

Dopamine as a Carbon Source: The Controlled Synthesis of Hollow Carbon Spheres and Yolk-Structured Carbon Nanocomposites**

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The synthesis of hollow carbon nanospheres or capsules has attracted considerable attention because of their potential applications in catalyst supports, fuel cells, gas storage and separation, and lithium-ion batteries, which result from their unique features, such as high surface-to-volume ratio and high structural stability.^[1] Templating is the method widely used to synthesize hollow carbon spheres. Typically, a spherical core-shell structure is synthesized by coating a carbon precursor on a hard template core, followed by carbonization and core removal to obtain hollow carbon spheres. The templating approach based on the use of solid molds also provides opportunities for developing various porous carbon composite nanostructures. Among them, the rattle-type or yolk-shell nanostructure is a novel and promising nanostructure, in which a movable core is encapsulated inside a carbon shell.^[2] Such a carbon shell not only functions as a barrier to prevent encapsulated nanoparticle from coalescence, the chemical and thermal stability and inherent electrical conductivity of such a carbon coating are especially beneficial for catalytic and electrochemical applications. For example, Pt@Carbon or Rh@Carbon and Sn@Carbon nanorattle structures shown excellent performance in catalytic hydrogenation reactions and lithium batteries, respectively.^[3]

Carbon precursors have an important effect on the preparation and final physical and chemical properties of

the resulting carbon framework.^[4] In addition to a good carbon yield, simple and effective uniform coating is another important issue in the templated synthesis of carbon materials. Recently, surface-initiated atom transfer radical polymerization (ATRP) from silica nanoparticles and mesoporous silicas has been used to make uniform polyacrylonitrile coating for the preparation of nanoporous carbon.^[5] More recently, White et al. have developed a novel hydrothermal carbonization method to synthesize carbon capsules using biomass as carbon source and polymer latex as template.^[6] Herein, we report a versatile and facile method to prepare hollow carbon spheres and yolk-shell carbon nanocomposites using dopamine as the carbon source. The essence of our method lies in the exploitation of 1) the conformal nature of polydopamine coatings and 2) high carbonization yield of polydopamine. To our knowledge, it is first time dopamine has been utilized in the construction of carbon-based nanomaterials.

Dopamine, a biomolecule that contains catechol and amine functional groups, can self-polymerize at alkaline pH values and spontaneously deposit polydopamine conformal films on virtually any surface.^[7] The thickness of such a conformal coating can be precisely controlled with a resolution of approximately 1 nm. The single-step solution-based deposition technique has demonstrated direct benefits in the construction of polymeric nanocapsules.^[8] In addition, polydopamine can further serve as an adhesion layer to immobilize biological molecules, amine- and mercapto-functionalized self-assembled monolayers, and metal films to the surface for secondary modification for various applications, such as biosensors, biomineralization, preparation of free-standing films, drug delivery, and cancer imaging.^[9] However, the use of dopamine or dopamine polymer as a carbon precursor has never been reported. The structural similarity of polydopamine to phenolic resins prompted us to think that polydopamine should have an excellent carbon yield. Taking advantage of its strong and versatile coating capability, dopamine is expected to show excellent performance in the preparation of carbon-coating materials.

As shown in Scheme 1, we used silica spheres as template to synthesize hollow carbon spheres. A spherical silica template with approximately 400 nm particle size (see Supporting Information, Figure S1) was prepared by the Stöber method.^[10] The dopamine coating was obtained by polymerizing dopamine onto silica spheres in 10 mM (pH 8.5) Tris-buffer.^[7] The polymer/silica nanocomposite thus obtained was then carbonized in N₂ to convert the coated polydopamine into carbon, followed by washing the carbon/silica composite in HF to remove the silica template to obtain

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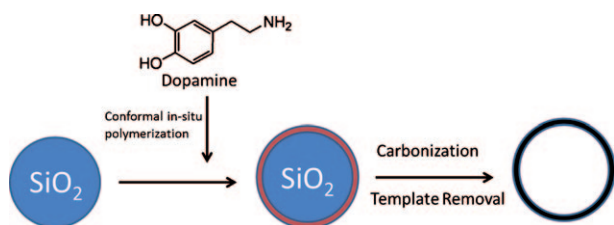
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Scheme 1. The synthesis of hollow carbon spheres using silica spheres (blue) as the template and dopamine (red ring) as the carbon source.

hollow carbon spheres. Scanning electron microscopic (SEM) image (Supporting Information, Figure S2) shows that the materials obtained preserve the structural integrity and spherical morphology with particle size of approximately 400 nm as their parent silica template. Energy-dispersive X-ray (EDX) analysis (Supporting Information, Figure S2) confirms the high purity of the carbon composition with a small amount of nitrogen left. Scanning transmission electron microscopic (STEM) analysis (Figure 1 A and B) clearly

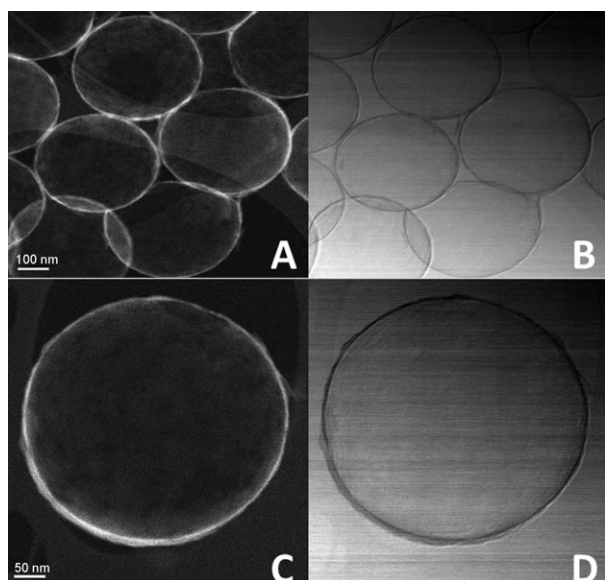


Figure 1. STEM images of hollow carbon spheres A),C) Z-contrast, B),D) bright field.

shows that the carbon capsules are monodisperse and uniformly spherical, with diameter of around 400 nm, which is consistent with the SEM result and the particle size of the silica template. STEM images in Figure 1 C and D reveal the characteristics of individual nanocapsules. The relative higher contrast of the shell with respect to the core in the Z-contrast image indicates that the nanoparticles are hollow. STEM images (Supporting Information, Figure S3) also show a clearly uniform shell with a 4 nm thickness full of micro-porosity of these spherical particles. Thermogravimetric analysis (TGA) provides more quantitative information about the carbon yield of polydopamine. Polydopamine formed on a silica glass under identical conditions was

scratched and tested in N_2 and air, respectively (Supporting Information, Figure S4). Pure polydopamine can produce nearly 60% carbon yield in N_2 at 800 °C. The above results clearly demonstrate that dopamine can work as a simple and effective carbon coating source.

The simple process for synthesizing hollow carbon spheres using dopamine as the carbon source can also be conveniently applied to convert other carbon-coated composites. As a demonstration of its versatility, monodispersed Au@Carbon (Au@C) nanorattle structures were synthesized and their use as nanoscale reactors for catalytic reactions was evaluated. Instead of silica spheres, Au@SiO₂ core-shell nanoparticles prepared using the reported sol-gel method^[11] were used as template (Supporting Information, Figure S5). Following a procedure similar to that described above, Au@SiO₂ was coated with polydopamine by simply mixing dopamine and Au@SiO₂ in 10 mM (pH 8.5) Tris-buffer. After carbonization in N_2 and etching in HF, Au@C nanorattle structures were obtained (see Scheme S1 and experimental details in Supporting Information). The EDX spectrum of composite materials (Supporting Information Figure S6A) clearly identifies the peaks of C and Au. SEM (Figure S6B) and STEM (Figure 2) images indicate that the Au@C preserves spherical

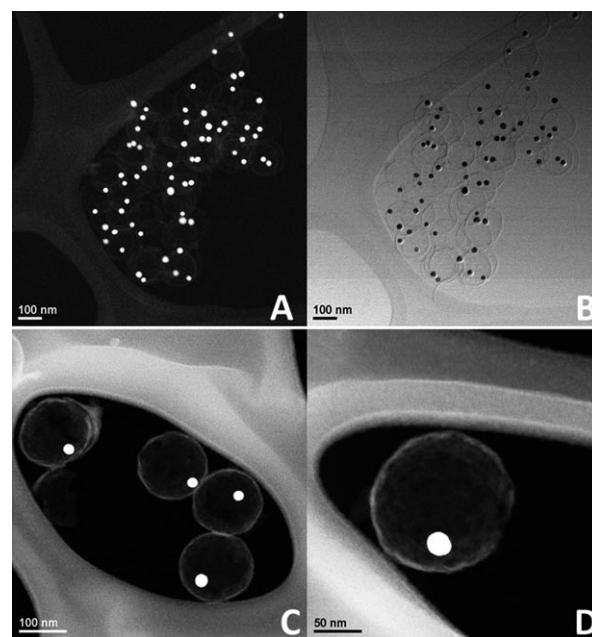


Figure 2. STEM images of Au@C yolk-shell nanocomposites A),C),D) Z-contrast, B) bright field.

morphology with particle size of approximately 100 nm, which is in accordance with the spherical structure of Au@SiO₂ (Supporting Information, Figure S5). The relative higher contrast of the shell with respect to the core in the Z-contrast image confirms the hollow structure, filled by metal nanoparticles with one metal nanoparticle in each carbon capsule, which is a typical characteristic of nanorattle or yolk-shell structures. From the SEM (Supporting Information, Figure S6B) and STEM images (Figure 2 C and D) of integral spheres, it is clear that gold nanoparticles appear as brighter

spots studded onto the inner surface of the hollow shells. The shell of the carbon capsule is about 4 nm thick, and the diameter of the metal nanoparticle is about 15 nm.

The gold-catalyzed reduction of 4-nitrophenol by NaBH_4 to 4-aminophenol was chosen as a model reaction to evaluate the catalytic ability of the synthesized Au@C. The reduction reaction does not proceed without the Au@C catalyst, as evidenced by a constant absorption peak at 400 nm. However, when Au@C yolk-shell catalyst was introduced into the solution, the absorption at 400 nm quickly decreased and absorption at 295 nm increased accordingly (Figure 3). The

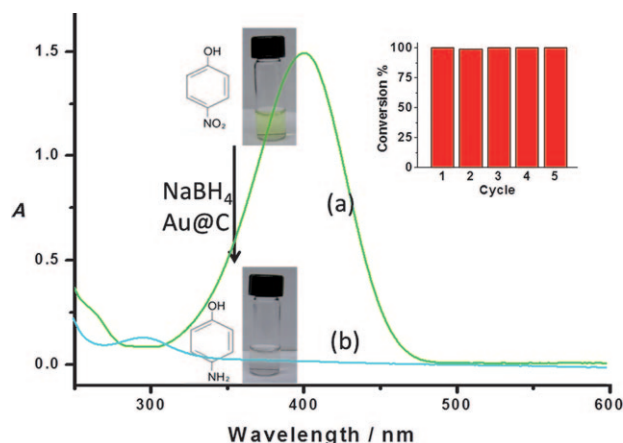


Figure 3. UV/Vis spectra of 4-nitrophenol reduction a) before and b) 5 min after the addition of the Au@C catalyst. Insets: reaction scheme and associated color changes and a graph of the conversion of 4-nitrophenol in 5 min versus the number of catalyst recycles.

reduction of 4-nitrophenol into 4-aminophenol was completely finished in 5 min. The complete conversion of 4-nitrophenol can also be visually appreciated by the color change of the solution, which was originally bright yellow and became colorless (Figure 3, insets). The fast reaction kinetics in nitrophenol reduction compared to the reported Au@SiO₂ and Au@polymer nanorattle structures^[12] is believed to come from a combination of Au@C nanorattle structure characteristics: the facile diffusion of 4-nitrophenol through the porous carbon layer sheet within a 4 nm ultrathin shell, the large free reaction voids inside the carbon sphere, and highly dispersed gold nanoparticles in each capsule. Stability against coalescence is a very important issue for nanocrystal-based catalysts.^[11,13] The stability of Au@C was investigated by performing the same reduction reaction with the same catalyst five times (Figure 3, inset). After each use, the catalyst was recycled by simple centrifugation, followed by washing with distilled water and drying in an oven overnight for the next cycle of catalysis. The catalysts were still highly active after five successive cycles of reactions, with conversion close to 100% within 5 min reaction periods. Apparently, the presence of a carbon shell was sufficient to stabilize the catalytic nanoparticles by preventing their aggregation. At the same time, the inherent chemical inertness and good mechanical stability of carbon materials renders Au@C with high catalytic

stability, giving the materials presented herein great potential as stable and highly active nanocatalysts.

In conclusion, we developed a versatile and facile method for synthesizing hollow carbon spheres and yolk-shell structured nanocomposites using dopamine as the carbon source. The uniform carbon capsules were obtained easily by a simple immersion of the template in a dopamine aqueous solution, and subsequent carbonization and template removal. The Au@Carbon yolk-shell nanocomposites obtained by the same process showed high catalytic ability and stability in the reduction of 4-nitrophenol. Since dopamine can self-polymerize and coat virtually any surface and can readily undergo secondary modifications, this highly efficient process may be applicable to various carbon-coating composites.

Experimental Section

Hollow carbon spheres: Silica spheres were synthesized as templates by Stöber method.^[10] Then, silica spheres (80 mg) were mixed with dopamine (80 mg) in Tris-buffer (25 mL, 10 mM; pH 8.5) for 24 h. The polymer/silica nanocomposite obtained was collected by centrifugation, then carbonized under N₂ atmosphere at 400 °C for 2 h with a heating rate of 1 °C min⁻¹, which was followed by further treatment at 800 °C for 3 h with a heating rate of 5 °C min⁻¹. After washing in 5% HF aqueous solution for 24 h, hollow carbon spheres were obtained.

Au@Carbon nanorattles: Au@SiO₂ core-shell particles were used as the template and prepared using the reported sol-gel method.^[11] The Au@SiO₂ (20 mg) and dopamine (20 mg) were stirred in Tris-buffer (10 mL, 10 mM; pH 8.5) for 24 h. Carbonization was carried out under N₂ atmosphere at 400 °C for 2 h with a heating rate of 1 °C min⁻¹, which was followed by further treatment at 800 °C for 3 h with a heating rate of 5 °C min⁻¹. After washing in 5% HF aqueous solution for 24 h, Au@C nanorattles were obtained.

Catalytic study: 4-nitrophenol (3 mL, 1 × 10⁻⁴ M) was mixed with freshly prepared aqueous solution of NaBH₄ (0.1 mL, 3 × 10⁻¹ M). Au@Carbon (5 mg) was then added with constant magnetic stirring. UV/Vis absorption spectra were recorded to monitor the change in the reaction mixture.

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