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The fabrication of size-tunable nitrogen-doped dual-mesoporous carbon nanospheres with excellent thermal stability via colloidal silica driving co-assembly strategy

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ABSTRACT

The synthesis of nitrogen-doped dual-mesoporous carbon nanospheres (N-DMCNs) with tunable sizes remains a great challenge due to the high cross-linking rate of carbon precursors and the weak interactions among the carbon precursors, inorganic components and templates. Herein, we demonstrated a colloidal silica nanoparticles (SN) driving co-assembly strategy for the first time to fabricate such N-DMCNs with hydrochloric acid (HCl) as a catalyst. Interestingly, SN not only acted as a pore-forming agent but also as a driving agent to induce the co-assembly of F127, carbon precursors and SN. The affinity between carbon precursor and template was enhanced by the Coulombic interaction originating from the $I^+X^-S^+$ mechanism driven by the protonation under highly acidic conditions. Furthermore, the mesoporous structure and particle sizes could be facilely tuned by varying the HCl concentration, which was elucidated by both reversible reaction and nuclei growth mechanism. The as-prepared N-DMCNs could be potentially used as drug carrier for poorly water-soluble drug carbamazepine by improving its aqueous release rate. Compared with previously reported method, the present strategy has striking features such as convenient, inexpensive and environmentally friendly, especially affording a paradigm for the preparation of spherical mesoporous carbon nanoparticles through driving-induced assembly engineering.

1. Introduction

Mesoporous carbon nanospheres (MCNs) have attracted considerable attentions due to the high dispersity, excellent thermal stability, uniform and controllable particle sizes. However, the practical applications of pristine mesoporous carbons are impeded by their high hydrophobic surface and the small number of specific active sites [1]. Fortunately, the above limitations could be solved by using the functional mesoporous carbon nanomaterials such as the oxidized MCNs, heteroatoms-doped MCNs (nitrogen, boron and sulphur etc.), which can tune the surface wettability, polarity and surface electron-distribution tendency of the carbon matrix [2,3]. Among these heteroatom modifications, nitrogen dopant appears to be an excellent choice because its atomic size and five-electron valence structure (sp^2 hybridization) allow it to naturally fit into a strong covalent network structure of carbon atoms [4]. The mesoporous carbon nanomaterials doped with nitrogen have been exploited in the aspect of the synthetic optimization and materials morphologic engineering, as well as boosted the application in adsorption, drug delivery, supercapacitors, and so on [5–7].

During the past decades, various synthesis strategies, such as hard-template assisted procedure [8], hydrothermal process [5,9], extended stober method [10–12], and one-step aqueous route [1,13,14], have been developed to fabricate nitrogen-doped MCNs (N-MCNs). Among these methods, one-step aqueous method exhibited better reproducibility, size-tunable pores and well-controlled morphologies, which was evaluated to be a more attractive route. Typically, Wang's group employed this strategy to fabricate N-MCNs with controllable particle sizes [15]. In this process, the key point was the selection of hexamethylenetetramine (HMT) as a slow release source of formaldehyde, which was an significant agent to separate the resorcinol-formaldehyde condense process and self-assembly process [16]. However, HMT would start to hydrolyze to form ammonia and formaldehyde at 70 °C in a non-

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acidic aqueous solution, which resulted in a relatively high energy consumption [17]. Otherwise, both this method and the aforementioned strategies used ammonia as alkaline catalyst, which showed the weak self-assembly ability between the carbon precursor and template [18]. As a result, the excessive cross-linking of carbon precursors would lead to macroscopic phase separation of the carbon precursors and templates [19]. Thus, it is highly desirable to develop a convenient and efficient method for the synthesis of mesoporous carbon materials with spherical morphology.

It is well-known that the self-assembly process between micelles and carbon precursors could be illustrated by the fundamental guiding principles including I^0S^0, $I^+X^-S^+$, $I{-}S^+$ mechanism (I^0 nonionic species, S^0 nonionic surfactants, I^+ soluble cationic inorganic precursors, X^- intermediate anion, and S^+ cationic surfactants) [20,21]. Under alkaline condition, the driving force of self-assembly process illustrated by the I^0S^0 principle is hydrogen-bonding interaction, which is rather weaker than the Coulombic interaction originating from the $I^+X^-S^+$ mechanism driven by the protonation under highly acidic conditions [22]. The latter feature exhibits enhanced affinity between carbon precursors and templates, which may benefit for matching a quick cross-linking rate of carbon precursors, thereby facilitating the formation of mesoporous structure. Furthermore, the principle of $I^+X^-S^+$ mechanism could also be applied to the cooperation of organic species and inorganic species such as the assembly of SN and phenolic derivatives [23]. However, under highly acidic condition (2 M), the polymerization rate of carbon precursors was extremely high, which made the polymer-rich phase easily separate from the aqueous solution, thus leading to a non-spherical morphology of the resulting carbon materials [24]. Therefore, it is challenging to keep the mesoporous structure as well as the spherical morphology during the rapid fabrication under highly acidic conditions. To the best of our knowledge, there is no report on the facile synthesis of N-MCNs with dual-mesoporous structure under high acid conditions so far.

In this contribution, we demonstrate a simple and efficient method for the first time to synthesize N-DMCNs through a SN driving co-assembly process with 3-aminephenol (AP) and formaldehyde as carbon precursors. Compared to previous reports, SN not only acts as a pore-forming agent but also as a driving agent to induce the participation of F127 into the assembly process. Moreover, HCl was used as a catalyst for the polymerization of AP and formaldehyde at an initial temperature of 35 °C. Both carbon resources and temples were highly protonated under high acid condition, and thus showed an enhanced Coulombic interaction originating from the $I^+X^-S^+$ mechanism with Cl^- as a mediator. The resulting N-DMCNs with well-defined dual-mesoporous structure (3.5 and 7.8 nm) displayed high specific surface areas (~642 m^2/g), large pore volumes (~0.86 cm^3/g), and their mesoporous structure as well as particle sizes could be facilely tuned by varying the HCl concentration. Inspiringly, the advantages of N-DMCNs, such as high dispersity, size controllable and high specific surface area made them a promising carrier candidate for drugs with poorly water-solubility like CBZ. The release testing was carried out to investigate the release behavior of drug-loaded N-DMCNs.

2. Experimental

2.1. Materials and preparation

F127 (Mw = 12,600 g/mol, $PEO_{106}{-}PPO_{70}{-}PEO_{106}$), carbamazepine (CBZ, >98%) and LUDOX AS-30 Colloidal silica (SN, 30 wt%) were purchased from BASF, Aladdin Reagent Inc and Sigma-Aldrich, respectively. Ethanol (>99%), hydrochloric acid (HCl, 37%), 3-aminophenol (AP, 98%), formaldehyde (37%–40% in water), sodium hydroxide (NaOH, >96%) and sodium lauryl sulfate were all purchased from Guangzhou Chemical Corp. (China). All chemicals were used as received without purification.

2.2. Synthesis of N-CNs, N-DMCNs

In a typical experiment, 0.84 g of F127 was dissolved in 43 mL of deionized water/ethanol solution (35:8, v/v), followed by adding 5 mL of 37% HCl solution (1.25 M) under magnetic stirring. Then 0.15 mL of SN and 0.20 g of AP were added. After stirring for 1 h, 0.18 mL of formaldehyde (37 wt%) was added dropwise. Afterwards, the above solution was further heated to 35 °C and stirred for 24 h. After centrifugation, purified and dried completely, the polymer nanospheres (PN) were obtained and denoted as PN-1.25. For the carbonization process, the polymer was heated to 410 °C, kept for 3 h and then further heated to 800 °C and kept for 3 h under flowing N_2 atmosphere with a heating rate of 1 °C/min. Then an etching treatment with 1 M NaOH at 70 °C was followed. The final product was denoted as N-DMCNs-x (x represents the corresponding HCl concentration). For comparison, the products synthesized without the addition of SN were denoted as N-CNs-x.

2.3. CBZ loading procedure

CBZ loaded into the nanospheres was via a procedure involving a combination of adsorption equilibrium and solvent evaporation. Firstly, 6, 12 and 20 mg/mL methanol solutions of CBZ were fabricated. Then, 100 mg of N-DMCNs-1.25 was transferred into 5 mL of the above CBZ solutions, respectively. The mixture was stirred for 24 h in a sealed container and then dried at 40 °C under vacuum for 24 h. The obtained powders were denoted as CBZ-N-DMCNs-x (x represents the corresponding concentration of CBZ solution), separately. For comparison, 100 mg of N-CNs-1.25 was added into 5 mL of methanol solution of CBZ (20 mg/mL) while keeping other parameters constant. The drug-loaded sample was referred to CBZ-N-CNs-20.

2.4. Determination of drug loading

Briefly, 20 mg of CBZ-N-DMCNs-x was added into 100 mL of methanol. These suspensions were sonicated for 10 min and subsequently put in a magnetic stir plate for 12 h. Following this, the nanoporous carbon products were separated from the CBZ solution by centrifugation. The supernatant layer was taken, filtered through a 0.22 μm PTFE syringe filter (Millipore, USA) and then the drug concentration was determined by UV spectrophotometer at 288 nm. The drug loading was calculated using the formula: Drug loading (%) = (the weight of CBZ in composite/weight of composite) × 100.

2.5. In vitro release profile

The release profiles were conducted by USP II paddle method. The drug-loaded sample (including 50 mg of CBZ) was dispersed into 900 mL of water containing 1% (w/v) sodium lauryl sulfate, and maintained at 37 °C with a rotation speed of 75 rpm. Afterwards, 10 mL of release medium was withdrawn at specified times and replaced with 10 mL of fresh release medium. The resulting medium was filtered and analyzed by UV spectrophotometer at 288 nm.

2.6. Characterization

Scanning electron microscopy (SEM) was performed with a Merlin high-resolution field emission electron microscope