Interface-mediated fabrication of bowl-like and deflated ballon-like hollow carbon nanospheres

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ABSTRACT

In our work, two kinds of hollow carbon nanospheres with controlled morphologies have been successfully prepared from low-cost and nontoxic glucose as the sole carbon precursor under neutral aqueous medium via a simple hydrothermal route. During the process, sodium dodecylbenzene sulfonate (SDBS) and triblock copolymer P123 ((EO)20(PO)70(EO)20) was skillfully selected as the structure-directing agent, respectively. SEM, TEM and AFM results revealed that the two products showed bowl-like and deflated-balloon-like morphology with uniform particle sizes, respectively. Based on the experimental observations, a possible formation mechanism was also discussed, in which the growth of the carbon nanospheres involved an interface-mediated assembly process. The present method was easy, green and mild. Apart from the unique nanostructure, the obtained bowl-like hollow carbon nanospheres exhibited excellent biocompatibility. In particular, it should be mentioned that the open window formed by the bowl-like morphology can facilitate ion transport, thus improving their performances.

1. Introduction

For the past two decades, porous carbon nanomaterials have been widely applied in catalysis, adsorption, energy and biomedical fields because of their unique electrical, optical, mechanical and biological characteristics [1–5]. By now, different types of carbon nanomaterials including carbon fiber, fullerene, carbon nanotube, and ordered mesoporous carbon have been fabricated, which will open more possibility for their further applications. Among them, hollow carbon spheres (HCS) with controlled nanostructures have received rapidly increasing interest due to their tailored morphologies, low density, high surface area, good insulation and electronic properties. Especially, HCS have been
investigated for potential applications such as lithium batteries [6–8], fuel cells [9,10], catalyst supports [11,12], supercapacitors [13,14], hollow spheres composites [15], or as templates for the synthesis of other hollow nanomaterials [10,16].

To date, many approaches towards hollow carbon spheres with various nanostructures have been developed regarding microfluidic approach [17], precursor-controlled pyrolysis [18,19], chemical vapor deposition [20,21] and hydrothermal routes [9,22]. However, in the first three methods, complicated synthesis processes, extreme reaction conditions or extra high temperatures are needed, which is generally time-consuming, high cost and unfriendly to the environment, thus hindering their further application as conventional methods. Comparatively speaking, the hydrothermal method is considered as an effective technique for fabrication the carbon nanospheres through the carbonization of carbonaceous precursors because of its simple, green, low-cost, and nontoxic character. The carbon precursors derived from glucose, resorcinol and formaldehyde were usually used. However, on account of ecological and economic concerns, the utilization of the renewable and inexpensive carbon sources has become a dramatic and exciting development in the production of carbonaceous materials, for example, typical glucose and sucrose. Recently, the work about hollow carbon capsules with unique nanostructure was reported through a facile hydrothermal route. As described in the study, the obtained carbon spheres had a controlled void core and tunable shell thickness [23]. Nevertheless, the morphology of the products is almost inhomogeneous with several micrometers in diameter. Therefore, it is of great significant to explore a simple and cost-effective route to fabricate HCS with small size and controlled morphology.

In this work, we present a simple hydrothermal method for one-pot synthesis of blow-like and deflated balloon-like hollow carbon nanospheres with controlled morphologies from low-cost glucose as the carbon precursor. The morphology and structure of the products obtained are characterized by the TEM, SEM, and AFM, XRD, Raman, FT-IR techniques, etc. Additionally, a series of products were prepared by changing the composition of precursor while keeping other constant. The growth process was observed by TEM technique, in which an interface-mediated assembly mechanism was also proposed.

2. Experimental

2.1. Materials

Triblock copolymer P123 ((EO)20(PPO)70(EO)20) was purchased from Sigma–Aldrich. Sodium dodecylbenzene sulfonate (SDBS), glucose, AgNO3, and ethanol were analytical pure, supplied by Sinopharm Chemical Reagent Co., Ltd. Cell Counting Kit-8 (CCK-8) was purchased from Dojindo Molecular Technologies (Japan). For cell culture medium, Dulbecco’s Modified Eagle’s Medium (DMEM), fetal bovine serum and glutamine were obtained from Invitrogen (USA), and penicillin/streptomycin was purchased from GIBCO (USA). Mesenchymal stem cells (MSC) were provided by Dr. Lu Zhang from Shanghai Jiao Tong University. All materials were used as received without any further purification. Distilled water was used throughout the experiments.

2.2. Preparation of hollow carbon nanoparticles

The hollow carbon nanoparticles (HCN) were prepared by using sodium dodecylbenzene sulfonate (SDBS) and triblock copolymer P123 as the morphology controller, respectively, and water as the solvent under mild conditions. In a typical procedure, 0.20 g of glucose and 0.14 g of SDBS were dispersed in 30 mL water by ultrasonic treatment for 10 min to form a clear solution. Then, the solution was transferred into a Teflon-lined stainless-steel autoclave and maintained at 180 °C for 6 h under autogenous pressure. Subsequently, the autoclave was cooled to room temperature naturally. The resultant precipitate was filtered, washed with water and ethanol for several times. Finally, the bowl-like hollow carbon nanospheres (denoted as BHCS) were obtained by dried at 60 °C for 12 h. In particular, the deflated balloon-like hollow carbon nanospheres (denoted as DHCS) were prepared by using P123 instead of SDBS under similar conditions (Typically, 0.20 g of glucose and 0.04 g of P123). In addition, a series of products were prepared by varying the compositions of precursors in order to further insight into the formation mechanism of hollow carbon nanoparticles. For comparison, the carbon spheres were also prepared by a similar procedure without the addition of any surfactant.

2.3. Preparation of Ag-loaded hollow carbon nanospheres

Typically, 0.02 g of newly prepared BHCS was dispersed in 10 mL of AgNO3 (0.03 M) aqueous solution, and the mixture were stirred for 10 min and aged for 1 h. Then, the solution was subjected to several centrifugation/water wash/redispersion cycles to remove residual Ag+ ions. The resultant was centrifuged, redispersed in the ethanol. Finally, the Ag-loaded BHCS were obtained by drying at 60 °C for 12 h.

2.4. Cell viability test

Mesenchymal stem cells (MSC) were grown in Dulbecco’s Modified Eagle’s Medium (DMEM) supplemented with 10% heat inactivated fetal bovine serum, 2 mM glutamine and 100 IU mL−1 penicillin and 100 μg mL−1 streptomycin in a humidified incubator with 5% CO2 at 37 °C. The morphology of cells was observed by using an optical microscopy (Leica, Germany). The viability of the cells in the presence of carbon nanoparticles was evaluated using the CCK-8 assay. MSC were seeded into 96-well plates at a density of 1 × 104 per well in 100 mL of media and grown overnight. The cells were then incubated at various concentrations of BHCS (5, 15, 25, 50 and 100 μg mL−1) for 12 and 24 h, respectively. Following this incubation, cells were washed with D-Hanks buffer solution and incubated in 100 μL fresh cell
culture medium containing 10 μL CCK-8 solution (5 mg/mL) for 4 h. Thereafter, the CCK-8 solution was removed and the precipitated violet crystals were dissolved in 100 μL of DMSO. The absorbance in cell test was measured at 450 nm using a microplate reader (Bio-TEK instrument, Inc). The following formula was used to calculate the viability of cell growth: Viability (%) = (mean of absorbance value of treatment group/mean absorbance value of control) × 100. The results were expressed as an average over six identical measurements of each time point.

2.5. Characterization

The hollow carbon nanoparticles were characterized by a transmission electron microscopy (TEM, JEOL 200CX), scanning electron microscopy (SEM, JEOL JSM-6700F), atomic Force Microscope (AFM, SHIMADZU SPM-9600). Elemental qualitative analysis was conducted by the energy-dispersive X-ray spectroscopy (EDS, OXFORD INCA) which was mounted on a JSM-6700F. X-ray powder diffraction (XRD) patterns were obtained on the Japan Rigaku D/max-2550 instrument operating at 40 kV and 40 mA using Cu Kα radiation (λ = 0.154 nm). Raman spectra were measured with Renishaw inVia Raman microscope using 514 nm lasers as a light source. Identification and characterization of functional groups were carried out using PerkinElmer FT-IR spectrometer in the range of 400–4000 cm⁻¹. N₂ adsorption–desorption isotherms were recorded on a QUADRASORB SI surface area and pore size analyzer at 77 K. Prior to the analysis, the products were annealed at 100 °C for 6 h. The Brunauer–Emmett–Teller (BET) surface area was calculated by using adsorption data.

3. Results and discussion

3.1. Structure and morphology

The BHCS was firstly prepared in the presence of small amount sodium dodecylbenzene sulfonate (SDBS) under neutral aqueous medium. The formation process of the carbon nanoparticles was briefly described, as shown in Scheme 1. Typically, appropriate amount of aqueous solution including glucose and SDBS was put in a Teflon-lined stainless steel autoclave and heated at 180 °C for 6 h. Followed by cooled down the autoclave to room temperature, the products at the surface of solution were collected after centrifugation and washed several times with ethanol and water. Fig. 1 shows the TEM images of BHCS prepared with different amounts of SDBS from 0 to 0.28 g when keeping other parameters constant. If no SDBS was added, only solid carbon spheres could be obtained, in agreement with our previously result (Fig. 1a) [16]. When increasing SDBS from 0.05 to 0.08 g (Fig. 1b and c), the hollow core size of the carbon nanospheres increased from 130 to 140 nm and the shell thickness decreased from 27 to 20 nm. Further increasing the amount of SDBS (Fig. 1d), the shells became slightly thinner (~18 nm). However, it was so thin that the carbon shells began to collapse surprisingly and finally deformed into bowl-like hollow nanospheres. Once the amount of SDBS increased to 0.21 and 0.28 g, too much SDBS leded to fracture of the spheres (Fig. 1e and f). As a result, some broken shells were formed, and even fragments began to appear. Hence, it was concluded that the addition of SDBS played a crucial role in the formation of the final products. Moreover, the shell thickness and the morphology of the carbon samples could be controlled by simply changing the amounts of SDBS. Therefore, the above results allow us to partially presume the mechanism of the transformation from solid carbon spheres to hollow nanostructures. During the hydrothermal reaction process, SDBS firstly enriched and formed vesicles in gas/liquid interface, which could be further served as the soft template, and provided the interface for the formation of BHCS. In the meantime, the carbonization of glucose also began to proceed under hydrothermal condition and then coated on the vesicles to form the carbon shell. Subsequently, the escape of SDBS through the channels happened. Finally, the hollow carbon spheres began to collapse and formed bowl-like hollow spheres with unique nanostructure, corresponding to the microscopic results [24].
Fig. 2 displays the structural property and morphology of the typical BHCS sample. Seen from the images, the carbon nanosphere has a dimension of \( \frac{C_{24}}{200 \text{ nm}} \) and a thin shell of 17–20 nm. Fig. 2a shows a side view of the “bowl” with a hemispherical shape. The EDS analysis (inset in Fig. 2a) confirms that BHCS is composed of C element, and while Si and Au elements could be ascribed to...
the silicon wafer used as a vector of samples and Au spraying used in SEM analysis. The morphology was further observed by Atomic Force Microscope (AFM) technique using a phase mode. Fig. 2b shows the hemispherical and stereoscopic result of BHCS, in accordance with SEM image. By closer observation, a “double-layer” structure was clearly seen owing to the collapse of the spherical structures, as displayed in the magnified TEM image (inset in Fig. 2c). Compared with the TEM image of Fig. 2c, the walls in Fig. 2a and b are much thicker, which may be due to the Au spraying and tip broadening effect, respectively. The size distribution curve of the BHCS according to the statistics about 200 nanoparticles is presented in Fig. 2d. The average diameter of BHCS is about 203 nm, which is in fairly good agreement with the TEM and SEM results.

Interestingly, when we try to prepare the carbon product by using triblock copolymer P123 as the morphology controller instead of SDBS under similar conditions, the deflated balloon-like hollow carbon nanospheres (DHCS) with uniform morphology can be achieved, which is obviously different with BHCS. Apart from the shape, the obtained DHCS has an average diameter of about ~1 μm, clearly larger than that of BHCS (Fig. 3a and b and Fig. S2). Analogously, it was founded that the amounts of P123 had also a profound influence on the formation of DHCS in the present system (Fig. S1). With the amounts of P123 tuning from 0.002 up to 0.08 with a fixed glucose dose of 0.20 g at 180 °C for 6 h, the morphology of carbon materials changed significantly. Consequently, we rationally presumed that the growth of DHCS may undergo similar interface-assembly process under hydrothermal conditions. Due to the larger molecular structure and intrinsic properties of P123, the results are totally different. The detailed mechanism for the formation of carbon spheres behind the assembly process is currently underway. Other techniques including XRD, Raman, and BET results were shown in ESI (Figs. S3–S5), all results confirmed that the hollow carbon nanospheres were successfully prepared with unique nanostructure and a certain degree of the graphitization in P123 system.

Fig. 4a depicts a representative Raman spectrum of BHCS. The intense and broadening G peak at 1581 cm\(^{-1}\) corresponds to an \(E_{2g}\) mode of carbon closely relating to the vibration of \(sp^{2}\)-bonded carbon atoms in a 2-dimensional hexagonal lattice [25]. On the other hand, a broad D band with a peak at 1343 cm\(^{-1}\) is related to the disorder or defects of the carbon materials. Generally, the relative intensity of the D band vs. G band (\(I_D/I_G\)) is used to characterize the disorder degree of carbon materials. The results indicated that the as-prepared BHCS were composed of carbonaceous material with a certain degree of the graphitization, in agreement with the observations reported by other researchers [26]. The crystal phase of the products was characterized by the XRD technique. Seen from the Fig. 4b (Fig. S3), there is an obvious diffraction peak centered at \(2\theta = 25.1^\circ\), which can be assigned to the (002) crystal plane [9], suggesting a graphitic nature and a low crystallinity of the BHCS and DHCS.

FT-IR technique is one of the useful tools to characterize the carbon framework. Fig. 4c clearly displays the existence of such hydrophilic residues attached to the carbon framework. The C=O peak at 1709 cm\(^{-1}\) and peaks of C–OH and –OH at 1394 and 1296 cm\(^{-1}\) imply the existence of residual –COOH groups in the product [9]. And peak at 1626 cm\(^{-1}\) is attributed to the C=C
stretching vibrations of the carbon framework. Additionally, the highly broadened and intense peak corresponding to the stretching vibrations of $-\text{OH}$ at 3423 cm$^{-1}$ indicates the existence of large quantity of adsorbed water of BHCS samples [27]. Besides that, the peaks at 2924 and 2820 cm$^{-1}$ corresponding to $-\text{CH}_2$ group can be inferred a restoration of the carbon basal planes [20].

The textural properties of the products were further investigated by N$_2$ adsorption–desorption isotherm analysis. As displayed in Fig. 4d, the prepared carbon materials exhibited a discern hysteresis loop at relatively high pressure, revealing their porous structures. The porous structure may be attributed to the removal of the organic moieties in the carbonization process. The specific surface area and pore volume of BHCS is $76.4 \text{ m}^2 \text{ g}^{-1}$ and $0.29 \text{ cm}^3 \text{ g}^{-1}$, respectively. Notably, the DHCSs products have similar some characteristics, as represented in Figs. S3–5.

3.2. Potential applications

To further expand the potential applications of the carbon products prepared in our work as biomaterial, the viability of mesenchymal stem cells (MSC) was firstly evaluated by using the cell counting kit-8 (CCK-8) assay. Fig. 5 shows the cell viabilities against BHCS with different concentrations from 5 to 100 $\mu$g mL$^{-1}$ for 12 h and 24 h, respectively. As was seen, the BHCS had almost no cytotoxicity after co-incubation with diverse concentrations of MSC for 12 h (Fig. 5a), even at the concentration as high as 100 mg mL$^{-1}$. Furthermore, to some extent, the MSC had a tendency to proliferation. When prolonging the co-incubation time to 24 h, the product only exhibited extremely low cytotoxicity even at the concentration of 100 $\mu$g mL$^{-1}$ (Fig. 5b), indicating the excellent biocompatibility of BHCS. Fig. 5d shows the corresponding optical photos of MSC after co-incubation with 100 $\mu$g mL$^{-1}$ of BHCS for 24 h. Compared with the blank control, there was nearly no cell apoptosis and all the cells still kept their normal

Fig. 5. Cell viabilities of BHCS against MSC at different concentrations for 12 h (a) and 24 h (b), respectively; Optical photos of MSC cells after co-incubation with 0 (c) and 100 (d) $\mu$g mL$^{-1}$ BHCS for 24 h.

Fig. 6. TEM image of Ag-loaded BHCS.
morphism (Fig. 5c). Therefore, the results are in line with our expectation for the BHCS, suggesting the carbon products will be a promising candidate in biomedical applications owing to their unique nanostructure, low density and highly biocompatibility, in comparison to other hollow nanospheres [28].

In addition, the Ag-decorated carbon spheres were also prepared by surface reduction of AgNO3 solutions at room temperature. It could be observed that Ag nanoparticles with an average diameter of about 10 nm were uniformly dispersed on the surface of the BHCS (Fig. 6). This phenomenon confirmed that the as-prepared BHCS could be readily functionized by noble metal nanoparticles or other organic groups, as reported by Li et al. [29] In particular, it should be mentioned that the open window formed by the brow-like morphology can facilitate ion transport, thus improving their performances [30]. All these are benefit for their more potential applications as the catalyst, energy materials, adsorbents, etc. Consequently, this work provides an extremely simple, mild and effective recipe to transform solid carbon spheres into hollow structures with various functions.

4. Conclusions

In conclusions, bowl-like and deflated balloon-like hollow carbon nanospheres with unique nanostructures have been successfully prepared via a simple and green hydrothermal route. Our results proved, for the first time, the possibility to obtain the hemispherically hollow carbon spheres with double-layer structure and small size (~200 nm) by simply pyrolysis of glucose in the presence of SDS. Furthermore, the shell thickness of the HCS can be easily controlled by varying the amount of templates (SDBS or P123). The formation of the carbon nanospheres involves an interface-mediated assembly process. Additionally, the bowl-like hollow carbon nanospheres show excellent biocompatibility. As a result, we expect that the hollow carbon spheres obtained in present method could be served as a promising candidate for more potential applications in the future such as drug delivery, catalysis, and lithium-ion batteries.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2015.04.027.

References