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# Low temperature fabrication of hollow carbon nanospheres over $Ni/Al_2O_3$ by the catalytic method

Haipeng Li [a,b], Naiqin Zhao [a,*], Chunnian He [a], Chunsheng Shi [a], Xiwen Du [a], Jiajun Li [a]

[a] *School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China*
[b] *School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300130, China*

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**Abstract**

A mass of hollow carbon nanospheres was fabricated by chemical vapor deposition of methane over $Ni/Al_2O_3$ catalyst at 600 °C. The products were characterized with scanning electron microscope, transmission electron microscope, and high-resolution transmission electron microscope images. The results showed that the external diameter of the hollow carbon nanospheres was 5–90 nm and the thickness of the wall was about 15 nm. And a possible formation mechanism of the hollow carbon nanospheres was discussed.


*Keywords:* Fullerenes; Nanostructures; Vapor deposition; Chemical synthesis; X-ray diffraction

## 1. Introduction

In recent decades, the fabrication of fullerenes [1], carbon nanotubes (CNTs) [2], and carbon onions [3] has attracted much attention in nanostructured carbon field. Various methods have been developed to synthesize these carbon nanomaterials with different structures [1–5], due to their unique properties and potential applications in the fields of conductive and high-strength composites, semiconductor devices, nanotweezers, field emission displays and gas storage media [6–10]. Besides, the synthesis of carbon nanocapsules has practical interest because they allow the encapsulation of different materials within the empty core domain. Therefore, hollow carbon nanospheres (HCNSs), which represent a special class of materials, are very promising as photonic crystals, excellent supports for catalysts, and anode in secondary lithium ion batteries, etc. [11–13].

Previously, various methods have been demonstrated for the synthesis of HCNSs [14–21], such as mixed-valent oxide-catalytic carbonization process [14], chemical vapor deposition method by using mesoporous silica [15], pyrolysis hydrocarbon via high temperature with certain catalyzers [16,17], shock compression from $C_{60}$ fullerene [18], media-reduction route [19,20], self-assembly approach [21], etc. Complicated processes or hazardous experimental conditions are necessary for the above methods. Nowadays, it is still a challenge to find an appropriate route to obtain hollow carbon nanostructures.

In this paper, we report a new process for synthesizing HCNSs. The method involves the preparation of the catalyst precursor $Ni(OH)_2/Al(OH)_3$ and the catalytic decomposition of methane over $Ni/Al_2O_3$ catalyst. Generally, the Ni nanoparticles favor the CNT growth. However, in this work the formation of CNTs was totally inhibited. Therefore, it is very worthy to investigate the structure and growth mechanism of our HCNSs and lead to the better control of the formation of high quality HCNSs.

## 2. Experimental

Previously [22,23], we have fabricated the Ni/Al catalyst using a precipitation route. Here we also used this process but excess NaOH (till the pH value of the solution arrived at 10) to produce binary colloid $Ni(OH)_2/Al(OH)_3$ (weight ratio Ni/Al = 2/3). After that the colloid was calcined in air to yield clusters made of Ni and Al oxides and then reduced in an $H_2$ flow (100 ml/min) at 600 °C for 120 min to form Ni nanoclusters supported on $Al_2O_3$.

To synthesize HCNSs, 50 mg $NiO/Al_2O_3$ distributed in a quartz boat uniformly was placed into a tube furnace. When the furnace reached 600 °C under

* Corresponding author. Fax: +86 22 27405874.
*E-mail address:* nqzhao@tju.edu.cn (N. Zhao).

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nitrogen, hydrogen (100 ml/min, 99.99% purity) was introduced to reduce the catalyst for 2 h. Then the hydrogen flow was stopped, and a mixture of $CH_4/N_2$ (60/420 ml/min, v/v) was introduced into the tube and maintained for 1 h. After the growth, the furnace was cooled to room temperature under $N_2$ and black powder was obtained.

The as-grown HCNSs were characterized using field emission scanning electron micrograph (FE-SEM) (JEOL JSM-6700F) and transmission electron microscope (TEM) (Philips Tecnai $G^2$ F20, 200 kV).

## 3. Results and discussions

The morphologies of the as-grown HCNSs were characterized by SEM and TEM. Fig. 1 shows a SEM image of the as-prepared hollow carbon nanospheres fabricated by the catalytic method over $Ni/Al_2O_3$ catalyst. From SEM image it is found that the most of the spherical nanoparticles are in the range of 5–90 nm and average is about 35 nm. In addition, we can find that some carbon nanowires coexist with the spherical nanoparticles, which may be from the catalytic growth of active Ni catalyst. In this work, after the synthesis of HCNSs, 50 mg $NiO/Al_2O_3$ (i.e. 45.47 mg $Ni/Al_2O_3$) catalyst can obtain 52.27 mg C–$Ni/Al_2O_3$ composite powder. That means the carbon yield is 6.8 mg/1 g $NiO/Al_2O_3$ catalyst.

A representative low-magnification TEM micrograph of the products is shown in Fig. 2(a). Based on large numbers of TEM observations, the proportion of HCNSs in the samples is estimated to be about 65%. The external diameter of the HCNSs is 5–90 nm and the thickness of the wall ranges from 2 to 50 nm. The diameter and wall thickness are much smaller than that of the HCNSs reported in the literatures [20,24]. Thus, the HCNSs may be important application in future nano-industry, especially for rising biological field.

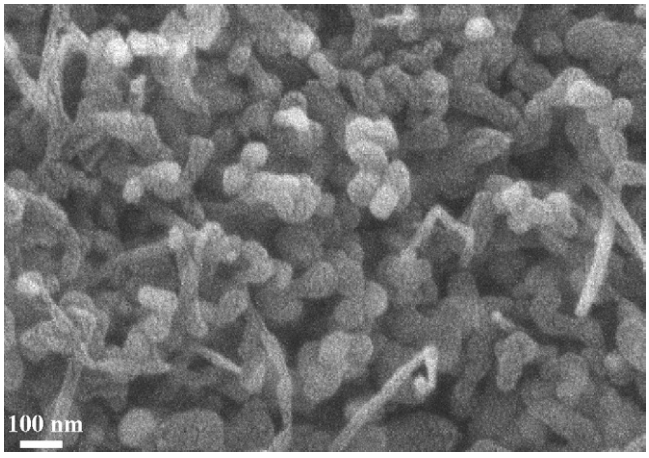


Fig. 1. SEM image of the as-prepared hollow carbon nanospheres fabricated by the catalytic method over $Ni/Al_2O_3$ catalyst.

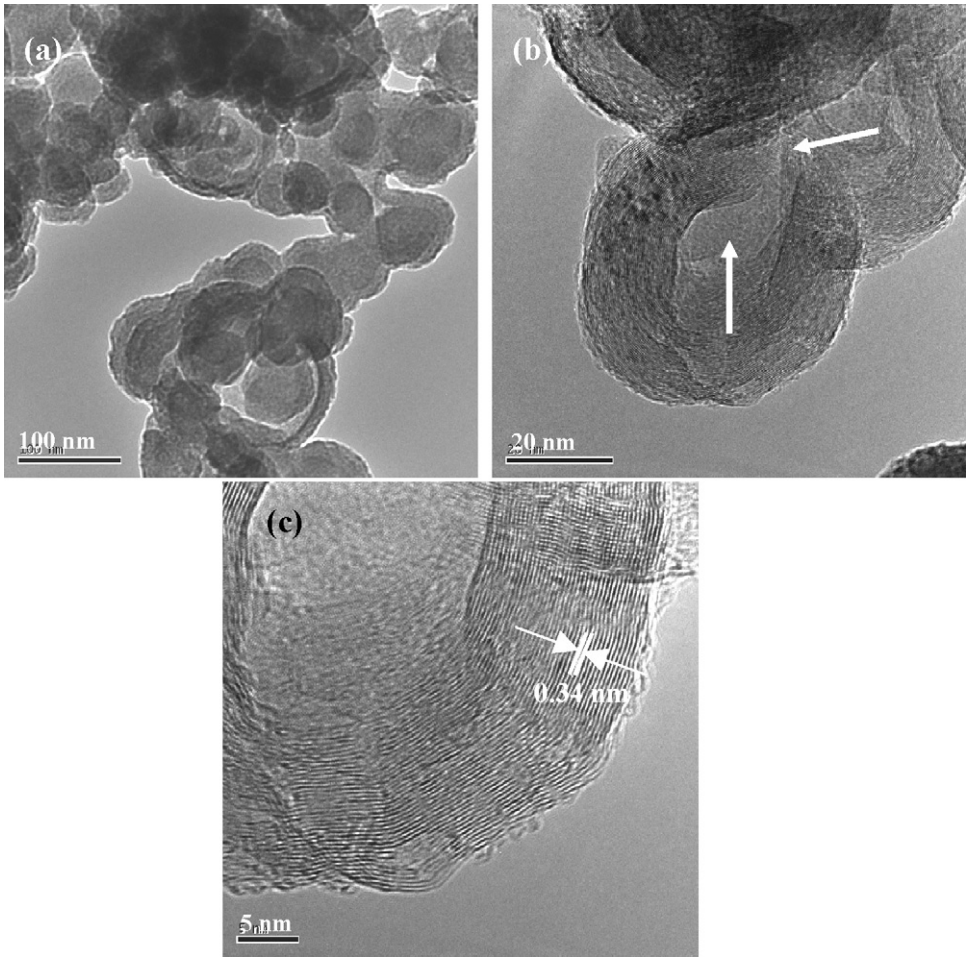


Fig. 2. Typical TEM images of the as-prepared hollow carbon nanospheres fabricated by the catalytic method over $Ni/Al_2O_3$ catalyst.

Typical HRTEM images of the HCNSs are presented in Fig. 2(b) and (c). Broken sphere (marked with arrow) and the strong contrast between the dark edge and pale center are revealed in Fig. 2(b), providing further proof of the hollow nature. Fig. 2(c) shows one typical HCNSs in high magnification. It indicates that the hollow spheres are composed of carbon sheets, and the average wall thickness of HCNSs is about 10 nm. The HCNSs shell consists of about 32 graphitic layers. Fig. 2(c) also reveals that the sheets are well graphitized and the interlayer spacing is about 0.34 nm, which is consistent with the d value of (0 0 2) plane of hexagonal graphite.

Except for the HCNSs, a few carbon coated Ni nanoparticles can also be found in Fig. 3(a), and the carbon coated Ni nanoparticles have almost the same inner and outer diameters as the HCNSs. HRTEM images of the carbon coated Ni nanoparticles are presented in Fig. 3(b) and (c). These images further reveal the presence of carbon coated Ni nanoparticles in the sample. The nanoparticles are composed of a metallic core and a carbon shell. The carbon shell present in the nanocapsules has a crystalline graphite structure. And the interlayer spacing between graphitic sheets is 0.34 nm, consistent with the ideal graphitic interlayer space (0.34 nm). The thickness of the coating shell of the nanocapsules is in the range of 5–50 nm. These thin carbon-coating shells can give effective protection of corrosion for the metal nanoparticles and not degrade the magnetic properties of the metal nanoparticles too much.

To achieve a controllable growth of the HCNSs with high quality, understanding of their growth mechanism is of importance, which still remains an open question. Recently, many studies on the HCNSs have discussed the reason for the formation of hollow core. Katcho et al. [25] have produced HCNSs by the chlorination of ferrocene at 900 °C, and proposed a speculation to elucidate their experimental results. They pointed out that iron might play a role in the making of the hollow carbon spheres. However, they have not found evidence by TEM of the presence of iron metallic particles that could catalyze the growth of the hollow spheres in a way similar to that occurring in the catalytic synthesis of carbon nanotubes. On the other hand, Genga et al. [26] have also obtained hollow carbon nanospheres through a ZnSe nanoparticle template route. They first produced carbon encapsulated ZnSe nanoparticles by non-catalytic one-step thermal evaporation method and then obtained carbon hollow spheres by a thermal conversion process. For the growth mechanism of HCNSs, they suggested that the thermal decom-

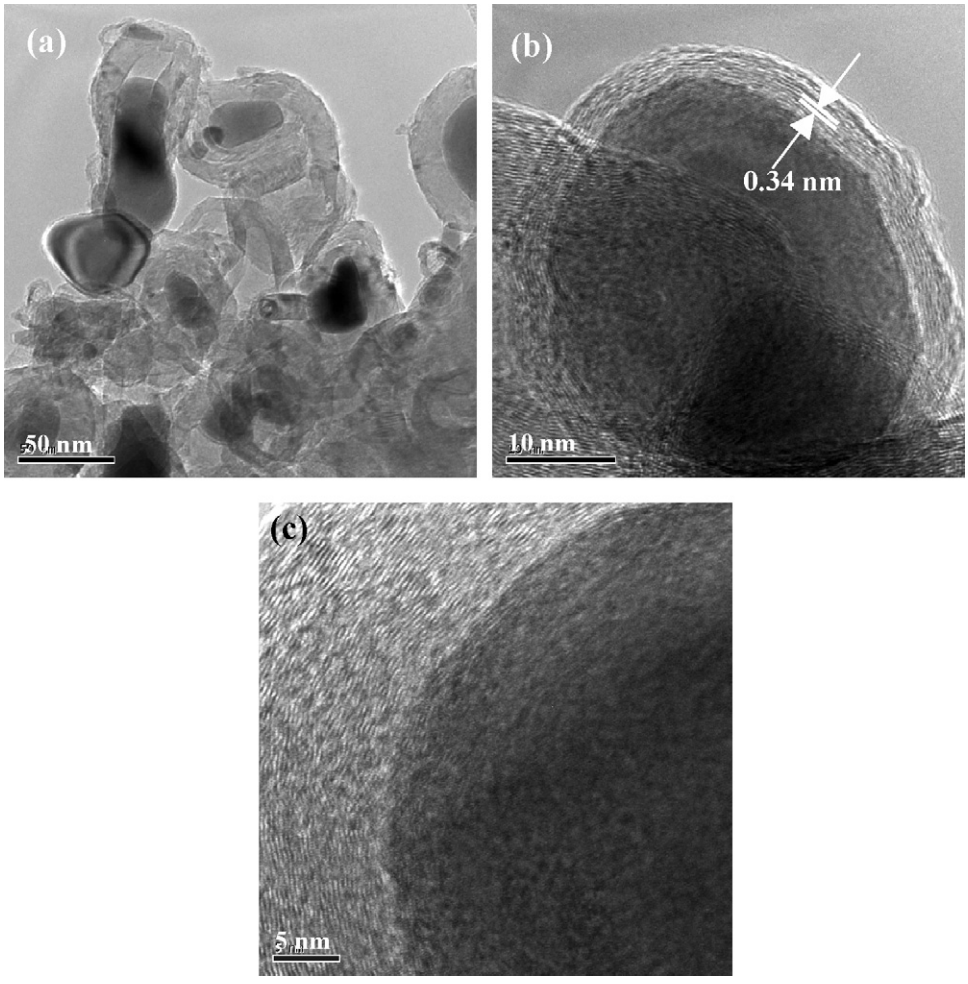


Fig. 3. Typical TEM images of a few carbon coated Ni nanoparticles coexisted with the hollow carbon nanospheres fabricated by the catalytic method over $Ni/Al_2O_3$ catalyst.

position of the toluene took place and produced carbon shells on the surface of the ZnSe nanoparticles. With increasing temperature, ZnSe pyrolysis took place and led to form the carbon hollow nanostructures. However, two above hypotheses cannot be used to explain our results due to different synthesis process of HCNSs in this work. Furthermore, another characteristic of our results consists in possessing two main different kinds of carbon nanostructures (HCNSs and carbon coated Ni nanopartilces), which also suggests that the growth of our HCNSs fabricated by CVD may follow a different mechanism. Therefore, a possible formation mechanism of our HCNSs and carbon coated Ni nanoparticles is proposed. At the beginning of the reaction, the methane decomposes into hydrogen gas and carbon atoms over active Ni catalyst. Then, these freshly formed carbon atoms grow into small graphite sheets because the growth rate of graphite along the *c*-axis is much lower than that along any other axis. When the graphite layers closed upon themselves due to that the Ni particles acted as a catalyst, inducing curvature in graphite layers, some Ni particles might be displaced before closure, while some others were trapped inside and could not escape, then the two different kinds of carbon nanostructures could be obtained.

## 4. Conclusion

A mass of hollow carbon nanospheres was fabricated by chemical vapor deposition of methane over $Ni/Al_2O_3$ catalyst at 600 °C. The products were characterized with scanning electron microscope, transmission electron microscope, and high-resolution transmission electron microscope images. The results showed that the external diameter of the hollow carbon nanospheres was 5–90 nm and the thickness of the wall was about 15 nm. A possible formation mechanism of the hollow carbon nanospheres was discussed.

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