



# Nitrogen-doped hollow carbon spheres derived from amination reaction of fullerene with alkyl diamines as a carbon catalyst for hydrogenation of aromatic nitro compounds



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## ABSTRACT

Hollow carbon nanospheres have received much interest by virtue of the special shape, low density and large interior void space, allowing their many potential applications. Here we report a template-free route to produce nitrogen-doped hollow porous carbon spheres (denoted as N-HPCs) through amination reaction of C<sub>60</sub> with alkyl diamines and subsequent carbonization. The size of wall thickness and cavity of hollow carbon spheres could be easily regulated by the chain length of alkyl diamines. After carbonization in Ar atmosphere, the obtained N-HPCs exhibited excellent activity and recyclability for hydrogenation of aromatic nitro compounds with hydrazine hydrate. The facile approach presented in this work provides a new way for preparation of doped hollow porous carbon spheres.

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## 1. Introduction

Porous carbon nanomaterials have received considerable attention owing to their unique properties such as high surface-to-volume ratio, low density, good chemical stability [1,2], allowing their many potential applications in catalysis [3,4], adsorption [5,6], hydrogen storage [7], supercapacitors [8] and lithium-ion batteries [9]. As one class of intriguing porous carbon materials, hollow porous carbon spheres (HPCs) possess a broad spectrum of attractive characteristics, including the spherical structure, shell permeability and large interior void fraction [10,11]. These features enable them served as unique reservoirs or artificial reaction cells, which is especially attractive for drug delivery, gas storage, nano-reactors and active material encapsulation [12,13]. Consequently, a wide variety of methods had been explored to prepare HPCs, including hard [14] and soft [15] templating, HTC [16], emulsion polymerization [17], self-assembly and Stöber synthesis [18].

In general, templating strategy based on hard/soft templates is the most frequently used synthetic method to prepare HPCs. During

hard-templating method, carbon precursors are usually first coated on the surface of core templates, followed by carbonization and finally removal of templates [19–23]. This strategy has the advantages in fine controlling the hollow size of carbon spheres. However, the removal of templates is time-consuming and unfriendly to the environment. The soft-templating method, which is based on the organic-organic self-assembly of thermosetting carbon precursors and thermally decomposable amphiphilic molecules, requires less synthetic steps [24,25]. Although soft-templating methods can be effectively adopted to prepare hollow carbon spheres, the possibilities to tune their textural properties and sizes are very limited [26]. Therefore, it is highly desirable to developing efficient template-free routes to produce HPCs.

Herein, we report a facile template-free strategy for synthesis of nitrogen-doped hollow porous carbon spheres (N-HPCs) based on amination reaction of C<sub>60</sub> with alkyl diamines. Moreover, the size of wall thickness and cavity of hollow carbon spheres could be easily regulated by using various alkyl diamines with different chain lengths. Alkyl diamines and H<sub>2</sub>O<sub>2</sub> play decisive roles in the hollow structure evolving process. After carbonization in Ar atmosphere, the obtained N-HPCs exhibited excellent activity and recyclability for hydrogenation of aromatic nitro compounds with hydrazine hydrate as the hydrogenation agent.

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## 2. Experimental

### 2.1. Materials

Toluene, hydrogen peroxide (30 wt%), ethanol, acetonitrile, 1-propanol, hydrazine hydrate (85 wt%), ethylenediamine (EDA) and 1,6-hexanediamine (HDA) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. C<sub>60</sub> was purchased from Suzhou Dade Carbon Nanotechnology Co., Ltd. 1,3-diaminopropane (PrDA), 1,4-diaminobutane (BDA), 1,5-diaminopentane (PeDA), ethanolamine (EOA), 3-amino-1-propanol (PrOA), 4-amino-1-butanol (BOA), 5-amino-1-pentanol (PeOA), 6-amino-1-hexanol (HOA), tetrabutylammonium hydroxide (40 wt% solution in water) and all the aromatic nitro compounds were purchased from Beijing InnoChem Science & Technology Co., Ltd. All the reagents were used without further purification.

### 2.2. Synthetic procedures

#### 2.2.1. Preparation of C<sub>60</sub>-alkyl diamines

C<sub>60</sub> 108 mg (0.15 mmol) was dissolved in 50 mL toluene, and this purple solution was labeled as A. 1,6-Hexanediamine 870 mg (7.5 mmol, 50 equiv.) was dissolved in 3.3 mL water, then it was mixed with solution A. After that, 5 drops of tetrabutylammonium hydroxide (40 wt%) as a phase transfer catalyst was added, then 1.7 mL H<sub>2</sub>O<sub>2</sub> (30 wt%, 15 mmol, 100 equiv.) was added. After stirring for 60 min at 60 °C, the upper toluene was removed, and 20 mL ethanol was added into the residual mixture. The solid was collected by filtration and washed with ethanol for 3 times. The product was dried at 60 °C for 12 h. The C<sub>60</sub>-EDA, C<sub>60</sub>-PrDA, C<sub>60</sub>-BDA and C<sub>60</sub>-PeDA were prepared in the same way except that ethylene, 1,3-diaminopropane, 1,4-diaminobutane and 1,5-diaminopentane were used instead of 1,6-hexanediamine.

#### 2.2.2. Preparation of C<sub>60</sub>-alcohol amines

The C<sub>60</sub>-HOA was prepared in the same method to that of C<sub>60</sub>-HDA. C<sub>60</sub> 108 mg (0.15 mmol) was dissolved in 50 mL toluene, and this purple solution was labeled as A. 6-Amino-1-hexanol 879 mg (7.5 mmol, 50 equiv.) was dissolved in 3.3 mL water, and it was mixed with solution A. After that, 5 drops of tetrabutylammonium hydroxide (40 wt%) as a phase transfer catalyst was added, then 1.7 mL H<sub>2</sub>O<sub>2</sub> (30 wt%, 15 mmol, 100 equiv.) was added. After stirring for 60 min at 60 °C, the upper colorless toluene solution was removed, and the lower deep red aqueous solution was precipitated by adding approximately 8 times volume of acetonitrile. The solid was collected by centrifugation and washed two times with acetonitrile. The obtained product was dried at 60 °C for 12 h. The C<sub>60</sub>-EOA, C<sub>60</sub>-PrOA, C<sub>60</sub>-BOA and C<sub>60</sub>-PeOA were prepared in the similar method except that ethanolamine, 3-amino-1-propanol, 4-amino-1-butanol, 5-amino-1-pentanol were used instead of 6-amino-1-hexanol.

### 2.3. Typical producers for hydrogenation of aromatic nitro compounds

Aromatic nitro compounds (0.5 g), hydrazine hydrate (85 wt%, 2 mL) and catalyst (10 mg) were added into a glass reaction flask. In order to promote the interaction between nitrobenzene and hydrazine hydrate, 1-propanol (1 mL) was added. Then, the mixture was stirred in a 100 °C oil bath for desired time. The products were analyzed by a gas chromatograph (Shimadzu GC-2010) equipped with a flame ionization detector (FID) and a Rtx<sup>®</sup>-5 capillary column (0.25 mm in diameter, 30 m in length). The identity was ascertained by GC-MS (Shimadzu GC-MS QP2010S). To study the reusability of the catalyst, the catalyst was washed one time with 1-

propanol and dried at 80 °C for 12 h before next cycle, and the reaction time was fixed to 4 h.

### 2.4. Characterizations

The morphology of the products was characterized by JEOL JEM-2100F transmission electron microscopy (operating at an accelerating voltage of 200 kV). Fourier transform infrared (FTIR) spectra were performed on a TENSOR-27 type infrared spectrometer. Elemental analysis was carried out on a Flash EA 1112 type elemental analyzer. The surface area was determined by N<sub>2</sub> adsorption-desorption isotherms using Quantachrome Autosorb AS-1 Instrument. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab 220i-XL electron spectrometer from VG Scientific using 300 W Al K $\alpha$  radiation. X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-2500 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV and 200 mA. Elemental mapping images were obtained by a JEOL-2100F TEM.

## 3. Results and discussion

### 3.1. Structural and chemical properties of the porous carbons

As illustrated in Fig. 1, the synthetic route for N-HPCSs was a two-step process. C<sub>60</sub> assembled hollow spheres were first prepared through amination reaction of C<sub>60</sub> and alkyl diamines in the presence of H<sub>2</sub>O<sub>2</sub>. Subsequently, N-HPCSs were obtained by a simple carbonization procedure under Ar atmosphere. The alkyl diamines used were ethylenediamine (EDA), 1,3-diaminopropane (PrDA), 1,4-diaminobutane (BDA), 1,5-diaminopentane (PeDA) and 1,6-hexanediamine (HDA), and the corresponding products were denoted as C<sub>60</sub>-EDA, C<sub>60</sub>-PrDA, C<sub>60</sub>-BDA, C<sub>60</sub>-PeDA and C<sub>60</sub>-HDA, respectively. The morphologies of products obtained in the first step were confirmed by TEM. As shown in Fig. 2a–e, all the products displayed the nearly monodispersed hollow sphere structures. The size of the hollow spheres increased from 500 nm to 780 nm while the size of cavity decreased gradually from 250 nm to 150 nm with the increased chain length of alkyl diamines from C<sub>2</sub> to C<sub>6</sub> (Fig. 2f). Besides the intriguing hollow structure, the reaction time was only 1 h under mild conditions, making the synthetic method a very facile and efficient route to produce carbon hollow spheres with tunable size.

Amination of fullerenes has been studied intensively in the literature [27–30]. Wudl and co-workers reported that primary and secondary aliphatic amines react readily with C<sub>60</sub> to give multiple adducts, which usually contain some oxygen if molecular oxygen is present in the reaction medium [31]. Ken Kokubo prepared a highly soluble fullerene derivative from hydrogen peroxide and ammonia, and proposed that an intermediacy oxidized fullerene C<sub>60</sub>O was produced with the nucleophilic attack of HOO<sup>-</sup>, which effectively formed from the equilibrium of H<sub>2</sub>O<sub>2</sub> by the assistance of NH<sub>3</sub> [32]. These studies confirmed that fullerenes were prone to react with amines in the presence of oxidizing agents, so H<sub>2</sub>O<sub>2</sub> was added as a green and cheap oxidant to accelerate the reaction between C<sub>60</sub> and amines. Generally, the obtained products are dissolved in the solvents. However, in this work, the products were insoluble in solvents and can be directly separated from the solution by filtration. We speculated that the products were cross-linked C<sub>60</sub> assemblies, in which alkyl diamines acted as crosslinking agents to connect the C<sub>60</sub> [33]. For comparison, alkyl alcohol amines including ethanolamine (EOA), 3-amino-1-propanol (PrOA), 4-amino-1-butanol (BOA), 5-amino-1-pentanol (PeOA) and 6-amino-1-hexanol (HOA), which possess similar structures and properties to their corresponding alkyl diamines, were also used to react with C<sub>60</sub> under the same conditions. The products obtained with alkyl alcohol amines were soluble in

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