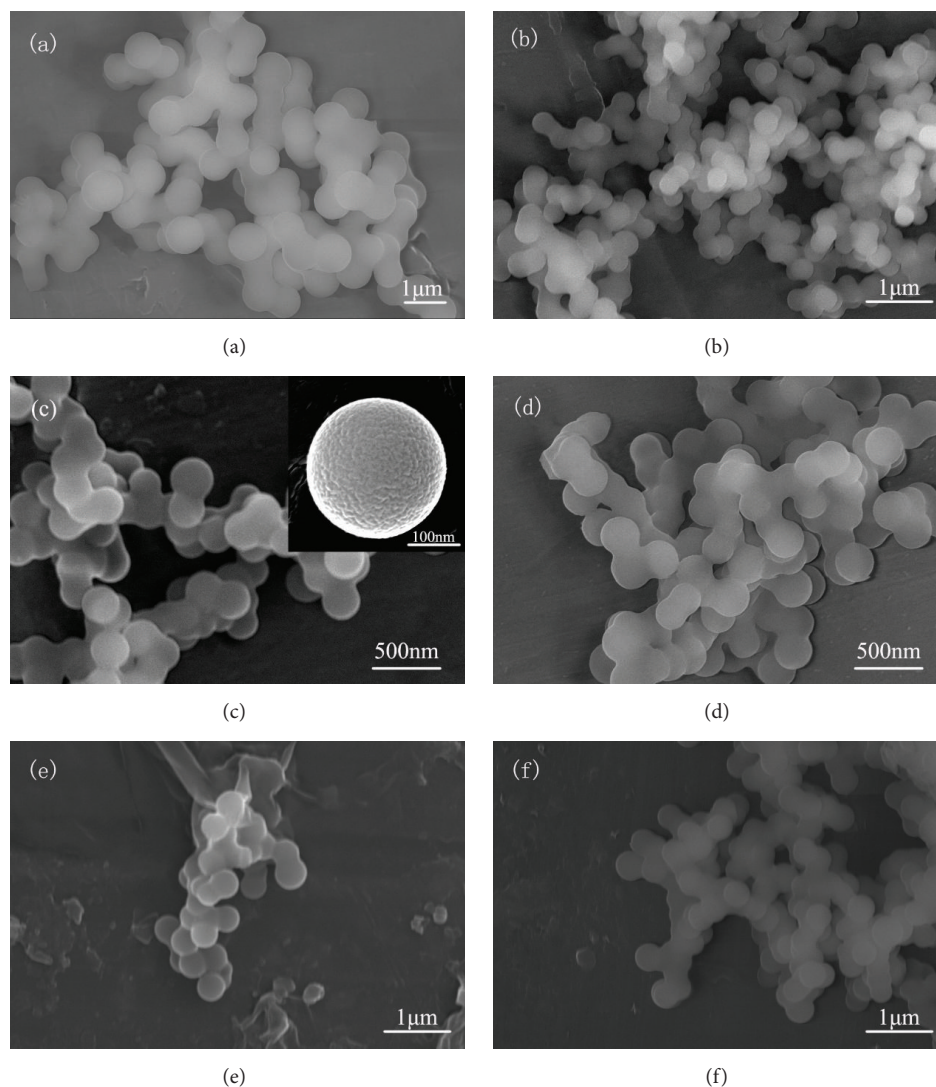
FIGURE 1: SEM photographs of carbon spheres prepared by different concentration of glucose, hydrothermal temperature, and time. (a) 0.5 mol/L, 220°C, 12 h; (b) 0.5 mol/L, 200°C, 12 h; (c) 0.5 mol/L, 180°C, 12 h; (d) 0.5 mol/L, 220°C, 10 h; (e) 0.5 mol/L, 220°C, 8 h; (f) 0.75 mol/L, 220°C, 12 h.

glucose (Beijing Chemical Reagent Factory, analytical purity) was dissolved in 90 mL deionized (DI) water to form a clear solution, which was then transferred to a 100 mL Teflon-sealed autoclave and maintained at certain temperature and time. The resultant black products were separated and purified by centrifugation and washed repeatedly in DI water and ethanol for three times, respectively, and finally dried in a vacuum oven at 80°C for 6 h. In order to regulate the dispersity and particle size of the as-obtained carbon spheres, the different hydrothermal treatment parameters and different kinds and amounts of the surfactants were used in the preparation of the carbon spheres.

2.2. Preparation of Metal Oxide Hollow Spheres.

Take TiO_2 as an example, the details of a typical experiment for the synthesis of TiO_2 hollow spheres are described as follows. Firstly, 5 mL tetrabutyl titanate was dissolved in 50 mL ethanol to form a clear solution, and then 0.1 grams of the newly synthesized carbon spheres was dispersed in the above suspension with the aid of ultrasonication. After stirred for 2 h, 20 mL of the mixed solutions of ethanol and DI water with the volume ratio of 5 : 1 was added dropwise to the suspension under vigorous stirring. The mixture was aged for 1 h and then subjected to centrifugation and washing to remove impurities and dried in a vacuum oven at 60°C for 5 h. Finally, the TiO_2 hollow spheres were obtained by strengthening the shell structure and removing the carbon spheres of the carbon-titania composites calcined in air at 450–850°C (heating rate of 2°C/min) for 4 h.

2.3. Characterization.

The calcination procedure was determined by the thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis. Nicolet Magna 750 was used to measure the FTIR spectra of carbon spheres, and the
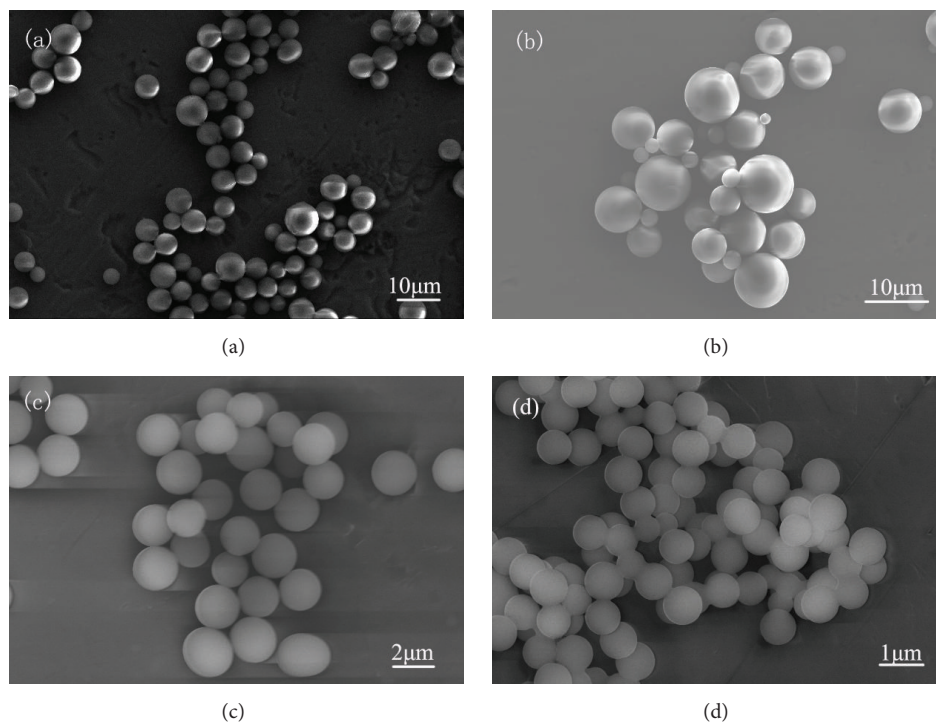
(a)

(b)

(c)

(d)

Figure 2: SEM photographs of carbon spheres prepared by adding different kinds and amounts of the surfactants. (a) 0.005 mol/L $NH_3 \cdot H_2O$; (b) 0.015 mol/L $NH_3 \cdot H_2O$; (c) 0.005 mol/L CTAB; (d) 0.015 mol/L CTAB.

wave number region ranged from 4000 to 500 cm^{-1} with 64 scans at 8 cm^{-1} resolution. X-ray diffraction (XRD) with the scanning speed of 4°/min from 20 to 80° was carried out on a Bruker D8-Advance diffractometer using Ni filtered Cu Kα radiation. The applied current and voltage were 40 mA and 40 kV, respectively. The microstructures of the carbon spheres and hollow TiO_2 spheres were observed by scanning electron microscopy (Carl Zeiss Jena scanning microscope, SEM) and transmission electron microscopy (JEOL JEM-2011, TEM). BET-surface area was measured by N_2 adsorption at liquid nitrogen temperature using a NOVA4000 automated gas sorption system.

3. Results and Discussion

3.1. Synthesis of Carbon Spheres. Figure 1 shows the SEM images of the as-prepared carbon spheres synthesized at different conditions. It can be seen that the dispersity and particle size of the as-synthesized carbon spheres were influenced by hydrothermal time, temperature, and concentration of glucose. With decreasing of the hydrothermal temperature, shortening of the hydrothermal time, and reducing of the concentration of glucose, the particle size of the colloidal carbon spheres decreased, and, meanwhile, the dispersity of the carbon spheres was improved. For example, the particle size of the carbon spheres decreased from 500 nm to 350 nm when the hydrothermal temperature decreased from 220°C to 180°C (Table 1). On the other hand, with increasing of the hydrothermal temperature and hydrothermal time,

the particle size of carbon spheres tended to be monodispersed. It also can be found that the as-synthesized carbon spheres exhibit rough and porous surface, which will impart the carbon spheres with low density and large specific surface area.

The hydrothermal synthesis of carbon spheres can also be divided into two stages, including nucleation and growth. The increases of temperature in the early stage of synthesis process led to dehydration and condensation of the glucose molecules, and the polysaccharide molecular was formed. With extending the hydrothermal time, the polysaccharide was further polymerized to form a polymer chain, and the carbon spheres nuclei were formed by the cross linking of polymer chain. Then polymer polymerization occurred in the surface of nuclei, namely, the growth of the carbon spheres, and after further dehydration and carbonization the carbon spheres with certain size were obtained.

In order to further regulate the dispersity and particle size of the carbon spheres, the hydrothermal temperature and time were fixed to 200°C and 10 h, respectively, and the different kinds and amounts of the surfactant were added in the solution. The typical SEM images are shown in Figure 2. It can be seen clearly that the morphologies and particle size of carbon spheres can be changed obviously when the surfactants were added, and the dispersity of the carbon spheres was improved, accompanied by decreasing the homogeneity of the carbon spheres. With increasing of the ammonia concentration from 0.005 mol/L to 0.015 mol/L, the particle size of the carbon spheres increased from 2–4 μm to 6–9 μm. The

TABLE 1: The diameter of the as-synthesized carbon spheres.

Concentration of the glucose (mol/L)	Hydrothermal temperature (°C)	Hydrothermal time (h)	Additives	Diameter of the carbon spheres
0.5	220	12	—	500 nm
0.5	200	12	—	400 nm
0.5	180	12	—	350 nm
0.5	220	10	—	450 nm
0.5	220	8	—	430 nm
0.75	180	12	—	450 nm
0.75	220	12	—	520 nm
1 m	220	12	—	600 nm
0.5	200	10	Ammonia 0.005 mol/L	2–4 μm
0.5	200	10	Ammonia 0.015 mol/L	6–9 μm
0.5	200	10	CTAB 0.005 mol/L	1-2 μm
0.5	200	10	CTAB 0.015 mol/L	700 nm

(a)

(b)

(c)
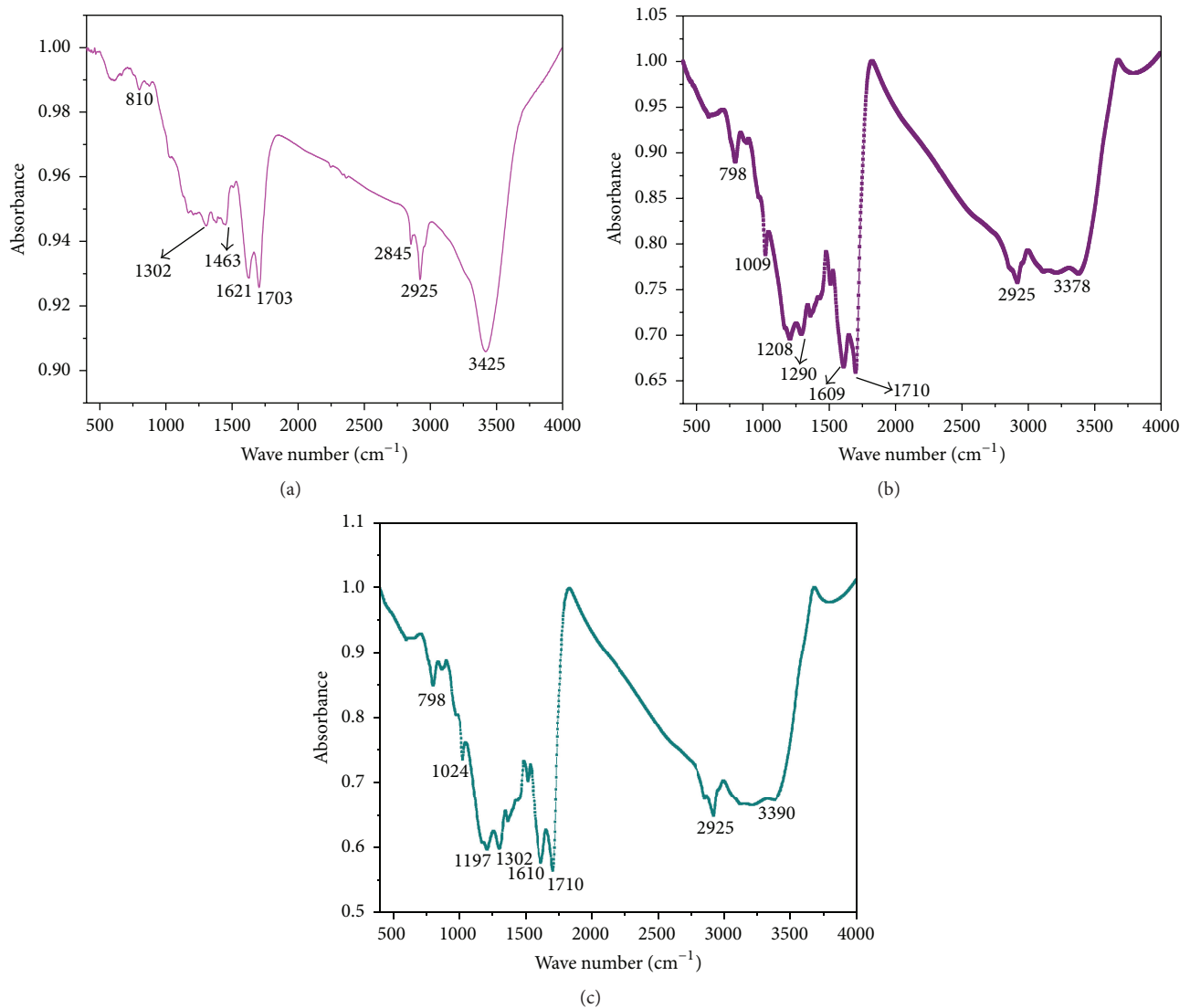
FIGURE 3: Fourier transform infrared spectroscopy FTIR spectra of carbon spheres. (a) no surfactant; (b) 0.015 mol/L $NH_3 \cdot H_2O$; (c) 0.015 mol/L CTAB.
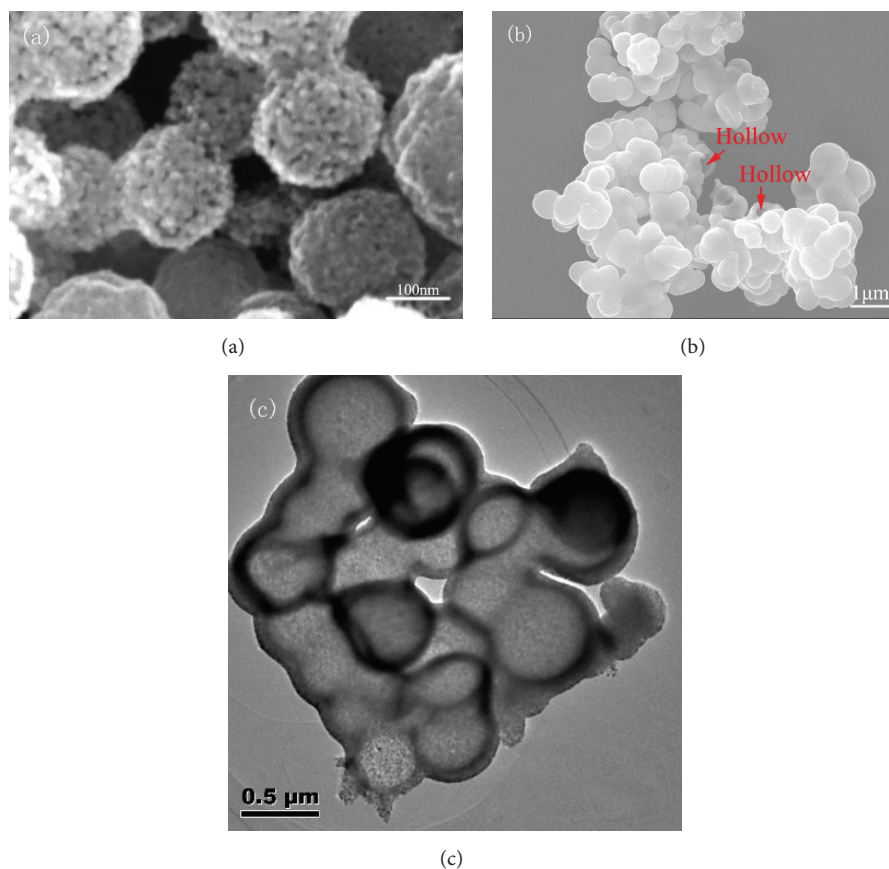
FIGURE 4: SEM images of (a) as-synthesized carbon-titania composites spheres; (b) titania hollow spheres; (c) TEM image of the titania hollow spheres.

monodispersed carbon spheres with the diameter of 700 nm can be obtained when adding the 0.015 mol/L cetyltrimethy-lammonium bromide (CTAB) under the hydrothermal conditions of 200°C and 10 h (Table 1).

Figure 3 presents the FTIR spectra of the as-synthesized carbon spheres under different conditions. It can be seen clearly that a large number of functional groups exist at the surface of the carbon spheres, including C-OH ($1710 \, cm^{-1}$), -OH ($3300 \sim 3500 \, cm^{-1}$), C=C ($1621 \, cm^{-1}$), C=O ($1302 \, cm^{-1}$), and C-H ($2925 \, cm^{-1}$) groups, and, among them, the absorption of the metal ions formed by hydrolysis of inorganic precursors and synergistic reaction with the precursors will be promoted by the presence of the C-OH and -OH groups, while the other groups are harmful to the coating process. Regardless of $NH_3 \cdot H_2O$ and CTAB, the -OH located at around $3300 \sim 3500 \, cm^{-1}$ decreased when the surfactants were added in the solution, which will affect the subsequent deposition process of metal ions.

3.2. Synthesis of Metal Oxide Hollow Spheres. Figures 4(a) and 4(b) show the SEM images of the carbon-titania composite spheres before and after the thermal treatment at 450°C for 4 h, and it can be seen that the coated carbon/TiO_2 composite spheres with monodispersed spherical shape were obtained,

indicating that the coating layer was uniform. There was a clear contrast between the edge and the center of the as-synthesized titania spheres which was observed in the TEM image (Figure 4(c)) indicating that they exhibited a hollow structure. The synthesis mechanism of the titania hollow spheres can be explained as follows. The replacement of the titanate groups and the -OH of the carbon spheres occurs when the carbon spheres are dispersed in the ethanol, and then the titanium atoms enter the hydrophilic surface of the carbon spheres through a -Ti-O- covalent bond. Once dropped in the mixed solution of water and ethanol, the hydrolysis and condensation reactions of titanate groups in the surface of the carbon spheres will occur, and with the increase of aging time the -Ti-O-Ti- groups are formed on the surface of carbon spheres, which will be trasformed to titania shell after subsequent calcination at certain temperature.

In order to determine the crystal phase of the as-prepared hollow TiO_2 spheres, XRD measurements were carried out and the results are shown in Figure 5(a). It can be seen that after the calcination of carbon-titania composite spheres at 450°C the titania precursor was transformed into anatase TiO_2. A distinct large hysteresis loop in the N_2 adsorption-desorption isotherms can be observed for all samples (Figure 5(b)), which is a typical IV isotherm with H1-shaped hysteresis loop, demonstrating the presence of
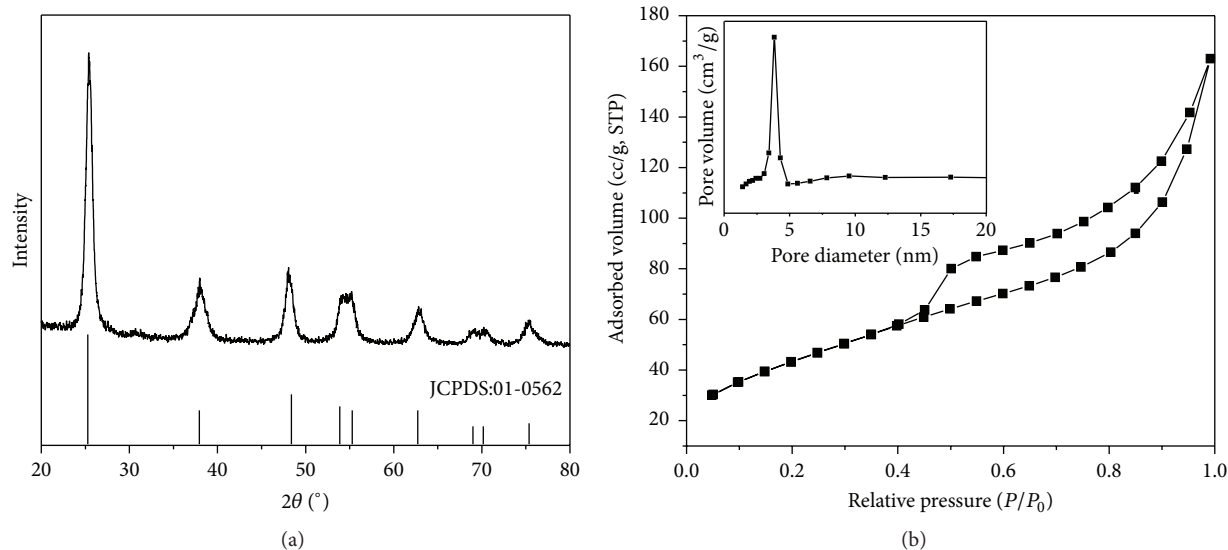
(a)

(b)

FIGURE 5: XRD pattern (a) and N_2 absorption-desorption isotherms of the titania hollow spheres, and the inset is the pore size distribution curve of the titania hollow spheres (b).
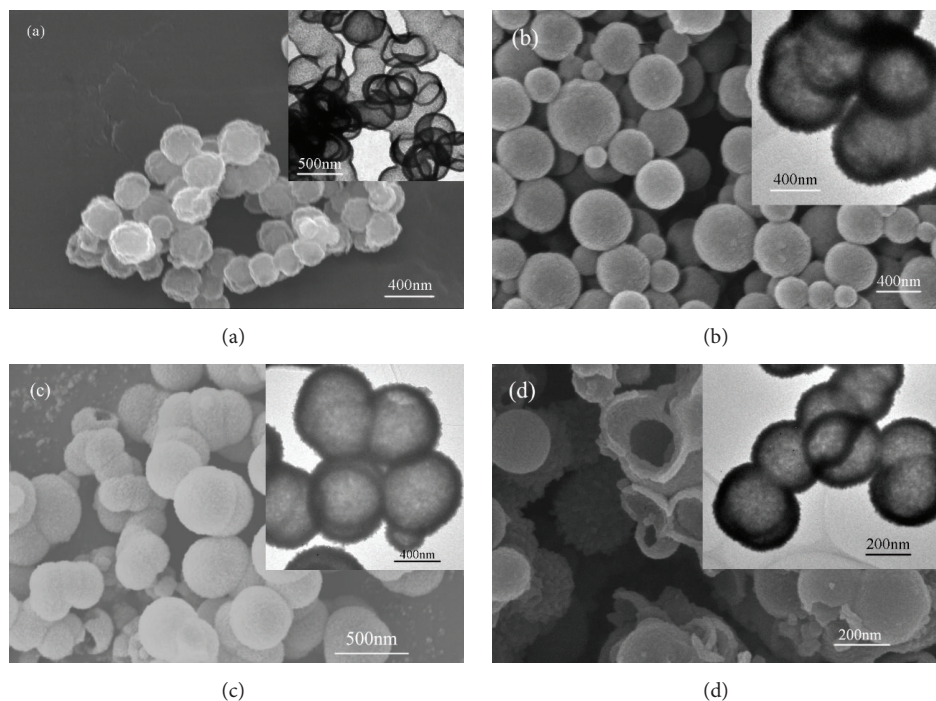

(a)

(b)

(c)

(d)

FIGURE 6: SEM images of SnO_2 (a), Co_3O_4 (b), YSZ (c), and CeO_2 (d) hollow spheres.

mesoporous structure. The titania hollow spheres with the maximum specific surface area of 100.179 m^2/g and pore volume of 0.110 cc/g can be obtained when the mass ratio of carbon spheres and tetrabutyl titanate was 1 : 30. The inset in Figure 5(b) shows that the pore size distributions of the hollow spheres exhibits a sharp peak, and the average BJH mesopore size is 3.76 nm, indicating a uniform mesopore distributed in the shell of the titania hollow spheres.

The size and pore structure of the hollow TiO_2 spheres can be easily regulated by adjusting the synthesis parameters.

For example, the diameter of hollow TiO_2 spheres can be controlled by using the carbon spheres prepared under different conditions as hard templates, while the wall thickness and specific surface area of the titania hollow spheres can be regulated either by adjusting the concentration of tetrabutyl titanate or by controlling the number of the functional groups located on the surface of the carbon spheres prepared with the presence of surfactants of different types and amount.

The synthesis strategy presented above provides a simple and general approach for the synthesis of hierarchically

porous metal oxide hollow spheres, which can also be widely applied to other systems. As shown in Figure 6, when other inorganic precursors, such as $SnCl_4$, $Co(NO_3)_2 \cdot 6H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, $ZrOCl_2 \cdot 8H_2O$, and $Ce(NO_3)_3 \cdot 6H_2O$ were employed as templates, the as-prepared SnO_2, Co_3O_4, YSZ, and CeO_2 hollow spheres with different compositions were successfully prepared by adopting this synthesis strategy. All the prepared hollow spheres with different inorganic salts as precursors possess the well-developed spherical morphology.

4. Conclusions

In summary, we have developed a simple and general approach for preparing the metal oxide hollow spheres by using the hydrothermally synthesized colloidal carbon spheres as hard templates. The wall thickness and textural properties of the hollow spheres can be easily tailored by adjusting the concentration of inorganic precursor. The monodispersed hollow spheres with perfect spherical shape and hierarchically pore structures can be used as catalysis, lithium-air battery, fuel cells, gas sensor, and so on.
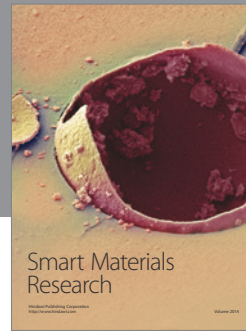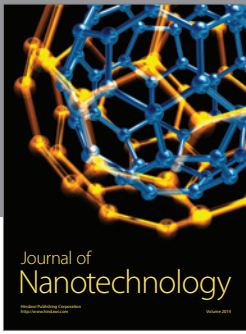
Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of the paper.

Acknowledgments

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