

A template-free nano-wrapping technique for the fabrication of copper hollow nanospheres smaller than 20 nm

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Received (in Cambridge, UK) 23rd July 2008, Accepted 30th September 2008

First published as an Advance Article on the web 4th November 2008

DOI: 10.1039/b812651h

A new template-free “nano-wrapping” method has been developed for the fabrication of copper hollow nanospheres with the smallest size of around 15 nm and its significance is highlighted to its composition tunability of the metal encapsulated inside the copper nanoshell.

This study reports the synthesis of the world's smallest copper hollow nanosphere with a diameter smaller than 20 nm using a template-free method. Because no template is required, metallic hollow nanospheres as small as 15 nm can be fabricated by this technique. A four-step mechanism is proposed to explain the formation of metal hollow nanospheres. This “nano-wrapping” method has also been applied to encapsulate metal nanoparticles inside the metal hollow nanosphere. This approach is an alternative for the fabrication of core-shell materials. It provides an opportunity to tailor the active metal elements inside the hollow metallic sphere. The hollow nanospheres have the potential to be packed into periodic three-dimensional metallic structures which have special optical and electronic applications. The findings in this study might open a new research area in the development of core-shell nanomaterials.

Hollow metallic nanospheres have drawn much attention recently. Because of their increased surface area, reduced densities, and tunable surface plasmon resonance (SPR) features,¹ hollow metallic nanospheres have great potential applications in many areas, including optical imaging,² surface enhanced Raman scattering (SERS),³ photothermal therapy,⁴ catalysis,⁵ optical material synthesis,⁶ bioapplication,⁷ and hollow microcapsule synthesis.⁸ The synthesis of nanospheres is normally carried out using a hydrothermal method requiring essential agents such as precursors of metal salts and an organic template followed by mixing, aging and calcination processes. The templating synthesis method, however, has a drawback that the size of the hollow metal shell is greatly dependent on the dimensions of template molecules. Thus, the final product has relatively large dimensions,⁹ in the range of around 50–100 nm in diameter.¹⁰ Liang and co-workers were able to make gold and platinum hollow nanospheres with a particle size of around 20 nm using silica as templates.¹¹ Xia's group has successfully synthesized hollow silver nanospheres with a dimension of around 11–15 nm by using a novel protocol of galvanic replacement reaction,¹² which is a template-free technique. However, the composition in the interior of the nanoshells is difficult to be tailored by these methods. Although the above methods are able to synthesize small hollow nanostructures of

noble or coinage metals such as platinum,¹¹ silver,¹² and gold,¹³ in the other hand, copper, which has been proved to be catalytically active,¹⁴ with hollow structures and small dimensions (~15 nm) cannot be found so far in the literature.

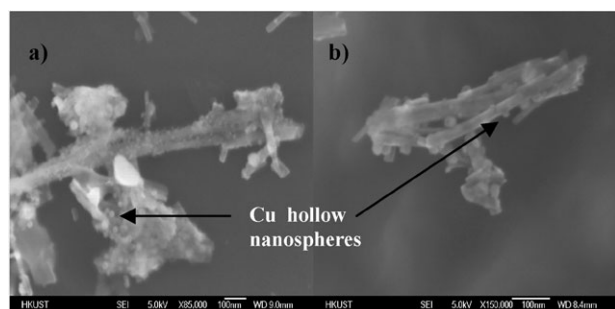
In this study we developed a new template-free protocol which can solve the problems of the conventional templating technique and tailor the active metal contents inside the hollow metal nanospheres effectively. Metal organic chemical vapor deposition (MOCVD), which is commonly used in the semiconductor industry, was used in this synthesis. By using zeolite 13X as the substrate, and carefully controlling the preparation, 20 nm nanoparticles can be fabricated. Based on our hypothesis, the formation of metal hollow nanospheres was shown to follow a four-step mechanism. We have also applied the “nano-wrapping” method to encapsulate metal nanoparticles inside the metal hollow nanosphere. More importantly, the reaction volume in the interior of this nanoparticle-encapsulated metallic hollow nanosphere is very significant compared to those of existing core-shell structured nanomaterials. This is exceptionally promising for nanoreactor design. Copper hollow nanospheres were synthesized by using metal organic chemical vapor deposition (MOCVD). Copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$) and zeolite 13X, supplied by Sigma-Aldrich and Alltech chemicals companies, were used as the precursor and the substrate, respectively. For each experiment, both precursor and substrate were mechanically mixed together in a mass ratio ($\text{Cu}(\text{acac})_2$: zeolite 13X) of 1 : 1. The mixture was heated to 190 °C with a ramping rate of 5 K min⁻¹ under a hydrogen flow of 0.5 mL s⁻¹ and kept at this temperature for 30 min for the deposition of a copper layer on the zeolite surface. It was then further heated to 350 °C with the same heating rate and kept at that temperature for another 30 min. The as-synthesized Cu hollow nanosphere/zeolite 13X was cooled down under the hydrogen flow and the final product was stored in a desiccator. For the synthesis of iron-encapsulated copper hollow nanospheres supported on zeolite 13X, an additional step was introduced. The iron precursor ($\text{Fe}(\text{acac})_3$) ($\text{Fe}(\text{acac})_3$: $\text{Cu}(\text{acac})_2$ = 1 : 3) was introduced after the deposition of the copper layer on the zeolite surface. Such a step would allow the iron element to be deposited on the copper layer. The iron precursor was heated at the same temperature (190 °C) for 30 min. The remaining steps were the same as for the copper hollow nanosphere formation.

Table 1 shows the compositions of the prepared zeolite-supported copper hollow nanospheres ($\text{Cu}/13\text{X}$) in comparison with blank zeolite 13X by using the XRF analytical technique. The tested samples were found to be mostly siliceous-based with some amount of other elements such as sodium, magnesium and aluminum. It is noted that after the MOCVD process copper has been loaded onto the zeolite 13X with an amount of

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Table 1 Compositions of zeolite 13X and zeolite 13X-supported copper hollow nanospheres by XRF analysis

Sample	Blank 13X	Cu/13X
O	61.8	57.5
Na	6.29	5.95
Mg	1.56	1.34
Al	10.3	9.63
Si	17.7	17.0
S	0.04	0.52
K	0.22	0.22
Ca	1.82	2.20
Mn	0.00	0.00
Fe	0.24	0.24
Cu	0.00	5.38

**Fig. 1** SEM images of Cu hollow nanospheres/zeolite 13X.

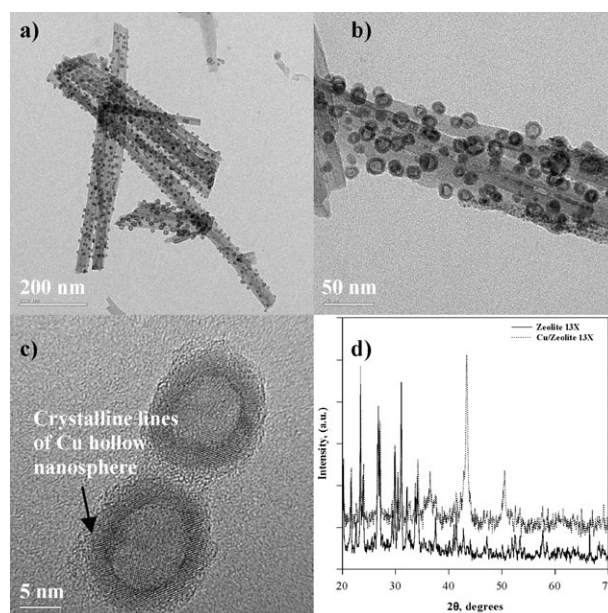
around 5.38 mol%. The copper was deposited as spherical objects on the surface of rod-shaped zeolite 13X crystals, as depicted in the SEM images in Fig. 1. The copper spheres are seen to distribute on the zeolite surface quite evenly in a close view (Fig. 1(b)). It is difficult to distinguish hollow nanospheres and nanoparticles in the SEM images. Therefore, TEM images were obtained for this purpose, as shown in Fig. 2.

Fig. 2(a) and (b) show that many copper hollow nanospheres are formed along the zeolite surface. The copper hollow nanospheres are spherical in shape and are distributed evenly over the substrate surface. It is also seen that the sizes of copper nanoshells have a narrow distribution. The reason may be that the self assembly process highly depends on the surface tension of copper element to the zeolite surface. A slight difference in the surface tension will cause the dimension variation of copper nanoshells.

The metallic status of the nanoshells can also be confirmed by XRD spectroscopy of Cu/13X, as shown in Fig. 2(d). Strong peaks at 43.3° (111) and 50.4° (200) are found, which are the blueprints of elemental copper to prove its existence with the corresponding crystalline planes.

The high crystallinity of elemental copper can be seen by the high intensity of the two peaks in the XRD spectroscopy and further confirmed by the clear parallel lines of the metallic shell in the TEM image displayed in Fig. 2(c). It is seen that the detached copper hollow nanospheres are around 15 nm in diameter with a shell thickness of around 2–3 nm. Moreover, clear parallel lines in different directions are observed in the image, implying that the copper shells are formed by random packing of copper atoms.

In order to have a better understanding of the formation mechanism of copper hollow nanospheres, we have also tested the same synthesis method for other substrates including

**Fig. 2** (a), (b) and (c): TEM images of Cu/zeolite13X; (d) XRD spectra of zeolite 13X and Cu/zeolite 13X.

bentonite clay, acid-treated bentonite clay,¹⁵ alumina and mesoporous silica (MCM-41 and SBA-15). No copper hollow nanospheres are observed when these substrates are used. However, for other zeolite substrates such as HZSM-5, NaY and 3A molecular sieves, copper nanoshells can be formed. This can be explained by the well known unique catalytic property of zeolitic material for organics synthesis. Since the precursor (copper(II) acetylacetonate) used is an organometallic compound, it can be catalyzed by the zeolitic surface to form self-assembled precursor molecules, followed by the detachment of organic ligand of the precursor in the presence of hydrogen, and copper hollow nanospheres are eventually formed. This new approach is beneficial because of its simple procedure (one-step synthesis) compared to conventional templating methods. More importantly, the hollow nanospheres obtained are of pure metal and are thermally stable up to a high temperature of 700°C . Pure metal nanostructures are difficult to be synthesized by a templating method because a calcination step is always involved in order to remove the organic ligands. Besides, some other metals such as iron and nickel have also been tested for nanoshell formation. However, iron can only exist as a layer or particle forms but not as a shell. For nickel, it can also form nanoshells.

The packing (formation) mechanism of copper hollow nanospheres on the surface of zeolite 13X is suggested as Fig. 3. The mechanism includes four steps: (a) free standing of precursor molecule, (b) self-assembly of precursor molecules on zeolitic surface, (c) detachment of precursor ligand by hydrogen reduction, and (d) the wrapping process of the deposited copper element.

In the chemical vapor deposition process, the solid precursor, $\text{Cu}(\text{acac})_2$, is first sublimed and occurs as free precursor molecules in the vapor phase during the heating process. At the same time, the gaseous precursor molecule will be gradually adsorbed on the zeolite surface by attaching with oxygen atoms of silanol groups.¹⁶ Because the incorporated aluminium ion on the zeolite surface has a high catalytic and polymerizing effect

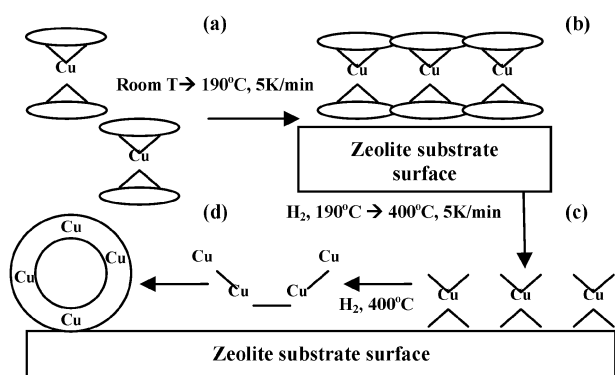


Fig. 3 A schematic hypothesis of copper hollow nanosphere formation.

towards carbon-containing ligands, the self-assembling occurs with the organic ligand attached onto the zeolite surface. As the temperature is increased from 190 to 400 °C, the adsorbed or oxygen-linked metal complexes are reduced by hydrogen and the subsequent volatile products (pentanedione) are detached from the deposited precursor, leaving elemental copper on the zeolite surface. The pure copper with vacant site at one end will agglomerate at this temperature due to the surface tension. Therefore, copper hollow nanospheres will be finally formed on the zeolite surface with an even distribution. Since such a synthesis method is driven by the self assembly process, the size of shell is believed to be the smallest possible. This mechanism is crucial to the incorporated aluminium element which plays an important role in the polymerizing and catalytic effects towards the organic metal complex ($\text{Cu}(\text{acac})_2$). This also explains why no copper nanoshells can be formed on MCM-41, SBA-15, alumina or silica, although they contain silanol groups.

To further validate this mechanism, an iron precursor ($\text{Fe}(\text{acac})_3$) is introduced in step (b) and the same procedures as in copper deposition were followed. Fig. 4(a) shows a general view of the synthesized Fe-encapsulated Cu/zeolite 13X. Some nanoparticles which are shown in dark regions have been encapsulated by copper hollow nanospheres. A more detailed close up image as shown in Fig. 4(b) reveals that an iron nanoparticle has been encapsulated in the copper hollow nanosphere that was supported on zeolite 13X. Three areas (A, B and C) in Fig. 4(b) were chosen for characterization by TEM-EDX which shows that both copper and iron nanoparticles have been enclosed by the copper hollow nanosphere. The results are listed in Table 2.

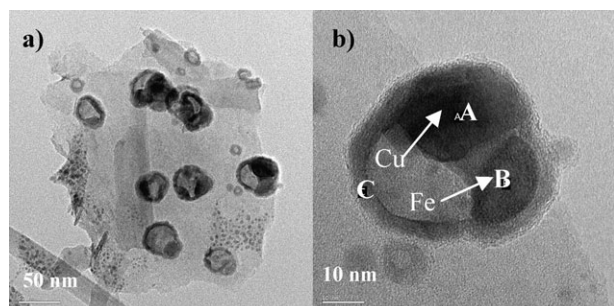


Fig. 4 TEM image of iron-encapsulated copper hollow nanosphere supported on zeolite 13X.

Table 2 Elemental compositions by TEM-EDX analysis of selected areas of an iron-encapsulated copper hollow nanosphere supported on zeolite 13X

	Area A		Area B		Area C	
	Peak area	Atom%	Peak area	Atom%	Peak area	Atom%
O K	155	4.86	476	17.57	352	27.6
Si K	0.00	0.00	124	1.97	680	22.89
Fe K	0.00	0.00	4245	74.68	72	2.69
Cu K	5051	93.95	204	4.47	945	43.93

Area B contains mainly iron (~75%) and the remaining detected elements are from the zeolitic substrate and the copper shell. For area C, copper is the main element in the nanoshell. Signals of silicon and oxygen are mainly from the background zeolitic substrate while the signal of iron is possibly originated from secondary electrons or fragments of the deposited amorphous iron. This demonstrates that the composition inside the hollow nanospheres can be tailored by depositing different metals. Moreover, the void space of copper hollow nanosphere is able to contain other active metal elements such as iron. Therefore, this new approach is particularly useful for the synthesis of microcapsular reactors as the interior composition can be tuned by depositing different active metal elements. It is believed that this approach can open a new application for the chemical vapor deposition method in the area of nanomaterial synthesis.

This project was supported by the HKUST grant No. HKUST2/CRF-SF/08.

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