



Self-catalyzed strategy to form hollow carbon nanospheres for CO₂ capture



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ABSTRACT

The hollow carbon nanospheres (HCNs) are synthesized by self-catalyzed method. The amino-functionalized silica nanospheres (NH₂-SiO₂) play the roles of template and catalyst. As a basic group, the amino provides slight alkaline conditions which can catalyze the polymerization of resorcinol-formaldehyde (RF) resin. Additionally, the amino group covering the outer surface of SiO₂ turns to be slight positively charged in the solution, which allows deposition of negatively charged RF on the surface of NH₂-SiO₂. The method has an advantage over previous method in terms of environment protection due to the absence of surfactant and ammonia. After carbonization and removal of the SiO₂ templates, the obtained HCNs completely copy the morphology of SiO₂, exhibiting uniform and monodispersed spherical structures with the diameter of ~290 nm and surface area of 777 m² g⁻¹. The sample exhibits a performance for CO₂ capture with the capacity of 3.65 mmol g⁻¹ at 298 K and 1.0 bar after activation with KOH.

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1. Introduction

Hollow carbon nanospheres (HCNs) are particularly fascinating due to their unique structural properties which make them suitable for several potential applications in lithium-ion batteries, catalyst supports, fuel cell electrodes, energy storage, gas storage and separation [1–5]. In recent years, hard template method is widely used to synthesize HCNs since it is straightforward to apply and has obvious advantages for controlling the size, shape and structure of the products by the pre-fabricated templates [6]. Among the hard templates, SiO₂ are ideal and popular due to their features of simple synthesis, and feasible modification. For example, Fuertes and co-workers reported the synthesis of SiO₂@resorcinol-formaldehyde (SiO₂@RF) nanocomposites under Stöber conditions using ammonia as catalyst and structuring direct agent [7]. In the alkaline conditions, NH₄⁺ in the emulsion can not only accelerate the polymerization of RF, but also supply the positive charges that adhere to the outer surface of SiO₂ (negatively charged) to prevent the aggregation of SiO₂ and form a stable colloidal suspension. The coating of RF on the surface of SiO₂ is an important process for preparing of HCNs. In order to obtain high quality RF coated SiO₂ nanostructures, surfactants (e.g. cetyltrimethylammonium bromide, CTAB) are usually used to modulate the surface properties of SiO₂ and reinforce the interactions

between RF resin and SiO₂. Previous reports reveal that in the absence of surfactant, no core-shell structures can be obtained [8]. Generally speaking, ammonia and surfactant are indispensable in synthesis of HCNs by employing SiO₂ as hard template. However, ammonia and surfactant are harmful to the environment, resulting in pollution problems. So, it is challengeable and desirable to develop more environment-friendly methods to synthesize HCNs.

Herein, we propose the synthesis of HCNs by using the amino-functionalized SiO₂ (NH₂-SiO₂) as hard template and catalyst, RF resin as carbon precursor via a self-catalyzed method. In the process, SiO₂ are first produced by classical Stöber method, and then modified with amino group by silicification with (3-aminopropyl) triethoxysilane (APTES). RF deposits on the NH₂-SiO₂ by a self-catalyzed process to form NH₂-SiO₂@RF without any added surfactant and ammonia. This self-catalyzed method is based on the following features: (1) the amino group on the surface of SiO₂ provides alkaline site promoting polymerization of resorcinol and formaldehyde; (2) positively charged NH₂-SiO₂ can induce spontaneous deposition of RF resin onto the surface of NH₂-SiO₂ [9]. On the basis of these features, the catalyzing and coating process is denoted by “self-catalyzed” method. The obtained HCNs have a uniform size and high surface area, as well as good performance for CO₂ capture after activation with KOH. This method can also be generalized to other resins to synthesize the HCNs and provides a novel synthesis strategy for HCNs.

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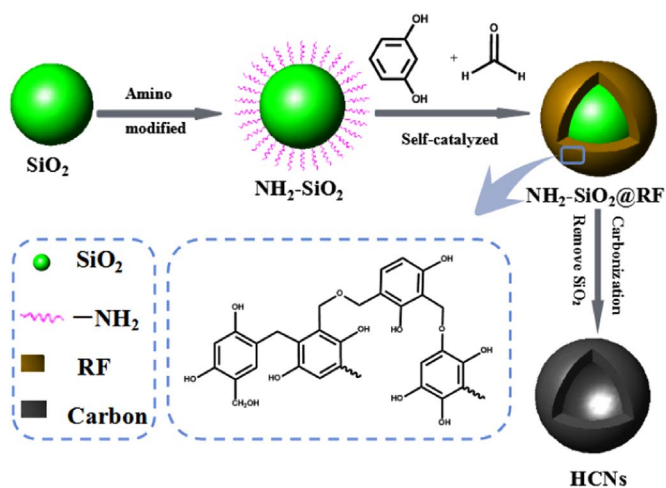


Fig. 1. The scheme of the formation of HCNs.

2. Experimental

The detailed pre-preparation of the raw material and fabricating process were shown in Supplementary Material. The fabrication of HCNs involves the following steps: (i) $\text{NH}_2\text{-SiO}_2$ was homogeneously dispersed in the mixture of resorcinol and formaldehyde, and then stirred at 35 °C for 24 h. (ii) The mixture was reacted in Teflon-lined autoclave container at 100 °C for 24 h. (iii) After collecting by centrifugation, carbonization and removing SiO_2 , the HCNs were obtained.

3. Results and discussion

The self-catalyzed mechanism is proposed for the formation of HCNs as shown in Fig. 1. The SiO_2 with a uniform diameter of 260 ± 20 nm are modified with amino and then used as template to synthesize the HCNs in the following process. With slightly positive charged surface and accessible alkaline site, the $\text{NH}_2\text{-SiO}_2$ catalyze the polymerization of RF resin and facilitate covering of RF resin outside the functional SiO_2 core, leading to core-shell structured $\text{NH}_2\text{-SiO}_2\text{@RF}$. The HCNs are then obtained through high temperature calcination and removing the SiO_2 templates with an appropriate amount of HF.

The morphologies and structures of HCNs are shown in Fig. 2. The SEM image of HCNs (Fig. 2a) shows that the HCNs are significantly monodispersed with smooth surface and spherical morphology (290 ± 20 nm). A broken carbon sphere can be clearly observed from Fig. 2b, which show the obvious hollow structure of HCNs. The hollow structure of the HCNs is further confirmed by the TEM images (Fig. 2c and d). Fig. 2c clearly exhibits uniform hollow nanostructures with a large void of 260 ± 20 nm in diameter, which is consistent with the size of the SiO_2 core, suggesting the RF resin can be adsorbed onto the surface of $\text{NH}_2\text{-SiO}_2$ uniformly by the self-catalyzed method. The thickness of the HCNs shell is around 15 nm, as measured from the high-magnification TEM image (Fig. 2d). It is remarkable that a large number of micropores are clearly observed from the Fig. 2d inset, which may result from shrinkage of RF during carbonization and removal of SiO_2 during etching process.

The N_2 adsorption-desorption isotherms of the resultant HCNs

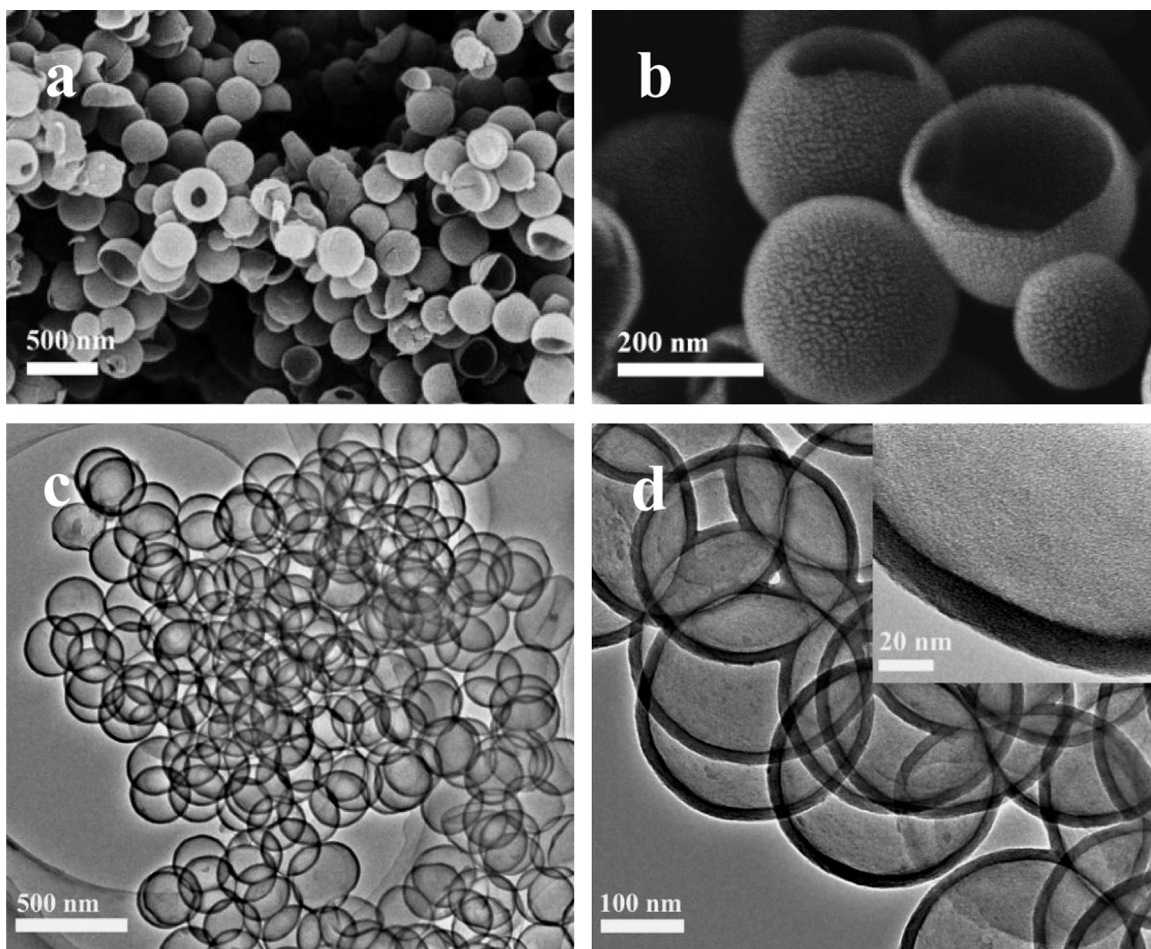


Fig. 2. SEM (a, b) and TEM (c, d) images of HCNs.

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