Graphitized hollow carbon spheres and yolk-structured carbon spheres fabricated by metal-catalyst-free chemical vapor deposition

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ABSTRACT

Hard-sphere-templating method has been widely used to synthesize hollow carbon spheres (HCSs), in which the spheres were firstly coated with a carbon precursor, followed by carbonization and core removal. The obtained HCSs are generally amorphous or weakly graphitized (with the help of graphitization catalysts). In this work, we report on the fabrication of graphitized HCSs and yolk-shell Au@HCS nanostructures using a modified templating method, in which smooth, uniform graphene layers were grown on SiO₂ spheres or Au@SiO₂ nanoparticles via metal-catalyst-free chemical vapor deposition (CVD) of methane. Our work not only provides a new method to fabricate high-quality, graphitized HCSs but also demonstrates a reliable approach to grow quality graphene on oxide surfaces using CVD without the presence of metal catalysts.

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1. Introduction

In recent years, the synthesis of hollow carbon spheres (HCSs) has attracted considerable attention because of the promising potentials of HCSs in energy storage and conversion [1–8] and in catalytic and adsorption-based application [1,9,10], owing to their many unique features, such as spherical morphology, low density, high specific surface areas, large void space fraction, outstanding thermal and chemical stability, etc. Hard-templating-based methods were widely used to synthesize the HCSs [1]. Typically, the templates, mainly silica spheres [2–6,9–16] and polymer spheres [7,8,17,18] having monodisperse size and spherical shape, were firstly coated with a thin layer of a carbon precursor (e.g., glucose [5–7], resorcinol-formaldehyde resin [3,4,9–13], dopamine [14,15], and petroleum pitch [16]) to form a core-shell structure, followed by carbonization of the shell and etching removal of the core. The as-synthesized HCSs preserved the morphology and size of the templates, forming negative replicas of the templates. Besides the HCSs, the template approaches also enable to synthesize novel yolk-shell structures, in which one or several movable nanoparticles are encapsulated inside a HCS (e.g., Au@HCS), when core-shell nanoparticles (e.g., Au@SiO₂) are used as the templates [14]. Such yolk-shell carbon structure is beneficial for catalytic and electrochemical applications [5,6,10,14].

The carbon shells of the HCSs fabricated by the templating methods are generally amorphous, which have poor electrical conductivity and are not ideal for some applications such as lithium-ion batteries [1]. To obtain graphitized carbon shells, graphitization catalyst, such as Fe-containing species [8,18], was frequently added into the carbon precursor coating layer in the coating process, which promoted the graphitization of carbon precursor in the carbonization process. However, the obtained carbon shells were only weakly graphitized, exhibiting turbostratic or localized graphitic structures. Herein, we report on the fabrication of graphitized,

monodisperse HCSs and yolk-shell Au@HCS nanostructures using a new, modified templating method, in which smooth, uniform graphene layers were grown on SiO₂ spheres or Au@SiO₂ nanoparticles via metal-catalyst-free chemical vapor deposition (CVD) of methane. Our work not only provides a new method to fabricate high-quality HCSs but also demonstrates a reliable approach to grow quality graphene on oxide surfaces using methane CVD without the presence of metal catalysts.

2. Experimental

2.1. CVD fabrication of hollow carbon spheres

The metal-catalyst-free CVD growth of graphitized HCSs was conducted in a tube furnace system using methane (CH₄) as the carbon source [19,20]. Two kinds of monodisperse SiO₂ spheres were used as the templates: micro-sized SiO₂ spheres with diameters of ~500 nm and nano-sized Au@SiO₂ core-shell spheres with diameters of ~50 nm. The micro-sized SiO₂ spheres were synthesized using the Stöber method [21]. The Au@SiO₂ core-shell nanospheres were prepared using the reported sol-gel method [22]. The spheres were spread on a Si wafer (or other substrates such as aligned carbon nanotube sheets) to form a thin layer of 3-D assembly of silica spheres, which was placed in the center of a horizontal tube furnace. The metal-catalyst-free CVD growth of graphitized carbon on SiO₂ sphere surfaces requires the growth temperature to be at 1100–1200 °C; below 1100 °C quality graphitized carbon spheres do not grow [19,20,23], and higher temperature (>1200 °C) can result in the sintering of the spheres [20].

Therefore, in this work, the growth temperature was fixed at 1150 °C. The other synthesis parameters were: methane flow rate, 5 sccm (standard cubic centimeters per minute); Ar flow rate, 150 sccm; growth chamber pressure, 150 Torr; and growth time, 1 to 10 min. After growth,

the samples were immersed in a 1 M HF aqueous solution for 2 h to dissolve the SiO₂ cores, followed by washing in methanol and drying in an oven at 80 °C for 1 h.

2.2. Morphology and structural characterization

The as-synthesized HCSs and Au@HCS yolk-shell nanostructures were examined using scanning electron microscopy (SEM; FEI Inspect F FEG SEM), transmission electron microscopy (TEM; FEI Titan S aberration-corrected TEM/STEM), and Raman spectroscopy (a Renishaw Raman 1000 system with a 514 nm argon ion laser; the laser power is about 1 mW).

3. Results and discussion

Figure 1a shows a SEM image of the micro-sized SiO₂ spheres. The spheres have a spherical shape with a uniform diameter of ~500 nm. After CVD reaction, the SiO₂ spheres were uniformly coated with a thin carbon layer, while the spherical shape of the spheres was perfectly preserved and no sintering between the spheres was observed (Fig. 1b). After the SiO₂ cores were removed by HF etching, HCSs which are the negative replicas of the SiO₂ spheres were obtained. Figures 1c, 1d,e, and 1f show the HCSs obtained after 3 min, 5 min, and 8 min of CVD growth, respectively. At shorter growth time (<3 min), there have small pores on some spheres, as indicated by the white line arrows in Fig. 1c. Occasionally, carbon hemispheres were observed, as indicated by the hollow arrow in Fig. 1c. However, no collapsed HCSs were observed, showing the rigidity of the spherically shaped spheres. At longer growth time (>5 min), carbon deposition occurred uniformly on the entire surface of each SiO₂ sphere, producing HCSs with microscopically smooth outer surfaces (Fig. 1d–f). Figure 1d–f clearly shows that due to the thin, conductive nature of the carbon shells, the HCSs are “transparent” to electron beam and the spheres located at deeper position can be clearly seen in SEM imaging. Moreover, Figure 1d–f also shows that the metal-catalyst-free CVD growth not only precisely replicate

Figure 1. SEM images of HCSs. (a) Micro-sized SiO₂ spheres. (b) Carbon-coated SiO₂ spheres (after CVD growth). (c) HCSs after 3 min growth. (d,e) HCSs after 5 min growth. (f) HCSs after 8 min growth. The white arrow heads in (c) indicate the holes on spheres. The hollow arrow head in (c) indicates a graphene hemisphere.

individual SiO₂ spheres but also perfectly preserve the 3-D assembly of SiO₂ spheres, showing the high penetration and uniform deposition of gaseous hydrocarbons in the CVD process.

The transparency and the spherical shape of the HCSs were verified by TEM/STEM imaging. Figure 2a shows a Z-contrast dark-field STEM image of a cluster of HCSs. In STEM, the hollow spheres resemble bubbles in water, exhibiting a perfectly round cross-section with a uniform shell thickness.

Figure 2. TEM images of HCSs. (a) Z-contrast dark-field STEM image of a cluster of HCSs. (b) HRTEM image of the wall of a HCS.

The microstructures and quality of the shells of the HCSs were examined using high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. HRTEM imaging (Fig. 2b) shows that the shell is well-graphitized even though no metal catalysts were used, with the graphitization degree comparable to that of the metal-catalyzed CVD multiwall carbon nanotubes [24]. The shell typically consists of >10 graphene layers after 5 min of growth. The HRTEM results were further verified by Raman measurements, as the typical Raman

spectrum shown in Fig. 3a. The Raman spectrum contains D ($\sim 1358\text{ cm}^{-1}$), G ($\sim 1584\text{ cm}^{-1}$), 2D or G' ($\sim 2708\text{ cm}^{-1}$), and D+G ($\sim 2928\text{ cm}^{-1}$) bands. The well-resolved G band as well as the strong 2D (G') band indicates the existence of significant sp^2 carbon in the HCSs. The broad 2D band and the low I_{2D}/I_G intensity ratio (~ 0.7) show the formation of multilayer graphene. The high D band intensity, however, suggests a relatively high level of disorders in the HCSs.

Figure 3. Raman spectra. (a) HCSs. (b) Au@HCS yolk-shell nanostructures.

Besides the microscale HCSs described above, we have also fabricated nanoscale HCSs encapsulating one or several Au nanoparticles, i.e., the Au@HCS yolk-shell nanostructures, by the metal-catalyst-free CVD using Au@SiO₂ core-shell nanoparticles as the templates. Figure 4a shows a SEM image of the Au@SiO₂ core-shell nanoparticles used in this study. The nanoparticles have a diameter of $\sim 50\text{ nm}$, and each particle contains one to three $\sim 10\text{ nm}$ Au nanoparticles. After CVD reaction followed by HF etching, HCSs that precisely preserved the shapes of the original SiO₂ nanoparticles were obtained and the Au nanoparticles were

encapsulated inside the spheres, as shown in Fig. 4b. Notably, despite the small size of the Au@SiO₂ nanoparticles, there is no apparent agglomeration of the particles during the high-temperature CVD growth.

Figure 4. SEM images of yolk-structures carbon nanospheres. (a) Au@SiO₂ core-shell nanospheres. (b) Au@HCS yolk-shell nanostructures.

The structural features of the Au@HCS yolk-shell nanostructures were further revealed by TEM/STEM imaging and Raman spectroscopy. Figures 5a and 5b show, respectively, the bright-field TEM and Z-contrast dark-field STEM images of a cluster of Au@HCS yolk-shell nanostructures. It is clear that the Au nanoparticles are indeed encapsulated inside the hollow spheres. High-magnification TEM imaging reveals that the Au nanoparticle is studded onto the inner surface of the hollow shell (Fig. 5c). Like the microscale HCSs, the shells of the nanoscale HCSs are graphitized and consist of around 10 graphene layers after 5 min CVD growth (Fig. 5d). However, the nanoscale HCSs contains a little higher degree of disorders than the microscale HCSs, as the stronger D Raman band shown in Fig. 3b.

Figure 5. TEM images of yolk-structures carbon nanospheres. (a) Bright-field TEM image of Au@HCS yolk-shell nanostructures. (b) Simultaneously acquired Z-contrast dark-field STEM image of the same area in (a). (c) Magnified TEM image of the boxed area in (a). (d) HR-TEM image of the boxed area in (c).

4. Conclusions

We demonstrated the synthesis of graphitized HCSs and Au@HCS yolk-shell nanostructures by metal-catalyst-free methane CVD using micro-sized SiO₂ spheres and nano-sized Au@SiO₂ core-shell spheres as the templates, respectively. Since the graphitization of the metal-catalyst-free CVD HCSs is comparable to that of the metal-catalyzed CVD multiwall carbon nanotubes, the significance of our work also lies in the capability of growing quality graphene on silica sphere surfaces using methane CVD without the presence of metal catalysts. This finding is significant for graphene growth because, compared with the popular metal-catalyzed CVD growth [25,26], the metal-catalyst-free CVD allows the growth of graphene on technologically important dielectric substrates (including SiO₂) for direct device fabrication, which can avoid the need for a complicated postgrowth transfer process [27]. Moreover, considering the diverse forms of SiO₂ structures (e.g., spheres, plates, porous foams, etc.) and the excellent coating capability of SiO₂ on other materials (e.g., metals, semiconductors, quantum dots, etc.), the metal-catalyst-free CVD technique provides a facile route to fabricate good quality, complex graphene structures with novel functionalities.

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