



Synthesize of large-sized porous carbon spheres with controllable N-content via spray-drying and photo-induced RAFT polymerization



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ARTICLE INFO

Keywords:

Large-sized carbon spheres
N-doped
Spray-drying
Photo-induced RAFT
Polyacrylonitrile
CO₂ capture

ABSTRACT

A method combined spray-drying process with light-induced reversible addition fragmentation chain transfer (RAFT) polymerization was used to synthesize N-doped carbon spheres (N-CS). Firstly, the common used carbon precursor phenolic resin which called Resol was modified with a chain transfer agent (CTA). Then, the mixed ethanol solution of CTA modified Resol, F127, TEOS, and HCl was used as starting material. After a typical spray-drying process, uniformed and discrete composite spheres in regular size (70 μm) were obtained. The RAFT polymerization of acrylonitrile was initiated under the irradiation of blue LED at the surface of spheres. Through such manner, controlled amount of polyacrylonitrile was introduced onto the surface of carbon sphere. After calcination at 900 °C and etching, the obtained porous N-CS (60 μm) showed controllable total N content up to 10.8 wt%, tunable high surface area up to 1130 m²/g and good CO₂ absorptivity which can up to 4.34 mmol/g at 273 K and 4.13 mmol/g at 298 K at 1.0 bar.

1. Introduction

Porous carbon sphere (CS) owned variety properties such as high surface area, low density, electric conductive, uniform morphology, electric conductive, tunable size, and porosity with excellent liquidity, which leads it play an important role at adsorption, separation, catalyst, energy conversion, and environmental purification etc. [1–5]. The performance of porous CS doped with heteroatoms such as nitrogen, sulfur, and oxygen etc. exhibits enhanced properties in specific areas especially in gas adsorption, super capacitors, and redox reactions [6–8]. Among them, N-doped porous CS (N-CS) attracted much more attentions than other heteroatom doped porous CS due to its high electrical conductivity, chemical reactivity, adsorption capability of acid gas, wettability and so on [9,10]. Two major methods for preparation of N-doped CS were reported in the literatures, the direct-synthesis method and the post modification method respectively. For direct-synthesis method, N-contained materials were used as the carbon precursor. Many examples could be found in the literatures, mostly including biomass or designed molecules, such as biomass derivant [6], melamine-formaldehyde [7], urea-formaldehyde [8], polypyrrole [9], polyaniline [10] and polyacrylonitrile (PAN) [11,12]. In the post-modification way, CS was modified by the reaction of CS with N-rich

precursors, such as NH₃ [13] and urea [18,19] at certain temperature. However, even there were enormous ways to synthesize N-CS, it was not easy to gain regular morphology and high N content simultaneously, which would be useful for improving its performance [14–16].

Size was one of the most key parameters of N-CS. It was reported that spheres with uniform large sizes in the range of 20–100 μm showed more suitable for applications such as chromatography, dynamic adsorption-desorption, catalysis and so on. However, spheres with other size may introduced bottlenecks when used in these fields [17–19]. The most common synthetic method of N-CS was applied through a Stöber-like method using RF resin as precursor [8,20,21]. The obtained N-doped CS has high surface area (up to 2200 m²/g) and high N content (up to 15 wt%), which also shows high CO₂ uptake capacity. But normally their size was small (< 1.2 μm), which limited their potentially application.

To prepare CS with large size (> 50 μm), different techniques have been explored. For example, Zhao et al. [17] firstly combined evaporation-induced self-assembly (EISA) with spray-drying for the preparing of mesoporous CS with uniform large size (~70 μm), large surface area up to 1930 m²/g, total pore volume 1.62 cm³/g and bimodal pores 2.0 nm and 5.5 nm. Such novel way provided the efficient way for producing CS on large scale. The precursor in their work was a widely

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<https://doi.org/10.1016/j.reactfunctpolym.2018.08.009>

Received 3 July 2018; Received in revised form 8 August 2018; Accepted 15 August 2018

Available online 24 August 2018

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used basic-catalyst phenolic-resin (Resol). The abundant of hydroxyl groups inside Resol can be further transferred to form methylene bridges under heating and crosslink inside finally. At the same time, the hydroxyl groups inside Resol also provides modification points for introducing of functionalities, such as polyacrylonitrile (PAN). The first example of using PAN as carbon precursor to synthesize ordered mesoporous carbon materials was reported at 2004 by Lu et al. [11]. By infiltration acrylonitrile into SBA-15 followed with atom transfer radical polymerization (ATRP) [22–24] and calcination, they prepared *N*-doped SBA-15 replica. Krzysztof Matyjaszewski [12] used different modified silica as templates and introduced PAN onto silica templates via surface-initiated ATRP. Such procedure confines the introduction of PAN on the surface of template uniformly and avoids the formation of excess PAN. The *N*-doped carbon materials with high pore volume, large pore diameter was obtained.

In our previously work [25,26], we found that thiocarbonate can generate radical under visible-light irradiation and initiate vinyl acetate, acrylonitrile (VAc, AN) polymerization under the controlled way through so called photo-induced reversible addition chain transfer polymerization [23](RAFT). Terminal carboxyl groups containing in thiocarbonate can react with hydroxyl group through esterification, which provided a modification way to introducing thiocarbonate into Resol. Use this modified Resol as precursor and through spray-drying process, it was hopefully to prepare spheres with surface chemical sites which can initiate AN polymerization by the stimulation of lights. The total *N* content can be controlled by the advantages of such living radical polymerization way. Best to our knowledge, there were few reports about using photo-induced RAFT to control the total *N* content of porous carbon spheres.

Following such hypotheses, we summarized the whole experiments in Scheme 1. The phenolic resin Resol was modified with a CTA in the first step. Then, the mixed ethanol solution of CTA modified Resol, F127, TEOS, HCl was used as precursor. After a typical spray-drying process, uniformed and discrete composite spheres in regular size (70 μm) were obtained. The surface initiated polymerization of AN can be carried out with the irradiation of blue LED. Finally, *N*-CS were obtained after calcination at 900 $^{\circ}\text{C}$ and silicon removal which showed tunable total *N* content up to 10.8 wt%, high surface area up to 1130 m^2/g and excellent CO_2 absorptivity (up to 4.34 mmol/g at 273 K and 4.13 mmol/g at 298 K).

2. Experimental

2.1. Materials

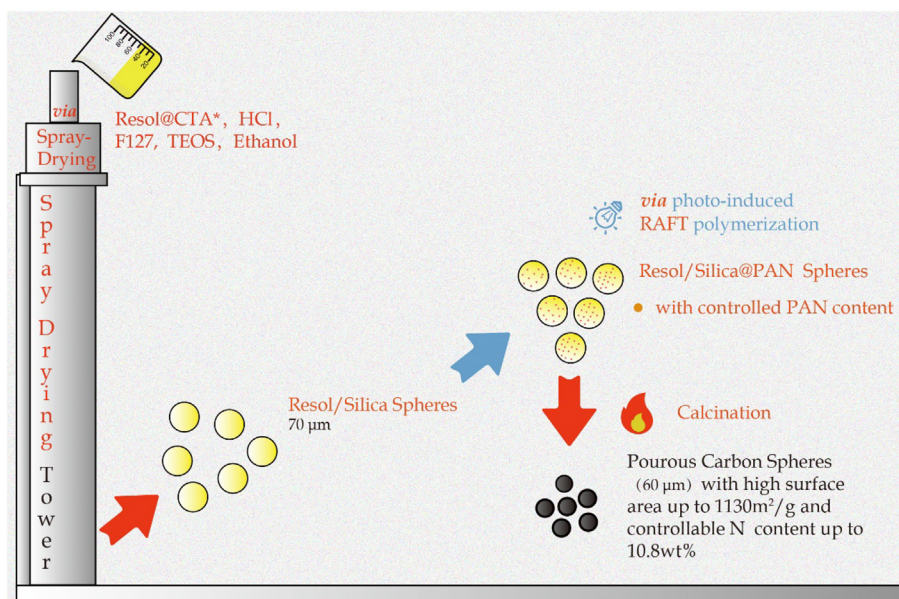
Phenol (98%), formaldehyde (37 wt%), tetraethylorthosilicate (TEOS), tetrahydrofuran (THF), acrylonitrile (AN), *N,N*-dimethylformamide (DMF), sodium hydroxide (NaOH), dodecanethiol, acetone, hydrochloric acid, carbon disulfide, ethanol, and hexane were purchased from Sinopharm Chemical Reagent Co. Ltd. China. 2-Bromopropanoic acid was purchased from Alfa Aesar China. Dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) were purchased from Adamas Reagent Co. Ltd. China. F127 and tetrapropylammonium bromide were purchased from Sigma Aldrich. AN was chromatographic separation in neutral alumina column before use. Other reagents were used as received. Deionized water was used in all experiments.

2.2. Synthesis of chain transfer agent

The chain transfer agent (CTA), 2-[(Dodecylsulfanyl)carbo-nothioly]sulfanylpropanoic acid (PADT), was synthesized according to the literature [27]. Briefly, NaOH aqueous solution (5 g 10 wt%) was dropwisely added into a mixture of 1-dodecanethiol (2.5 g, 12.5 mmol), acetone (40 mL) and 0.27 g tetrapropylammonium bromide with stirring. The resulting solution was cooled in an ice bath and added with carbon disulfide (0.95 g, 12.5 mmol). After stirring for another 30 min, 2-bromopropanoic acid (1.91 g, 12.5 mol) was added. The mixture was further stirred at ambient temperature for 12 h. The solution was evaporated to half of the original volume. Then it was slowly acidified with 0.5 M hydrochloric acid (200 mL). The precipitate was collected and recrystallized several times from hexane to give the desired trithiocarbonate as fine yellow platelets (3.6 g, yield 80%).

2.3. Synthesis of Resol & Resol@CTA

The Resol used in this work was synthesized through a slightly modified method reported by Zhao et al. [28]. Typically, NaOH solution (1.68 g, 42 mmol) was added into melting phenol (8.0 g, 85 mmol) at $\sim 45^{\circ}\text{C}$ under a nitrogen atmosphere and followed by 10 min stirring. Then, 13.76 g formaldehyde aqueous solution (13.76 g, 37 wt%, 170 mmol) was added. After further stirring for 1 h at $\sim 78^{\circ}\text{C}$, the



Scheme 1. An overview scheme for the preparation of *N*-doped porous carbon spheres within this study.

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