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Direct triblock-copolymer-templating synthesis of ordered nitrogen-containing mesoporous polymers

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ABSTRACT

Ordered nitrogen-containing mesoporous carbonaceous polymers have been synthesized via a direct triblock-copolymer-templating process by using soluble, low-molecular-weight urea–phenol–formaldehyde (UPF) resin as an organic precursor and amphiphilic triblock copolymer Pluronic F127 as a template. Characterization using small-angle X-ray scattering (SAXS), N_2 sorption, transmission electron microscopy (TEM), elemental analysis, thermogravimetric analysis (TG), Fourier transform infrared (FTIR), and water adsorption techniques reveals that the obtained nitrogen-containing mesoporous polymers possess ordered structures, high surface areas (385–420 m^2/g), large pore sizes (3.1–3.6 nm) and pore volumes (0.25–0.44 cm^3/g), and high nitrogen content (2.69–2.94%). Various mesostructures, such as two-dimensional (2-D) hexagonal (space group, $p6mm$) and 3-D body-centered cubic ($Im\overline{3}m$) symmetries, can be obtained by simply adjusting the mass ratio of UPF/F127. The content of nitrogen in the mesoporous polymers can also be easy varied by changing the amount of urea and the reaction time of UPF resin precursors. Compared with the nitrogen-free mesoporous polymer, the obtained mesoporous carbonaceous polymers show a more hydrophilic nature and thus evidently higher water adsorption capacity. The presence of nitrogen groups can also significantly improve the adsorption performance of Fe(III) ions.

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1. Introduction

Mesoporous materials have attracted much attention owing to their large surface area, uniform pore size, specific channels, structural regularity, and thus potential applications in many fields, such as separation, adsorption, catalysis, bioreactors, dielectrics, and sensors [1–6]. Until now, a large number of ordered mesoporous materials with various compositions and structures have been successfully synthesized, including two-dimensional (2-D) hexagonal or/and 3-D cubic mesostructured silicates [7–9], metal oxides [10], metal sulfides [11], metals [12], polymers, and carbons [13–16]. In addition, further modification of these mesostructures can endow the materials with additional physicochemical functions, and therefore improve their performance in practical applications. For example, nitrogen-containing mesoporous materials have shown an excellent performance of adsorption for transition metal ions [such as Fe(III) and Cr(VI)] [17,18] and gas storages [19], because of the coordination and hydrogen-bonding affinity [20]. Moreover, for catalysis, the introduction of nitrogen species can improve the basicity and the ability to activate oxygen via the formation of O_2^{2-} superoxide, which has tremendous effects on oxidation reaction [21]. The role of nitrogen is usually linked to the surface chemistry and ability to increase the polarity of the surface, which can enhance the interaction with polar species via electrostatic forces or hydrogen bonding. On the other hand, carbon materials for electrochemical supercapacitors have been studied extensively in recent years, these nitrogen-containing porous carbons have attracted more and more attention due to their pseudocapacitance and provide the most promising method for enhancing capacity while maintaining the super-cycleability of the supercapacitor [22].

Up to now, the conventional methods to synthesize nitrogen-containing mesoporous polymers involve a nanocasting strategy [23], surfactant-templated cocondensation [24,25]. A frequently used approach to fabricate ordered N-containing mesoporous polymers is a nanocasting process by using mesoporous silicates (such as SBA-15, KIT-6) as a hard template. Mesoporous polymer replicas can be obtained through the following procedures: irrigating the nitrogen-containing monomers into the silica channels, polymerization at a certain temperature, and removing the hard templates

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by using HF or NaOH solution. It is an obviously multistep preparation procedure and time-consuming, and sacrifices both templates, thus fussy and expensive. The cocondensation method uses the anionic surfactant sodium dodecyl sulfate (SDS) and non-ionic surfactant Brij35 [$C_{12}H_{25}(CH_2CH_2O)_{20}OH$] *in situ* polymerization of anilines [24]. However, it results in a wormhole-like disordered mesostructure.

A block-copolymer self-assembly approach to prepare ordered mesoporous carbonaceous polymers has been recently reported by several research groups [15,16]. For example, Meng et al. demonstrated a reproducible synthesis of highly ordered mesoporous polymers from an organic–organic assembly of phenolic resins, and commercial amphiphilic PEO–PPO–PEO triblock copolymers [26]. A family of ordered mesoporous resins and carbons have successfully been synthesized, including 2-D hexagonal (space group, $p6mm$) (FDU-15) [16], bicontinuous cubic $Ia\bar{3}d$ (FDU-14) [27], body-centered cubic $Im\bar{3}m$ (FDU-16) [16], and face-centered cubic $Fd\bar{3}m$ (FDU-17) [28] and $Fm\bar{3}m$ (FDU-18) [29] symmetries. However, up to now, the functionalization of these ordered mesoporous carbonaceous polymers with nitrogen groups has rarely been reported. As the hard templating method, the drawbacks for the incorporation of nitrogen groups include the blocking of the active sites, thus resulting in a significant decrease of the micropore volume. While for the surfactant-templating method, it is the absence of efficient nitrogen-containing precursors that can assemble with the amphiphilic surfactants, and then rarely obtain the ordered nitrogen-containing mesoporous carbonaceous polymers.

Herein, we report a direct triblock-copolymer-templating method for the synthesis of nitrogen-containing ordered mesoporous polymers. The low-molecular-weight and water-soluble urea–phenol–formaldehyde (UPF) resin was used as an organic precursor, which was polymerized from urea, phenol, and formaldehyde under a simple alkaline catalysis condition. Triblock copolymer Pluronic F127 was selected as a structure-directing agent. Ordered N-containing mesostructured polymers are produced via the evaporation-induced triblock-copolymer self-assembly process associated with the thermopolymerization of UPF resins by calcination under N_2 atmosphere. The structure and nitrogen content of the mesoporous polymers can be controlled by adjusting UPF/F127 ratios, urea content, and the prepolymerization time of UPF.

2. Materials and methods

2.1. Chemicals

Triblock poly(ethylene oxide)-*b*-poly (propylene oxide)-*b*-poly (ethylene oxide) copolymer Pluronic F127 (Mw = 12600, PEO_{106}–PPO_{70}–PEO_{106}) was purchased from Acros Corp. Other chemicals were purchased from Shanghai Chemical Corp. All chemicals were used without further purification. Deionized water was used in all experiments.

2.2. Preparation of UPF resin precursor

The UPF resin, a low-molecular-weight and soluble modified phenolic resin, was prepared with urea phenol and formaldehyde via a basic catalyzed process. In a typical preparation, 0.61 g of phenol was melted at 45 °C in a flask, followed by addition sodium hydroxide (NaOH) aqueous solution (0.13 g, 20 wt.%). After being stirred for 10 min, 1.05 g of formalin (37 wt.% formaldehyde) was added. The mixture was stirred for another 30 min at 70—75 °C. Then a certain amount of urea and formaldehyde was added, and the reaction was carried out at 65 °C for a setting time. After being cooled to room temperature, the pH value of the above mixture was adjusted to neutral (pH $\sim$ 7.0) with HCl (0.6 M) solution. Water was removed by vacuum evaporation at 50 °C. The final product was dissolved in ethanol (20 wt.% of ethanol solution) while sodium chloride was separated as a precipitate at the same time.

2.3. Synthesis of ordered mesoporous polymers

Nitrogen-containing mesostructured polymers were synthesized via an evaporation-induced self-assembly (EISA) method with Pluronic F127 as a template. For a typical preparation procedure, 0.25–1.0 g of F127 was dissolved in 2.5–10 g of ethanol, and then the above dilution of UPF resol precursors in ethanol solution was added by stirring for 10 min to obtain a homogeneous solution. The solution was poured into dishes to evaporate ethanol at room temperature for 5–8 h, followed by thermopolymerization in an oven at 100 °C for 24 h. The as-made products were scraped from the dishes and crushed into powders. In order to remove the Pluronic F127 templates, the as-made samples were calcined in a tubular furnace under nitrogen atmosphere with a flowing rate of 60 cm^3/min at 380 °C for 5 h.

2.4. Adsorption of Fe(III) cations

Adsorption performance of the obtained mesoporous carbonaceous polymers for Fe(III) ions was tested in a procedure similar to the previous reports [30,17]. Forty milligrams of the nitrogen-containing mesoporous polymer and the nitrogen-free mesoporous polymer was suspended in 10 mL of $FeCl_3$ aqueous solution (0.5 mM), respectively. The suspensions were put under ultrasound for 1.5 h, and then the solids were filtered off. The concentration of Fe(III) in the filtrate was monitored by measuring the UV absorption intensity at λ_{max} of 295 nm.

2.5. Characterization

The small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small-angle X-ray scattering system (Bruker, Germany) using Cu Kα radiation. The d-spacing values were calculated by the following formula: $d = 2\pi/q$. Nitrogen adsorption/desorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 analyzer. Before measurements, the samples were degassed at 180 °C for at least 6 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}), using adsorption data in a relative pressure (P/P_0) range from 0.04 to 0.2. The pore volume and pore size distributions were derived from the adsorption branch of the isotherms by using the Barrett–Joyner–Halenda (BJH) model. The total pore volume, V_t, was estimated from the amount adsorbed at a relative pressure P/P_0 of 0.995. Transmission electron microscopy (TEM) experiments were conducted on a JEOL 2011 microscope operated at 200 kV. The samples for TEM measurements were suspended in ethanol and dried on a holey carbon film on a Cu grid. Fourier transform infrared (FTIR) spectra were collected on a Nicolet Fourier spectrophotometer with spectral width of 4000–400 cm^{-1}, using KBr pellets of the solid samples. The thermal decomposition behaviors of the products were monitored by using a Mettler Toledo TGA/SDTA851 analyzer from 25 to 900 °C under nitrogen with a heating rate of 5 °C/min.

3. Results and discussion

The as-made mesoporous polymers and calcined samples prepared with different molar ratios of urea:phenol:formaldehyde:F127 (1:1:2.5:0.0025) and urea:phenol:formaldehyde:F127 (1:1:2.5:0.010) with reaction time of 4 h were particularly investi-

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