

A Novel Route for Preparation of Hollow Carbon Nanospheres Without Introducing Template

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Abstract A newly developed route for the synthesis of hollow carbon nanospheres without introducing template under hydrothermal conditions was reported. Hollow carbon nanospheres with the diameter of about 100 nm were synthesized using alginate as reagent only. Many instruments were applied to characterize the morphologies and structures of carbon hollow nanospheres, such as XRD, TEM, and Raman spectroscopy. The possible formation and growth mechanism of carbon hollow spheres were discussed on the basis of the investigation of reaction influence factors, such as temperature, time, and content. The findings would be useful for the synthesis of more materials with hollow structure and for the potential use in many aspects. The loading of SnO₂ on the surface of carbon hollow spheres was processed, and its PL property was also characterized.

Keywords Synthesis · Nanostructure · Carbon hollow nanospheres

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Introduction

Inorganic hollow spheres with tailored structural, optical, and surface properties represent an important class of materials that may find applications in a wide range of areas such as delivery vehicle systems, photonic crystals, fillers, and catalysts [1–4]. Generally, the synthesis of inorganic hollow spheres can be realized by means of sacrificial templates, including “hard templates”, such as silica spheres, polystyrene latex spheres, and resin spheres [5–8], and “soft templates”, such as vesicles, liquid droplets, emulsion droplets as well as block copolymer micelles [9–11]. But synthesis of hollow structures without introducing templates has scarcely been reported in recent years.

Researchers have paid great attention to carbon spheres, as they have significant application in the preparation of diamond films, lubricating materials, and special rubber additives, owing to their properties similar to fullerene and graphite [12–14]. However, harsh environment was necessary for the synthesis of these hollow carbon spheres up to now [15–18]. Hydrothermal method provide a comparatively mild circumstance and is widely used in the synthesis of carbon materials. Till now, only hollow carbon spheres with the diameter of few microns were obtained through this method [19]. In this report, hollow carbon nanospheres with the diameter of about 100 nm were reported through hydrothermal treatment without introducing template, and this process was seldom reported in the synthesis of inorganic hollow structures, especially in the synthesis of carbon hollow spheres. SnO₂ nanoparticles loading on the surface of these hollow spheres were synthesized and the fluorescence property of the complicate materials was also be characterized.

Experimental Works

Synthesis of Hollow Carbon Nanospheres

All chemicals were purchased from Sinopharm group chemical reagent Co. Ltd with analytic-grade purity and used directly without further treatment. The carbon spheres were synthesized under hydrothermal conditions. In a typical procedure, 0.3 g sodium alginate was dissolved in 16 mL deionized water and ultrasonic processed for 20 min and sealed in a 20 mL Teflon autoclave and maintained at 180 °C for 10 h. The autoclave was naturally cooled down to the room temperature when the reaction was complete. The black products were collected by using a centrifuge and washed several times with distilled water and absolute ethanol, respectively, and dried under vacuum at 80 °C for 5 h.

Loading of SnO₂ on the Surface of Hollow Carbon Nanospheres

The loading of SnO₂ on the surface of hollow carbon nanospheres was performed referring to coating of SnO₂ nanoparticles on the surface of carbon nanotubes in the Zhou's report [20]. Using a desired amount of HCl acid (0.7 ml of 38% HCl in 40 ml H₂O) is the key to obtaining uniformly dispersed SnO₂ nanoparticles loading on the surface of hollow carbon nanospheres.

Characterization

The structures of synthesized products were measured with X-ray powder diffraction (XRD) and Raman spectroscopy. XRD measurements were recorded using a Netherlands 1,710 diffractometer with graphite monochromatized Cu K α irradiation ($\lambda = 1.54056 \text{ \AA}$) and Raman spectroscopy using Renishaw company, equipped with an Ar + laser at 514.5 nm. Infrared spectrum was characterized by a Nicolet 5DX FTIR spectrometer equipped with a TGS/PE

detector and a silicon beam splitter with 1 cm⁻¹ resolution. The micromorphologies of products were inspected by transmission electron microscopy (TEM) (JEOL JEM2010, Japan) at an accelerating voltage of 200 Kv. Emission spectra were measured on a Perkin-Elmer LS-55 fluorescence spectrophotometer. All the measurements were taken at room temperature.

Results and Discussion

Morphologies and Structure

XRD as a kind of important manner can be used to characterize the phase and structure of samples. The XRD pattern of products obtained in the hydrothermal system is shown in Fig. 1a. The broad peak indicates that the amorphism of product is because of poor crystallization. As a kind of usual fashion, Raman spectroscopy is a powerful technique for characterizing the carbon materials. Figure 1b displays the Raman spectrum of synthesized materials that verifies carbon structure of products. A strong peak at 1,588 cm⁻¹ and a weak peak at 1,333 cm⁻¹ corresponding to typical Raman peaks of graphitized carbon spheres are observed. The peak at 1,333 cm⁻¹ could be assigned to the vibrations of carbon atoms with dangling bonds in planar terminations of disordered graphite. The peak at 1,588 cm⁻¹ (G-band) corresponds to an E_{2g} mode of graphite and is related to the vibration of sp²-bonded carbon atoms [21, 22]. The high intensity ratio of D to G band suggests the poor graphitization of the products, which is consistent with the XRD pattern. FT-IR is also used to characterize the function group of the hollow carbon nanospheres.

In our experiment, FT-IR spectrum (Fig. 1c) was used to identify the functional groups of the hollow carbon nanospheres for the sake of further understanding the structure

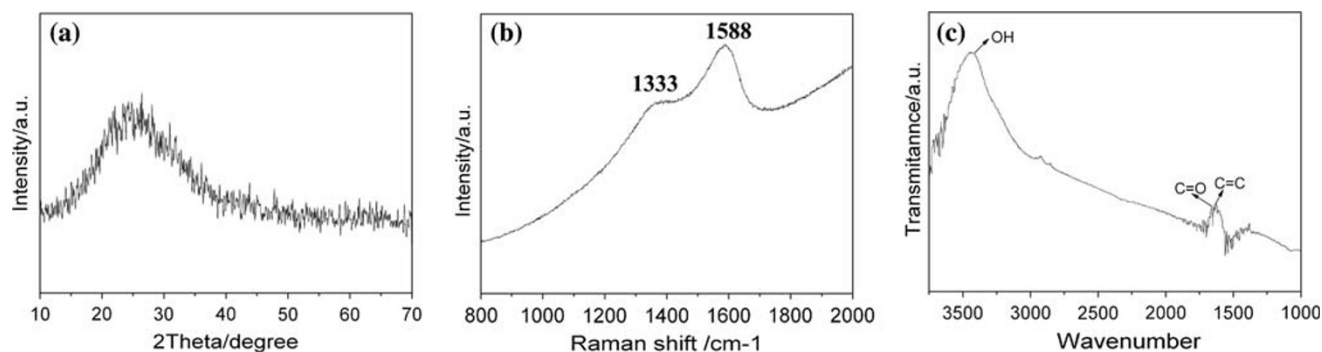


Fig. 1 **a** XRD patterns of synthesized products after hydrothermal process 5 h at initial content = 0.3 g; **b** Raman spectrum of synthesized products; **c** IR spectrum of synthesized products

of carbon. As a kind of amylose aggregated from monoglucuronide, aromatization is usually regarded as a process of decreasing the number of functional groups [23]. The bands at 1,710 and 1,620 cm^{-1} can be attributed to $\text{C}=\text{O}$ and $\text{C}=\text{C}$ vibrations, respectively. These results reveal that aromatization of chitosan has taken place during hydrothermal treatment. Compared with the aromatization of glucose under hydrothermal condition [24], the bands in the range of 1,000 \sim 1,300 cm^{-1} are hardly seen in the FT-IR spectrum of our products, indicating few $\text{C}-\text{OH}$ stretching and OH bending vibrations and implying few residual hydroxyl groups appear. This is in accordance with the polymer structure of alginate. The residues of CHO groups are covalently bonded to the carbon frameworks, which makes it more potential application as templates for hybrid complex structures and opens a new way to hollow core-shell materials.

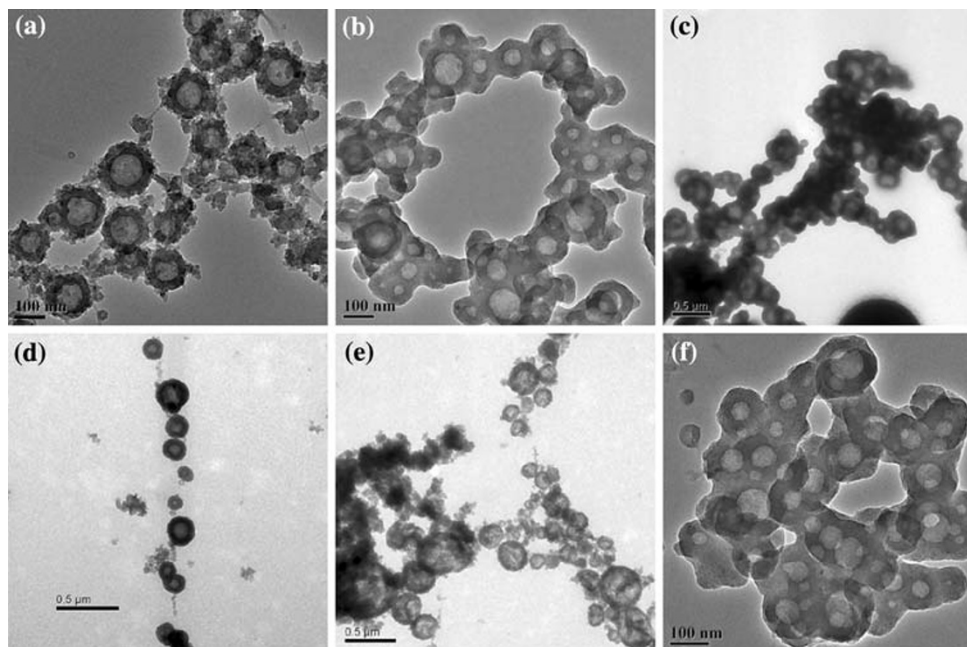
Typical TEM images of hollow carbon nanospheres obtained in 0.3 g sodium alginate solution after hydrothermal process for 5 h are presented in Fig. 2a. The strong contrast between the dark edge and the pale center of the spherical particles evidences their hollow structure. The diameter of the hollow carbon spheres is about 70–120 nm, with an average diameter of about 100 nm, and the wall thickness is about 20 nm. The related electron diffraction pattern (not shown) is circular, indicating the amorphous structure of carbon, consistent with the XRD pattern and Raman spectrum. The possible reason might be that a low temperature process leads to the poor crystalline.

The Influence Factors of Reaction

The time-dependent experiments were also carried out to investigate the influence of reaction time on morphologies of products. Hollow carbon nanospheres were obtained in a series of experiment times. When the reaction time was less than 2 h, carbon could not be formed. That is, complete carbonization of alginate is not possible at this reaction time. This result showed the importance of reaction time on the formation of carbon spheres. Extending the reaction time to as long as 12 h, the products remained hollow carbon nanospheres. The hollow nanospheres obtained changed from single hollow nanospheres (in Fig. 2a) to a ringlike structure of walled hollow nanospheres (in Fig. 2b) and then to a linear structure of walled hollow nanospheres (in Fig. 2c) when the reaction time is 5, 7, 10 h, respectively. No distinct changes in the thickness of the wall of synthesized hollow nanospheres were found and the network made of many hollow nanospheres appeared with the prolonged time. Probably, the reason for the occurrence of these phenomena lies in the linear polymer structure.

The content-dependent experiments were carried out to monitor the influence of the initial content of the product. The different amounts of alginate were put into autoclaves, and other parameters were kept constant. Some typical TEM images are given in Fig. 2. The TEM images showed that morphologies of obtained products gradually changed from a few single hollow nanospheres (Fig. 2d) to a great deal of hollow nanospheres (Fig. 2e) and then to cross-

Fig. 2 TEM images of prepared hollow carbon nanospheres at different reaction time and content. **a, b, c** products after 5, 7, 10 h, 0.3 g sodium alginate **d, e, f** products after 7, 10, 18 h, 0.1 g sodium alginate



linked hollow nanospheres (Fig. 2f) when the content changed from 0.1 to 0.3 g and then to 0.5 g (the reaction condition is kept at 180 °C for 7 h in all reactions). These varieties of products revealed that the content is a crucial factor for preparing carbon nanospheres in a large scale. Because the carbonization process was actually a defunctionalization process, the content of reagents largely affected the collision rate among base groups. These results reveal that carbon spheres could be achieved only the alginate is up to a certain content. The alginate solution is up to critical supersaturation and nucleation burst when these macromolecules dehydrate gradually.

The influence of temperature on products was also explored. When the reaction temperature is decreased to 160 °C, even if reaction time is kept at 12 h, carbonization reaction could not be complete and brown reaction solution was obtained when the content was reduced to 0.1 g, which identified the occurrence of aromatization. While a higher temperature (200 °C) was used, it led to accelerated dehydration of alginate intermolecules and a burst nucleation around spherical chain, which could result in the formation of cross-linked hollow spheres. These results revealed that temperature was a key factor in the preparation of carbon nanospheres through dehydration, aromatization, and carbonization. At lower temperatures, the energies of intermolecular collisions and of intramolecular collisions were not high enough to carbonize, leading to the failure of formation of carbon nanospheres. Compared with the carbonization of glucose [24], the carbonization of alginate was slower and needed higher temperature although glucose and alginate sodium were a kind of saccharide. The possible reason lies in the polymer structure of alginate. On the one hand, the polymer structure contained fewer –OH group and slowed the dehydration intermolecular process. More time and higher temperature were needed to realize polymerization and carbonization of alginate according to the theory of the rate of chemical reaction.

The filling ratio as an important parameter of hydrothermal systems has a critical influence on the reaction

pressure, solubility of solute, viscosity, density, and dielectric constant of solution at constant temperature in a sealed hydrothermal system. To investigate the influence of filling ratio on the obtained products, a series of parallel experiments were performed with different filling ratios from 40 to 80% at 180 °C for 8 h. Obtained products congregate more easily and become randomly when the filling ratio of the reagent is low to 40%, compared with the filling ratio is up to 80%. It is well known that the viscosity of alginate depends on temperature, density, and the stirring rate. With the decrease in filling ratio, the alginate solution becomes denser, which makes carbonization reaction more intense.

Formation Mechanism

The formation mechanism of hollow carbon nanospheres was also explored. At first, the formation of carbon spheres was a nucleation and growth process (Fig. 3). At a certain temperature, the alginate solution can form spherical micelles and further nucleate by dewatering. Compared with the dehydration of glucose [24], the dehydration of glucose became more difficult because less –OH group made intermolecular dehydration take place only when reaction system had higher energy. It may be explained why carbonization of alginate needed higher temperature than for carbonization of glucose. Then nucleation of alginate took place when critical supersaturation of alginate was got to. Finally, the growth of nucleus is controlled by diffusion or carbonization reaction according to the theory of Ostwald ripening [25].

The comparative experiment was made without ultrasonic processing, and irregular carbon chips were obtained. That is, ultrasonic process was key to the formation of the hollow structure. So we speculated that the formation of hollow structure was as follows: At first, sodium alginate was wholly dissolved in the water by heating the solution. Then hollow sodium alginate nanospheres were formed by cavitation of ultrasonic process. A great number of air bubbles formed and grew in the zone of negative pressure,

Fig. 3 Formation mechanism of hollow carbon nanosphere

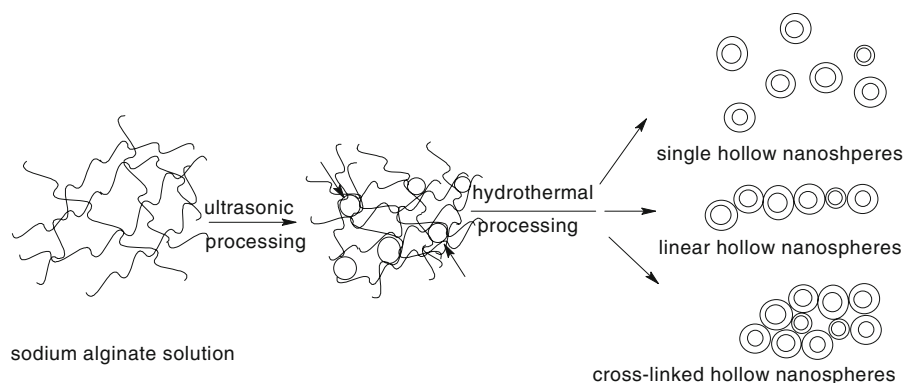
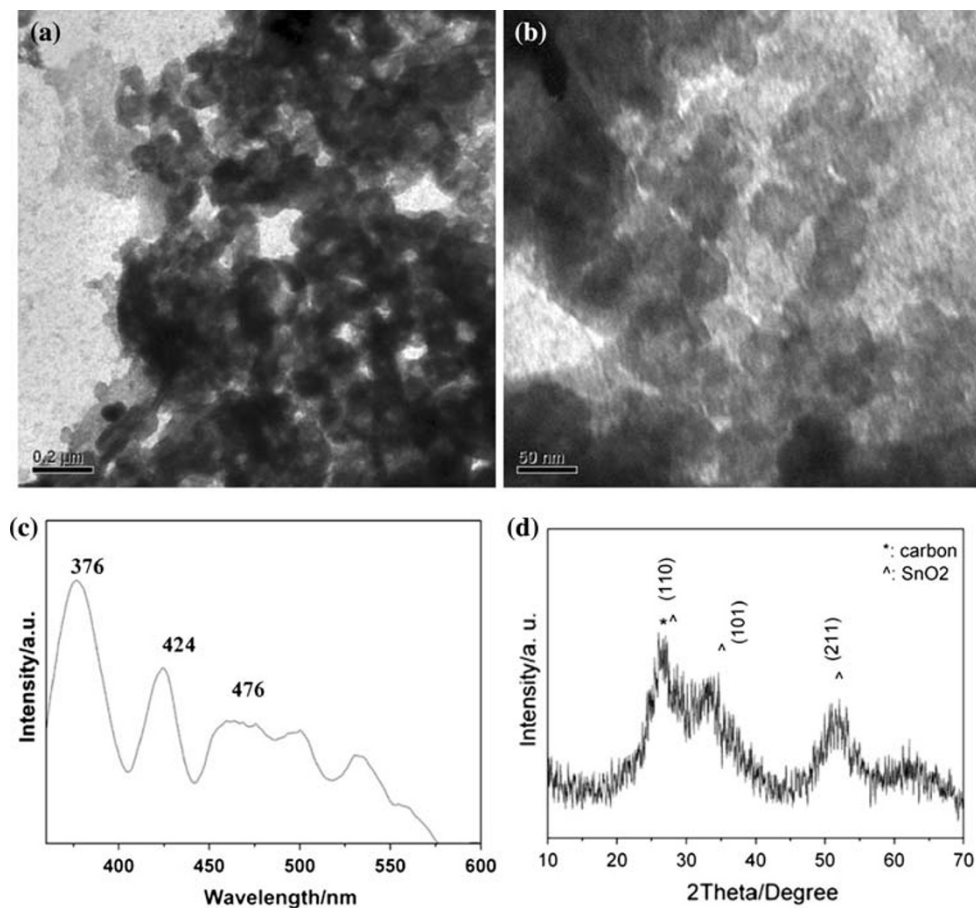


Fig. 4 **a, b** TEM and amplified TEM images of synthesized $\text{SnO}_2@\text{C}$, **c** its PL properties and **d** XRD pattern of synthesized $\text{SnO}_2@\text{C}$ composite



and they were occluded in the zone of positive pressure during the ultrasonic process. This kind of cavitation led to air bubbles formed in the molecular of alginate. When the solution was placed in the hydrothermal condition at some temperature, carbonization took place in situ, and hollow carbon nanospheres were synthesized. According to the content of reactant, different structures made of hollow nanospheres were formed.

The Loading of SnO_2 Nanoparticles

Carbon hollow structures, typically in the form of capsules converted from their core-shell precursors, exhibited higher current and power density when used as a catalyst support in the direct methanol fuel cell [26]. SnO_2 -nanoparticles-coated carbon spheres are useful functional nanocomposite in many applications including gas sensors, batteries, and optics. The special configuration in this nanocomposite is expected to prevent the SnO_2 nanoparticles from aggregation and to increase its conductivity, hence the performance. In this article, SnO_2 nanoparticles are loaded onto the surfaces of hollow carbon nanospheres by room-temperature surface oxidation method. To reveal the composition and structure of the above sample, XRD was carried

out. Figure 4d shows the XRD pattern, in which all diffraction peaks were in good agreement with tetragonal rutile SnO_2 (JCPDS No: 41-1445). The morphology of this kind of complicate material was characterized with TEM. The TEM image and amplified TEM image are given in Fig. 4a and b. SnO_2 nanoparticles of several nanometers were loaded on the surface of hollow carbon nanospheres. The PL spectrum of the composite material was characterized by two peaks at 376 and 424 nm, and a broad peak centered at 476 nm in the wavelength of range 450–516 nm under excitation at 310 nm. The emission in the wavelength range 450–550 nm may be related to the intrinsic defect structures, in particular the oxygen vacancies originated from the oxygen deficiency [27] induced during the growth. The prominent band at 420 nm is attributed to the recombination of the deep-trapped charged and photogenerated electron from the conduction band [28].

Conclusion

To conclude, hollow carbon nanospheres with the diameter of 100 nm were synthesized without template under

hydrothermal condition via ultrasonic pretreatment. And the wall thickness was about 20 nm. The influence of the reaction time and the content was also observed. Then a possible forming mechanism was given. Hollow carbon nanospheres loading SnO₂ nanoparticles were synthesized and its photoluminescence peak appeared at 376, 424, and 476 nm. The hollow carbon nanospheres and their loading structure have potential application in many fields such as carriers, storage, and catalysts.

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