

General Synthesis and Gas-Sensing Properties of Multiple-Shell Metal Oxide Hollow Microspheres**

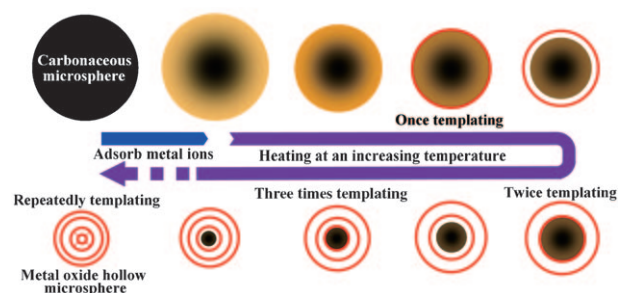
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Hollow spheres with nanometer-to-micrometer dimensions, controlled internal structure, and shell composition have attracted tremendous attention because of their potential application in catalysis, drug delivery, nanoreactors, energy conversion and storage systems, photonic devices, chemical sensors, and biotechnology.^[1] Single-shell and double-shell hollow spheres of various compositions have been synthesized by a number of methods, such as vesicles, emulsions, micelles, gas-bubble, and hard-templating methods.^[2] More recently, efforts have focused on the fabrication of hollow spheres with multiple shells, as these materials are expected to have better properties for applications such as drug release with prolonged release time, heterogeneous catalysis, lithium-ion batteries, and photocatalysis.^[3] For example, multiple-shell hollow microspheres of Cu_2O have been prepared by vesicle templating and an intermediate-templating phase-transformation process.^[3a,b] Multiple-shell azithromycin hollow microspheres were fabricated by hierarchical assembly.^[3c] Cao and co-workers reported the synthesis of triple-shelled SnO_2 hollow microspheres by chemically induced self-assembly in the hydrothermal environment which exhibited enhanced electrochemical performance.^[3d] Yao and co-workers reported excellent cycle performance and enhanced lithium storage capacity of multiple-shell Co_3O_4 hollow microspheres synthesized by oriented self-assembly.^[4] These preparative methods, however, are suited for each specific material and cannot be applied generally to a wide range of materials. Currently, there is no general synthetic approach

for fabricating multiple-shell hollow nanostructures of any desired material.

Herein, we present a straightforward and general strategy to prepare metal oxide hollow microspheres with a controlled number of shells. Carbonaceous microspheres were used as sacrificial templates. The microspheres were saturated with a desired metal salt solution and then heated in air; the carbonaceous template evaporates and templates the formation of metal oxide shells. The number of shells is controlled by the metal ion loading and the process is general for a wide range of metal oxide materials.

Scheme 1 illustrates the general process of fabricating multiple-shell hollow metal oxide microspheres. The key to this process is the use of carbonaceous particles rich with surface functional groups available for metal ion adsorption.^[5]



Scheme 1. Illustration of the sequential templating approach to multi-shell hollow metal oxide microsphere synthesis.

Multiple shells are generated by supplying enough shell precursor material to the sacrificial carbonaceous spheres. Recently, our group reported the synthesis of hollow core-shell ferrite microspheres,^[5b] demonstrating that carbonaceous particles can absorb a significant amount of metal ions within the interior of the particle (Figure S1 in the Supporting Information). In this work, we extend these methods and demonstrate the general and facile synthesis of multiple-shell hollow microspheres of a wide range of different metal oxides.

Figure 1a,b shows a transmission electron microscopy (TEM) image of hollow microspheres of $\alpha\text{-Fe}_2\text{O}_3$ obtained by soaking carbonaceous microparticles in an 2 mol L^{-1} iron nitrate solution (detailed synthesis procedures are presented in the Experimental Section). The hollow microspheres have a double-shell structure of a $0.45\text{ }\mu\text{m}$ diameter shell with an outer shell of about $1.5\text{--}2.0\text{ }\mu\text{m}$ in diameter. Scanning transmission electron microscope (STEM) imaging and energy-dispersive X-ray microanalysis (EDS) line scans (Figure S2) confirmed the hollow double-shell structure of the particles

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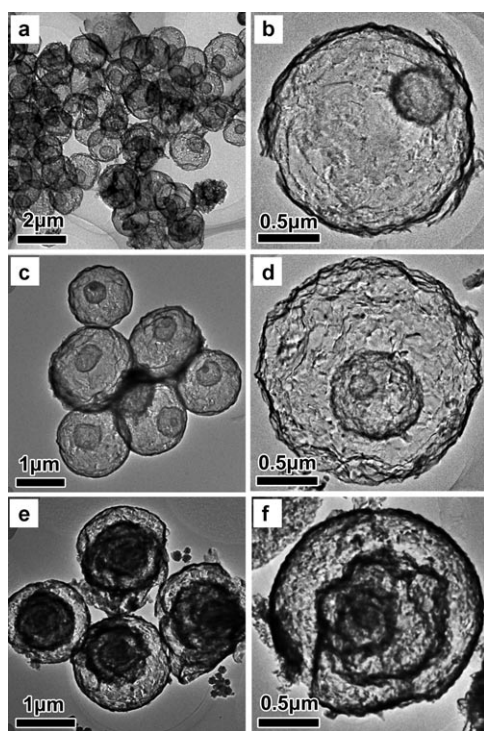


Figure 1. TEM images of a,b) double-shell α -Fe₂O₃ hollow microspheres; c,d) triple-shell α -Fe₂O₃ hollow microspheres; e,f) quadruple-shell α -Fe₂O₃ hollow microspheres.

and their homogeneous composition. Increasing the concentration of the iron nitrate solution to 3 mol L⁻¹ yielded α -Fe₂O₃ hollow microspheres with three shells (Figure 1c,d). Further by increasing the concentration of the iron nitrate solution to 5 mol L⁻¹, hollow microspheres with four shells were also obtained (Figure 1e,f). Powder X-ray diffraction (XRD) confirmed that the all the multiple-shell hollow microspheres were composed of crystalline α -Fe₂O₃ (JCPDS 33-0664) without any other phases present.

The shell formation process was studied in more detail by carrying out the reactions at various temperatures (Figure 2 and Figures S3 and S4). Carbonaceous microspheres were soaked in the iron nitrate solution and heated to 500 °C at the

rate of 2 °C min⁻¹. The products were characterized after different times in the heating process. Relative to the carbonaceous particle at room temperature in Figure 2a, the TEM image in Figure 2b showed that there is no visible change when the sample is heated to 270 °C except for the decrease in diameter from 3.4 to 2.4 μm. A reaction temperature of 350 °C led to the formation of a shell around a solid sphere (Figure 2c). The characteristic peaks of resultant materials in Raman spectra of Figure 2f suggest the formation of hematite, which is also evidenced by its XRD data in Figure 2g, whereas the reduction of Raman signals of carbon reveals the degradative oxidation of carbonaceous template. When the temperature reaches 430 °C, the outer hematite shell somewhat shrunk but the inner solid core sharply contracted and also changed to a core-shell sphere, resulting in a core-double shell structure (Figure 2d). Increasing the temperature further to 500 °C led to a hollow core, or a triple-shell hollow structure shown in Figure 2e. Thermogravimetric analysis (TGA) results suggest carbon template could be completely removed (Figure S5a).

The studies of the various reaction conditions confirm that the multiple-shell metal oxide hollow microparticles form by a sequential templating process. There are two prerequisites for this method to work: 1) there must be a large penetration depth of iron ions within the carbonaceous microsphere, and 2) the rate of metal oxide shell formation must match with the rate of carbonaceous microsphere disintegration. When the annealing temperature is relatively low, the contraction of the carbonaceous microspheres by degradative oxidation is slow (Figure S5b), allowing iron to concentrate within carbonaceous template matrix and cross-link to form the iron oxide shell. At higher temperature, separation occurs between the iron oxide shell and the shrinking carbonaceous template owing to their different rates of formation and disintegration. If the penetration depth of iron ions within the carbonaceous microspheres is too short, all the iron ions distribute in the narrow region near the surface and very likely form a single shell because of the shorter ion diffusion length. Sequentially, hollow spheres with only a single shell form, as there is not enough iron to sustain the formation of more shells (Figure S6). When the penetration depth of iron ions within the carbonaceous microspheres is large enough, only a fraction of the iron within the carbonaceous microspheres joins in the creation of first outer shell of hematite, whereas the others remain within inner carbonaceous microsphere and supply iron resource for the creation of inner shells. Larger penetration depth of iron ions within the carbonaceous microspheres possibly lead to the formation of more shells. A large number of methods are available for increasing the penetration depth of iron ions, such as adjusting the concentration of precursor solution (in this case) or changing the solvent, absorption temperature, or time.

Moreover, TGA provided another estimate of the rate of size decrease of the carbonaceous microsphere during heating (Figure S5b), which was consistent with that observed by TEM images of intermediate products (Figure 2). We also note that the size of second shells in double-shell, triple-shell, and quadruple-shell structures is different from each other, possibly deriving from shell formation in different stages of

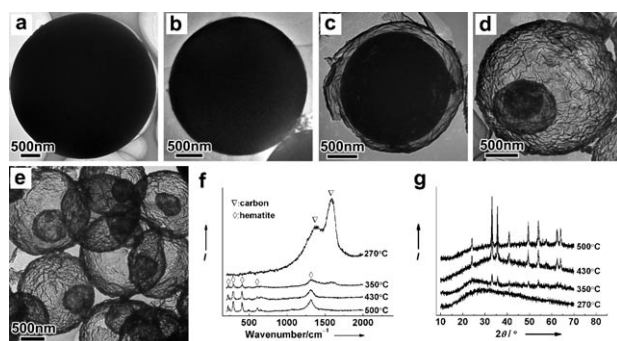


Figure 2. TEM images of carbonaceous microspheres after soaking in a 3 mol L⁻¹ solution of iron nitrate: a) before heating, and after heating at b) 270 °C, c) 350 °C, d) 430 °C, and e) 500 °C. f,g) Corresponding Raman spectra (f) and XRD patterns (g).

carbonaceous microsphere contraction (i.e. the different template sizes). The rate of carbonaceous microsphere shrinkage could be slowed by heating in an N_2 atmosphere, instead of air. As a result, microspheres soaked in iron nitrate solution (3 mol L^{-1}) gave only single-shell hollow microspheres (Figure S7). These results suggest the possibility of adjusting the textural parameter of multiple-shell hollow structure through controllable contraction of carbonaceous microsphere by various techniques, such as heating rate and atmosphere type., which may be favorable for their practical application.

The hollow structure morphology of hematite can be expected to dramatically benefit surface-related applications, such as gas sensing. Hollow iron oxide microspheres were tested as an ethanol-sensing material. The gas sensitivity is defined as the resistance ratio $R_{\text{air}}/R_{\text{gas}}$, in which R_{air} and R_{gas} are the electrical resistances for sensors in air and in ethanol gas, respectively. Figure 3 shows the gas-sensing behavior of

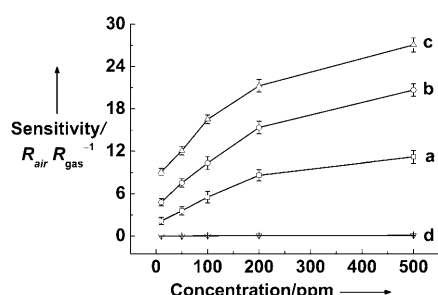


Figure 3. Sensor response in the presence of ethanol from $\alpha\text{-Fe}_2\text{O}_3$ hollow spheres with different numbers of shells: a) single-shell, b) double-shell, c) triple-shell, and d) bulk $\alpha\text{-Fe}_2\text{O}_3$ particles.

$\alpha\text{-Fe}_2\text{O}_3$ hollow microspheres with different numbers of shells in the presence of ethanol. Solid $\alpha\text{-Fe}_2\text{O}_3$ particles used as a reference sample were found to be nearly insensitive to the presence of ethanol. In contrast, the resistance of the hollow shells was very sensitive to ethanol. This sensitivity may be attributed to the larger specific surface areas of the latter (85 , 80 , and $48 \text{ m}^2 \text{ g}^{-1}$ for single-shell, double-shell, and triple-shell hollow microspheres respectively; Figure S8) than that of the former ($4 \text{ m}^2 \text{ g}^{-1}$), which allows them to absorb more gas molecules. The sensitivity of the electrical resistance to ethanol is also increased significantly when the particles had an increasing number of shells. A number of factors in addition to specific surface area (such as grain size, and porosity) can affect the gas sensitivity of a semiconductor^[6] and the underlying reasons for the observed behavior still need further study. Nevertheless, these results exhibit the considerable advantages of multiple-shell hollow microspheres, which could be potentially useful in gas detection.

Different types of multiple-shell hollow microspheres, such as Co_3O_4 , NiO , CuO , and ZnO , could also be fabricated by soaking the carbonaceous microspheres in solutions with the corresponding metal ion species (Figure 4a–f and Figures S9 and S10). Furthermore, binary metal oxide (ZnFe_2O_4) and heterogeneous metal oxide ($\text{ZnO@ZnO/ZnFe}_2\text{O}_4\text{@ZnO/ZnFe}_2\text{O}_4$) multiple-shell hollow microspheres were also

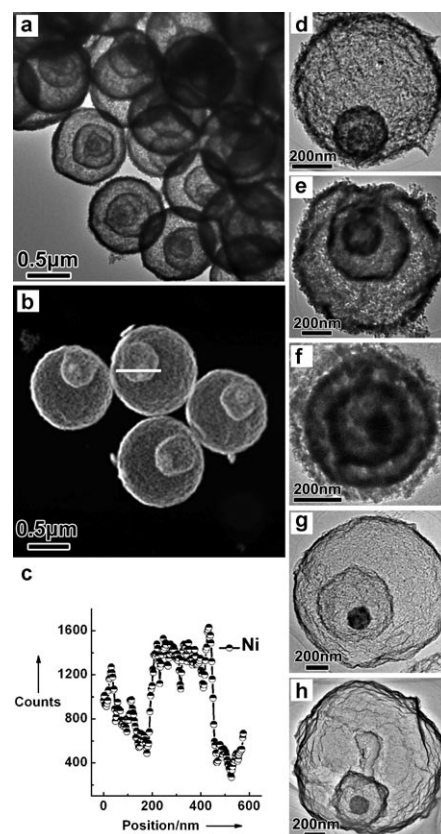


Figure 4. a) TEM image of quadruple-shell NiO hollow microspheres; b) STEM image and c) EDS line scanning of triple-shell NiO hollow microspheres; TEM images of other multiple-shell hollow microsphere of d) Co_3O_4 , e) CuO , f) ZnO , g) ZnFe_2O_4 , and h) $\text{ZnO@ZnO/ZnFe}_2\text{O}_4\text{@ZnO/ZnFe}_2\text{O}_4$.

prepared by the simultaneous or successive use of different metal ions (Figure 4g,h and Figures S11–S17). Moreover, we noted that only a minority of metal oxides in which the diameter of outer shell and inner hollow cores are relatively close could have their cores in the center of the core–shell configuration (for example, those in Figure 1f and Figure 4a,f), but the position of cores in others is random. This result may suggest that these inner hollow cores are not fixed on the outer shell but are movable. Those cores in the former have very limited movable region (since its diameter is close to that of outer shell) and thus tend to stay at the center, whereas those cores in the latter possess relatively broad movable region and have not fixed position. Nevertheless, all these results suggest the generality of the present synthesis method. In particular, the formation of all shells and the removal of template were completed by a simple one-step heating treatment, which is highly desirable for large-scale production.

In summary, a general and facile method for the synthesis of multiple-shell metal oxide hollow microspheres by using carbonaceous microsphere as a template was demonstrated. All of the shells were created by a one-step thermal treatment. The number and composition of shells could be rationally designed by adjusting the heating conditions and the concentration and type of metal salt species used. The

strategy used herein could be expected to prepare other multiple-shell hollow structures with different shapes, sizes, and compositions by choosing appropriate template and precursor material. The research may open up new opportunities for preparing advanced materials based on various complex multiple-shell hollow structures for multipurpose applications.

Experimental Section

All reagents were analytical grade and purchased from Beijing Chemical Co. Ltd., and used without further purification. Hydrated metal nitrates ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were used as metal precursors. Taking $\alpha\text{-Fe}_2\text{O}_3$ triple-shell hollow microsphere as an example, a typical synthesis process is described as follows: Carbonaceous microspheres were synthesized through the emulsion polymerization reaction of sugar under hydrothermal conditions as described elsewhere.^[5b] Newly prepared carbonaceous microspheres (0.4 g) were dispersed in iron nitrate solution (20 mL; 3 mol L^{-1}) with the aid of ultrasonication. After ultrasonic dispersion for 15 min, the resulting suspension was aged for 6 h at room temperature, filtered, washed, and dried at 80°C for 12 h. The resultant composite microspheres were heated in air at 2°C min^{-1} up to 500°C , kept at this temperature for 4 h, and cooled naturally to room temperature. As-formed products, $\alpha\text{-Fe}_2\text{O}_3$ triple-shell hollow microspheres, were accumulated. Other metal oxide multiple-shell hollow microspheres, such as Co_3O_4 , NiO , CuO , and ZnO , were also synthesized by following a similar procedure.

Powder X-ray diffraction (XRD) patterns were recorded with an X'Pert PRO MPD [$\text{Cu}_{\text{K}\alpha}$ radiation (λ , 1.5405 Å)], operating at 40 kV voltage and 30 mA current. Scanning electron microscopy (SEM) images were obtained using a JSM-6700 microscope operating at 5.0 kV voltage. Transmission electron microscopy (TEM) images were taken on a FEI Tecnai F20 instrument at an acceleration voltage of 200 kV. Raman spectra were performed on LabRAM HR800 spectrometer manufactured by Horiba Jobin Yvon company, France. The laser excitation wavelength was 514 nm. The thermal analysis was carried out up to 800°C on a Labsys Evo apparatus (SETARAM, Caluire, France) at a heating rate of 2°C min^{-1} in air. The nitrogen adsorption-desorption isotherms at the temperature of liquid nitrogen (-196°C) were measured on a Quantochrome Autosorb-1 sorption analyzer with prior degassing under vacuum at 200°C overnight. The gas sensors were fabricated by coating an ethanol suspension of $\alpha\text{-Fe}_2\text{O}_3$ onto alumina tubes with gold electrodes. The fabrication and measurements of the gas-sensing of alcohol vapor were similar to that for ZnFe_2O_4 core-shell hollow microspheres.^[5b]

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