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Nitrogen-doped hollow carbon spheres with engineered large tunable mesoporous (~20 nm) shells are successfully synthesized for the first time by using dual-template method.
Nitrogen-doped Hollow Carbon Spheres with Large Mesoporous Shells Engineered from Diblock Copolymer Micelles

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Nitrogen-doped hollow carbon spheres with engineered large tunable mesoporous (~20 nm) shells were successfully synthesized for the first time by using the colloidal silica and the diblock copolymer PS-b-PEO as the dual-template and dopamine as the precursor. The unique structural properties enable them to be promising materials as adsorbents, catalyst supports, electrode materials, drug delivery carriers and hosts for active substances.

Future fabrication of advanced nano-devices will rely largely on the ability to control synthesis of nanomaterials possessing unique structural features and multifunctional properties. Porous carbon materials have been universally applied in dozens of fields due to their stable physicochemical properties, good electronic conductivity, low cost and abundant storage. Compared with other morphologies, the hollow spherical structure has many fascinating properties, including a high surface-to-volume ratio, low density, and large interior void fraction. Hollow carbon spheres have consequently attracted a great deal of interest, generating abundant research efforts. Up to the present, hollow carbon spheres have been fabricated by means of various synthetic approaches, including the hard-templating and soft-templating methods. The hard-templating method has been commonly adopted to synthesize uniform hollow carbon spheres by coating the surface of the spherical template core with a carbon precursor (e.g. resol, pitch, glucose, pyrrole), followed by carbonization and subsequent template etching. The retained carbon shells and hollow cores originate from the sacrificial colloidal hard templates, including monodispersed silica nanoparticles.

spherical polymers (e.g. polystyrene spheres), and metal oxides. Soft-templating method, which based on the organic-organic self-assembly of thermostetting carbon precursor and thermally decomposable amphiphilic molecules, requires less synthetic steps. Only a few hollow carbon spheres are obtained by using soft-templating method. These uniform hollow carbon spheres exhibit excellent potential for applications in adsorption, catalysis, and energy storage, due to their stable physicochemical properties, good electronic conductivity and unique structural property, including high surface area, accessible porous shell and high internal volume. In addition, the internal void provides a confined space which is especially attractive for drug delivery, gas storage, nanoreactors, and active material encapsulation.

Research designed to promoting applications of carbon materials have shown functionalized carbon materials with heteroatoms (e.g. N, B, P) to offer an effective approach to modifying intrinsic physicochemical properties of carbons. Nitrogen-enriched carbons with hierarchical pore structures present extraordinarily high capacitance per unit surface area (>30 μF·cm⁻²), due to the pseudocapacitance obtained from the high nitrogen content. The success of nitrogen-doped carbon materials in these applications depends on the increases in active surface sites, electrical conductivity, and the electron-donor effect between nitrogen and carbon in the nitrogen-doped carbons. In this context, nitrogen-doped hollow carbon spheres have recently been the subject of extensive research efforts. Since the first report in 2011 by Dai and coworkers, dopamine has been demonstrated to be a suitable precursor for synthesis of nitrogen-doped carbon materials. Compared with other carbon precursors, dopamine has many unique features. First, dopamine is a nontoxic biomolecule that can self-polymerize under alkaline conditions at just room temperature and, at the same time, coat almost any surface. Secondly, polymerized dopamine has a high carbonization yield of 50 wt.%, even at a temperature of 1000 °C, and nitrogen can be preserved in the final carbons in the form of graphitic-N and pyridinic-N. Very recently, we have demonstrated a strong interaction between dopamine and the high-molecular-weight diblock copolymer PS-b-PEO, and have...
successfully obtained solid nitrogen-doped carbon spheres consisting of abundant large mesopores (up to 16 nm) for the first time.\textsuperscript{[28]}

Although nitrogen-doped hollow carbon nanospheres have been developed by different synthetic strategies, including the use of dopamine as the precursor and silica spheres as the hard template,\textsuperscript{[29,30]} most have only random micropores or small mesopores (3-5 nm) in the shell.\textsuperscript{[4,11,19]} To the best of our knowledge, there are few reports that focus on precision engineering of the porous architecture of the shell in the hollow carbon spheres. Recently, monodispersed asymmetrical carbon nanohemispheres filled with ordered mesopores have been realized by Zhao’s group, but the size of the pores in the shell is still less than 6 nm.\textsuperscript{[31]} Hence, it remains a challenge to fabricate nitrogen-doped hollow carbon spheres with large mesopores in the shell, which could be more interesting for their ability to act as accessible pathways for mass transport, especially of large molecules. Inspired by the conformal deposition nature of polydopamine on solid surfaces, and the strong interaction between polydopamine and diblock copolymer PS-b-PEO, we report herein the synthesis through a dual-template method of nitrogen-doped hollow carbon spheres with large tunable mesopores (~20 nm) in the shell (NHCS-LM). Dispersed silica nanoparticles with sizes of ~350 nm were used as the hard template, and the diblock copolymer PS\textsubscript{173}-b-PEO\textsubscript{270} was selected as the micelle soft template for the generation of mesopores in the shell.

Figure 1. Schematic illustration of the preparation of NHCS-LM

A schematic illustration of the preparation of NHCS-LM is displayed and the formation mechanism is proposed in Figure 1. In the experimental process, the diblock copolymer PS\textsubscript{173}-b-PEO\textsubscript{270} dissolved in tetrahydrofuran (THF) solution, silica nanospheres well-dispersed in ethanol solution and dopamine (DA) dissolved in water were consecutively mixed together under continuous stirring. Under these conditions, the diblock copolymer PS\textsubscript{173}-b-PEO\textsubscript{270} existed as micelles in the hybrid solution. The PS\textsubscript{173}-b-PEO\textsubscript{270} micelles were surrounded by DA molecules because of the hydrogen bond interaction between the -OH group in the PEO block and the inherit catechol and N-H groups in the DA molecules.\textsuperscript{[25,32,33]} The solution was then adjusted to become alkaline by adding a certain amount of ammonia solution. The pH value of the alkaline reaction solution was measured to be 11.35. The DA molecules proceeded to self-polymerize and continued to coat the surface of the silica spheres at this stage.\textsuperscript{[25,32]} In the meantime, the micelles interact strongly with the polymerized dopamine (abbreviated as PDA) due to the catechols/quinone groups present in the PDA,\textsuperscript{[25, 32]} and were thus forcibly co-deposited onto the surface of the silica spheres together with PDA to obtain core-shell silica@PDA/micelles composite spheres. Carbonization was conducted at 800 °C under an inert atmospheres. This involved converting the PDA into nitrogen-doped carbon, simultaneously removing the PS\textsubscript{173}-b-PEO\textsubscript{270} micelles and creating large mesopores in the shell. The obtained sample was named as silica@NMCS at this stage, where NMCS refers to the nitrogen-doped mesoporous carbon shell that is inherited from the PDA/micelles shell. Finally, the silica template was etched with hydrofluoric acid to obtain the macroporous core, and leading to the formation of the target product, nitrogen-doped hollow carbon spheres with macroporous cores (~350 nm) and large mesoporous (~20 nm) shells (NHCS-LM).

Figure 2. SEM images of (a,b) silica@PDA/micelles, (c) silica template, (d) micelles of diblock copolymer PS\textsubscript{173}-b-PEO\textsubscript{270}, (e,f) silica@NMCS, and (g,h) NHCS-LM

The practical morphology of the samples in each stage was revealed by scanning electron microscope (SEM) images. As shown in Figure 2a, the prepared core-shell silica@PDA/micelles preserve the spherical morphology of their parent silica templates, but they exhibit a larger average diameter of 395 nm (inset in Figure 2a) compared with the silica core templates with an average diameter of 350 nm (Figure 2c). A high resolution SEM image of the individual particles of silica@PDA/micelles is shown in Figure 2b-1. Many round bumps with sizes of ~30 nm, a configuration matching the morphology of PS\textsubscript{173}-b-PEO\textsubscript{270} micelles (Figure 2d), can be clearly seen from the exposed hemispheres. The appearance of the silica@PDA/micelles is similar to our previously reported PDA/micelles spheres, demonstrating successful formation of a shell composed of PDA and PS\textsubscript{173}-b-PEO\textsubscript{270} micelles.\textsuperscript{[28]} Most of the spheres retained their integrity. When a random cracked shell...
was observed (Figure 2b-2), it revealed that the PDA/micelles layer coated the surface of the silica core uniformly and displayed a shell thickness of 24 nm, which explains the increased diameter of the silica@PDA/micelles compared with the parent silica spheres. After carbonization at 800 °C under a nitrogen atmosphere, the PDA could be converted to a nitrogen-doped carbon shell and those thermal pyrolysis PS-b-PEO micelles were simultaneously removed to leave mesopores (Figures 2e,f). Finally, the silica template was etched by hydrogen fluoride aqueous solution (HF) to produce the nitrogen-doped hollow carbon spheres with large-sized mesoporous shell (NHCS-LM, Figure 2g). As definitely observed from the high-magnification SEM image (Figure 2h), the shells of NHCS-LM possess large mesopores (~20 nm). This result has never been realized by other studies. In addition to the large mesopores that are replicated from the removal of the micelles, abundant micropores and small mesopores that originated from the pyrolysis of PDA are co-exist in the shells, which are not clear on the SEM image and can be estimated by nitrogen adsorption–desorption isotherms in the following section. Moreover, as verified in our previous study, the large mesopore size in the shell inherited from the diblock copolymer micelles can be easily adjusted by regulating the different molecular weights of the PS blocks in PS-b-PEO, which provides flexibility for tailored applications.

![Figure 3](image-url)

Figure 3. TEM images of NHCS-LM with identical average macroporous core diameter of 350 nm but varied shell thickness: (a,b) 17 nm and (c,d) 50 nm

The hollow structure and mesoporous shell of NHCS-LM were confirmed by transmission electron microscopy (TEM) images. As clearly shown in Figure 3a, NHCS-LM have a central hollow core with a diameter of around 350 nm, which matches the size of the silica template. The average porous shell thickness in NHCS-LM is about 17 nm, however, which is thinner than the PDA/micelles layer (24 nm), due to shrinkage of the PDA polymer during carbonization. The large mesopores that inherited from the diblock copolymer micelles in the shell also seem to appear in the TEM images (Figures 3a,b). The nitrogen content in NHCS-LM roughly estimated by energy-dispersive X-ray analysis (EDXA) is ~8 wt% (Figure S1). We further demonstrate that the thickness of the mesoporous shell is adjustable by controlling the coating time. After silica@PDA/micelles composite spheres were obtained, for example, these composite spheres have been dispersed into the ethanol solution and added to the primary solution composed of PS-b-PEO and dopamine, after which the process of coating the PDA/micelles layer has been repeated. The following carbonization and template etching steps are similar. As presented in Figures 3c,d, NHCS-LM after twice-repeated coating have an increased shell thickness of ~50 nm.

The carbon state in NHCS-LM was identified by XRD and Raman spectroscopy. As shown in Figure S2a, NHCS-LM presents two broad diffraction peaks at 2θ of 24° and 44°, which can be indexed to the (002) and (101) diffraction plane of the carbon and which suggest a predominantly amorphous nature of NHCS-LM. As shown in Figure S2b, the Raman spectra of NHCS-LM show two distinct bands located at 1360 (D band) and 1590 (G band) cm⁻¹, respectively. The D band is generally related to the vibrations of sp² hybridized carbon and defects in the plane terminations, and the G band is associated with vibrations of sp²-bonded ordered graphitic carbon sheets. Thus, graphitic and disordered carbons co-exist in NHCS-LM, which corresponds with the XRD result. The porosity and electric state of nitrogen were also determined by nitrogen sorption analysis (Figure S2c) and X-ray photoelectron spectroscopy (XPS) (Figure S2d). The details were explained in the supporting information.

The NHCS-LM synthesized by the dual-template method in this study have a mesoporous shell with a large pore size (~20 nm) which has never been reported before. Combined with their large internal void space, abundant nitrogen functional groups, and large surface area and pore volume, NHCS-LM have a wide spectrum of potential applications. The NHCS-LM can be used, for example, as electrode materials in electric double-layer capacitors. The electrochemical properties of a NHCS-LM electrode implemented in a supercapacitor architecture were investigated and the details was explained in supporting information (Figure S3).

In summary, we have described a dual-template approach to nitrogen-doped hollow carbon spheres with macroporous cores and tailored large mesoporous shells (NHCS-LM). The sizes of the mesopores in the tunable shells can be easily adjusted by adopting diblock copolymers with different molecular weight. Due to the unique structural properties of NHCS-LM, including their possession of abundant nitrogen functional groups, high specific surface area of 427 m²g⁻¹, large tunable mesopores in the shell and confined internal space, NHCS-LM are expected to be promising materials for applications as adsorbents, catalyst supports, drug delivery cargos, and hosts for active substances.

Notes and references