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Tetraethyl orthosilicate-assisted synthesis of nitrogen-containing porous carbon spheres

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ABSTRACT

It is shown that the pore size and pore volume of carbon spheres (CSs) can be effectively tuned by varying the amount of tetraethyl orthosilicate (TEOS) during the one-pot modified Stöber synthesis that involves polymerization of resorcinol and formaldehyde in the presence of ethylenediamine used as a basic catalyst and nitrogen source. Namely, an increase in the amount of added TEOS caused a considerable reduction in the micropore volume accompanied by a three-fold increase in the total pore volume. This substantial increase in porosity was achieved after dissolution of the TEOS-generated silica and additional activation. Importantly, the controlled addition of TEOS was effectively used to tune the structure of the composite carbon-silica spheres to obtain, for instance, the composite spheres with uniformly distributed carbon and silica, and core-shell structures with single shells (silica core/mixed silica-carbon shell), and double shells (silica core/mixed silica-carbon shell/silica shell), which upon suitable post-synthesis treatment can be respectively converted to mesoporous CSs, hollow mesoporous CSs, and yolk-shell silica spheres. Beside the well-developed porosity and interesting morphology, the resulting CSs were N-doped and featured high surface area in the range of 1000–1439 m^2/g.

1. Introduction

In recent years, nanoporous carbon spheres have attracted considerable attention due to their versatility in wide range of applications as adsorbents, catalyst supports, and electrodes in supercapacitors and batteries [1–5]. Depending on the precursors used and synthesis conditions, they combine the fascinating characteristics of carbon materials including good electrical conductivity, chemical inertness, high surface area, well-developed porosity and biocompatibility allowing them to outperform many previously reported materials [6]. Moreover, their size, structure and spherical morphology can be advantageous in various uses ranging from adsorbents, catalysts, separation media, electric double-layer capacitors and batteries to biomedical applications, where mass transport is the matter of primary concern since it provides short passage pathways [1,7].

So far, various strategies have been developed for the fabrication of nanoporous carbon spheres including hard templating (HT) [8–10], soft templating (ST) methods [11,12], hydrothermal carbonization (HTC) [13,14], emulsion polymerization [15] and Stöber-like synthesis [1,16]. Since most of these methods either involve extra preparation and removal of hard templates (HT), require soft templates (ST), or may lead to the aggregated products (HTC and emulsion polymerization) [1], there is an urgent need to develop facile and low cost methods for the fabrication of uniform monodispersed polymer/carbon spheres with proper porosity and size.

A great popularity of the proposed Stöber method in 1968 for the synthesis of colloidal silica spheres with tailorable sizes and narrow particle size distribution [17], stimulated many researches toward development of non-silica colloidal spheres such as carbon spheres. In 2011, Liu et al. [16] extended this popular method to fabricate monodispersed phenolic resin spheres using NH_3 as a catalyst and resorcinol and formaldehyde as polymerization precursors in ethanol-water phase. A similar reaction mechanism of TEOS condensation and resorcinol-formaldehyde (RF) polymerization was the key factor towards the aforementioned extension of the Stöber method. The subsequent carbonization of the resulting phenolic resin spheres in inert atmosphere generated microporous carbon spheres. The particle size of these polymer and carbon spheres could be effectively tuned by simply adjusting the alcohol/

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water ratio, concentration of ammonia, and the amount of resorcinol or by changing the type of alcohol during synthesis [16]. The above mentioned extension of the well-known Stöber synthesis has opened new opportunities in the advancement of polymer and carbon spheres as clearly indicated in previous report [18] and subsequent reports showing their functionalization and doping with heteroatoms such as N, P, S and F [19–23] and nanostructure tuning [24–26]. The use of polymer precursors with appropriate functionality has been commonly employed strategy for doping carbon spheres with various heteroatoms [2]. It was shown that nitrogen doping of carbons can improve their surface, adsorption and catalytic properties making them potential materials for energy storage, catalysis and adsorption, for instance electrodes, CO_2 capture and so on [2,27,28]. In spite of easy functionalization, the main drawback of heteroatom doped carbon spheres fabricated by Stöber method is their solely microporous nature [16,18] which limits their applications where facile diffusion of ions and/or molecules is essential. Therefore, the presence of mesopores in carbon spheres is critical to facilitate diffusion of ions and molecules inside pores, which is important in many applications such as energy storage devices including Li-ion batteries, drug loading, and adsorption of small as well as larger molecules.

Stimulated by previous studies devoted to the templating synthesis of mesoporous silica spheres [29], Choma et al. performed one-pot Stöber-like synthesis of phenolic resin spheres in the presence of Pluronic F127 block copolymer. Since this synthesis was in alkaline conditions, the use of block copolymer did not result in the creation of mesopores but in controlling the size of spheres. By increasing the amount of Pluronic F127 in this synthesis, the size of spheres was decreased from 1000 nm to 30 nm [18].

Two major findings, a similar reaction mechanism of resorcinol-formaldehyde (RF) polymerization and TEOS condensation under basic conditions and faster kinetics of TEOS condensation as compared to RF polymerization, inspired Fuertes and coworkers to explore one-pot polymerization of resorcinol, formaldehyde and TEOS under alkaline conditions (Stöber synthesis) to obtain silica core/carbon shell particles [30]. They further claimed that these silica core/carbon shell particles can only be formed in EtOH/water (E/W) (v/v) ratio between 2 and 7. However, this one-pot synthesis has been rarely used for obtaining composite silica-carbon spheres beyond the aforementioned E/W ratio. Recently, Dai and coworkers [31] proposed “silica-assisted self-assembly” strategy where one-pot polymerization of resorcinol, formaldehyde and TEOS was carried out using lower ethanol-water ratio (1: 4.75 up to 1: 2.38) in the presence of hexadecyltrimethylammonium chloride. Various types of structures like homogeneous and hollow phenolic resin-silica spheres were synthesized by using the TEOS/resorcinol ratio 0.95 and 1.90, respectively, and even yolk-shell phenolic resin-silica spheres were obtained by additional hydrothermal treatment of hollow phenolic resin-silica spheres. Further, these spheres were converted into mesoporous carbon spheres, hollow mesoporous carbon spheres and yolk-shell mesoporous carbon spheres, respectively, upon carbonization and silica dissolution. Similarly, Cao and coworkers [32] demonstrated that the addition of surfactant during one-pot polymerization of RF and TEOS leads to the formation of polymer-silica-surfactant (PSS) composite spheres. Interestingly, the nanostructure of PSS composite spheres was effectively tuned by simply changing ethanol-water ratio to obtain hollow mesoporous silica-carbon tubes or spheres, rattle-type mesoporous carbon tubes or spheres after suitable treatment. Liu et al. [26] further reported the structure transformation from hollow to rattle-type structure by varying the amount of EDA during the synthesis performed at the E/W ratio = 0.4 in the presence of cetyltrimethylammonium chloride (CTAC) surfactant keeping the fixed amount of TEOS. Note that all the above mentioned synthesis conditions refer to quite low E/W ratio. The use of surfactants is the key factor in this synthesis, which makes it more expensive and industrially unfeasible.

Robertoo et al. successfully synthesized SiO_2 nanoparticles of controlled size ranging from 10 nm to 600 nm by changing water-ethanol relative concentration. At high water content, a large amount of hydrolyzed monomers is formed favoring nucleation process. Moreover, they inhibit condensation process (where more H_2O is produced) according to the Le Chatelier's principle. Thus high water content promotes formation of smaller silica nanoparticles [33]. Carcouet et al. [34] investigated the progress of growth of silica nanoparticles using cryo-TEM, pH monitoring, and ^{29}Si MAS NMR to better understand the initial formation of primary silica particles (~2 nm). At their low concentration (0.54 mg/mL), the primary particles remained stable for long period of time. However, at higher silica concentration (25 mg/mL) achieved by simple evaporation of water, primary particles assembled into larger particles (~7 nm), which suggests that the size of silica nanoparticles (NPs) is highly dependent on the silica concentration. The observed dependence of the size of NPs on the water content, silica concentration and their inability to form core-shell structures at lower ethanol-water ratios has encouraged us to study the one-pot polymerization of RF and TEOS at the E/W ratio 0.4 under Stöber conditions by varying the TEOS amount.

Herein, we demonstrate one-pot synthesis of monodispersed N-doped porous carbon spheres under Stöber conditions by using resorcinol and formaldehyde as carbon precursors, TEOS as silica precursor and EDA as basic catalyst and nitrogen source. The initial Stöber-like synthesis reported by Liu et al. [16] was carried out at the E/W ratio = 0.4 and produced microporous carbon spheres. A gradual porosity tuning from micropores to mesopores could be achieved by varying the amount of TEOS added during synthesis followed by silica dissolution. Interestingly, the structure of the resulting spheres could be changed from the composite spheres with uniformly distributed carbon and silica to core-shell structures with single shells (silica core/mixed silica-carbon shell) and double shells (silica core/mixed silica-carbon shell/silica shell) and respectively, to mesoporous carbon spheres, hollow porous carbon spheres (upon silica dissolution) and yolk-shell porous silica spheres (after burning off carbon in air).

2. Experimental

2.1. Materials

Resorcinol ($C_6H_4(OH)_2$, 98%), formaldehyde (HCHO, 37 wt%), tetraethylorthosilicate (TEOS), ethylenediamine (EDA) and Rhodamine B were purchased from Acros Organics (Geel, New Jersey, USA). Sodium hydroxide was purchased from Fischer Scientific (Fair Lawn, New Jersey, USA). Technical grade ethanol and deionized water were used in all experiments.

2.2. Synthesis of N-containing phenolic resin-silica and carbon-silica composite spheres

A series of nitrogen-containing phenolic resin-silica composite spheres was fabricated by slightly modifying the Stöber synthesis reported by Liu et al. [16]. In a typical synthesis, 1.2 g of resorcinol was added and stirred for 30 min in a water-ethanol solution, which was prepared by mixing 48 mL of ethanol and 120 mL of distilled water. Next 1.8 mL of ethylene diamine was added and stirred for additional 20 min. Thereafter, a proper amount of TEOS (2.5, 5, 7.5, or 10 mmols) was added to the reaction solution, followed by dropwise addition of 1.68 mL of formaldehyde. The reaction mixture was vigorously stirred for 24 h at room temperature