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Synthesis of nitrogen-doped graphitic carbon nanocapsules from a poly(ionic liquid) for CO_2 capture

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Abstract: A poly(ionic liquid) was prepared from an ionic liquid monomer that was obtained by the reaction of 1-vinylimidazole, 4-vinyl-benzene chloride with 2,6-di-tert-butyl-4-methylphenol. The poly(ionic liquid) was mixed with $K_3[Fe(CN)_6]$ and a 5 nm silica colloidal sol, carbonized at 900 °C for 4h, and sequentially treated with HNO_3 and NaOH to remove the iron and silica to obtain nitrogen-doped graphitic carbon nanocapsules. The iron and silica acted as a graphitization catalyst and template, respectively. The nitrogen-doped graphitic carbon nanocapsules have a diameter of 50 nm and a wall thickness of 6 nm and have a high adsorption capacity and good recyclability for CO_2 capture. The addition of SiO_2 nanoparticles in the synthesis significantly increased the specific surface area from 100.4 to 865.7 m^2 g^{-1} and the CO_2 adsorption capacity from 0.76 to 2.14 mmol g^{-1}.

Key Words: Ionic liquid; Nitrogen doped; Graphitic; Carbon nanocapsules; CO_2 capture

1 Introduction

Nitrogen-doped carbon materials are promising candidates for CO_2 capture, catalyst support, and so on[1,2]. Nitrogen doping can be achieved by either direct pyrolysis of nitrogen-containing precursors or post-treatment of carbons. The latter method incorporates nitrogen by surface functionalization, which can't modify the properties of the bulk material. The amount and distribution of nitrogen are uncontrollable as well. In contrast, in situ doping using nitrogen-containing precursor favors a homogeneous distribution of nitrogen with a controlled chemistry[3, 4].

As a kind of nitrogen-containing precursor, ionic liquids (ILs) have attracted much attention owing to their high heteroatom doping and excellent stability[5]. Moreover, ILs could be used to synthesize mesoporous carbon through a template-free route[6]. Nitrogen-doped carbon materials derived from ILs present favorable electric and electrochemical properties[7]. Our previous research revealed that nitrogen-doped hollow carbon spheres could be synthesized from ILs[8].

Herein, nitrogen-doped carbon nanocapsules (N-CNC) with a graphitic structure were prepared using ionic liquid polymer as a carbon-nitrogen precursor. $K_3[Fe(CN)_6]$ catalyst was employed to facilitate the catalytic graphitization and to form a macroscopic hollow architecture. In addition, silica nanospheres of 5 nm were optionally introduced to form uniform mesopores and therefore to improve the specific surface area. Nitrogen-doped carbon nanocapsules with a wall thickness of 6 nm and a diameter of 50 nm were achieved successfully, which possessed a graphitic structure and a considerably high surface area. The graphitic nitrogen-doped carbon nanocapsules may serve as promising candidates for CO_2 capture.

2. Experimental

2.1 Synthesis

The poly(ionic liquid)s (PILs) as a carbon-nitrogen precursor were prepared according to the literature[9]. 1-Vinylimidazole (12.3 g, 0.131 mol) was added dropwise under argon to a mixture of 4-vinylbenzene chloride (20 g, 0.131 mol) and 2,6-di-tert-butyl-4-methylphenol (89.5 mg, 0.4 mmol). After an addition of 30 mL methanol, the mixture was stirred at room temperature for 30 minutes, then at 60 °C for 22 h. The reaction mixture was poured into 500 mL diethyl ether to obtain a precipitate. The resulting solid was purified by dissolving in methanol and precipitated in diethyl ether. Remaining solvent was removed under high vacuum till constant weight to obtain the ionic liquid (IL) monomer. 2 wt% azodiisobutyronitrile (AIBN) was dissolved in the IL monomer at room temperature. Under argon, pieces of the porous glass were infiltrated with the IL mixture at 30 °C for

20 h. The IL-mixture within the porous glass was heated to 100 °C for 20 h and finally to 200 °C for 20 h. The infiltrated silica disks were removed manually from the bulk poly(ionic liquid) (PIL) and treated with 1 M NaOH to remove the template. The PIL was washed with water and acetone and dried at 40 °C under vacuum.

The nitrogen-doped graphitic carbon nanocapsules were obtained as follows: 2 g PILs, 0.5 g $K_3[Fe(CN)_6]$ and 20 mL water were mixed at 25 °C. Subsequently, a colloidal sol consisted of 5 nm silica nanospheres was added. Then the composite was kept at 900 °C for 4 h in N_2 flow, followed by treatments with HNO_3 and NaOH separately to remove iron and silica. According to various conditions, the synthesized samples were labeled as N-CNC prepared without $K_3[Fe(CN)_6]$ and SiO_2, N-CNC-Fe prepared with $K_3[Fe(CN)_6]$ but without SiO_2 and N-CNC-Fe-Si prepared with $K_3[Fe(CN)_6]$ and SiO_2.

2.2 CO₂ capture measurement

The CO_2 adsorption measurements were carried out using a Micrometitics TriStar 3020 volumetric adsorption analyzer at 25 °C from 0.01 to 1.0 bar. The temperature during sorption was controlled by a circulating bath. Before the measurement the samples were degassed at 120 °C under vacuum for 24 h to remove any moisture and CO_2 molecules adsorbed in the pores. After each sorption, the sample was kept under vacuum for 10 min, and then allowed to adsorb CO_2 again. This adsorption-desorption cycle was repeated twenty times at 25 °C and 1.0 bar.

2.3 Characterization

X-ray diffraction (XRD) patterns were achieved using a Rigaku D/MAX-2500 X-ray diffraction system (Cu Kα radiation, λ=0.15406 nm) operated at 40 kV and 40 mA. Scanning electron microscopy (SEM) was performed on a HITACHI S-4800-I scanning electron microscope. High-resolution transmission electron micrographs (HR-TEM) were obtained on a JEOL JEM-2010 electron microscope. Nitrogen adsorption-desorption isotherm measurements were performed on a Micrometitics TriStar 3020 volumetric adsorption analyzer at -196 °C. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area of each sample, and the average pore size distribution was derived from the adsorption branch of the corresponding isotherm using the Barrett-Joyner-Halenda (BJH) method. The total pore volume was estimated from the amount of N_2 adsorbed at the relative pressure of p/p_0=0.97. XPS data was acquired using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer. The atomic concentrations were calculated using the Casa XPS software (version 2.3.14) and a Shirley baseline with Kratos library relative sensitivity factors (RSFs).

Raman measurements were performed under ambient conditions using a 532 nm (2.33 eV) laser in the backscattering configuration on a Jobin-Yvon HR800 Spectrometer.

3 Results and discussion

For all three samples, two XRD diffraction peaks at $2\theta =$ 26° and 43° are observed (Fig. 1a), which correspond to (002) and (100) diffractions of graphitic carbon. The (002) d-spacing is 0.337 nm, which is very close to that of graphite (0.335 nm) [10, 11, 12]. N-CNC-Fe shows a considerably shaper and higher (002) diffraction intensity than that of N-CNC, indicating that $K_3[Fe(CN)_6]$ could facilitate catalytic graphitization significantly. It should be noted that the incorporation of SiO_2 maintains the graphitization degree of the carbon materials.

The Raman spectrum of N-CNC-Fe-Si is illustrated in Fig. 1b. *G* band at 1576 cm^{-1} is mainly assigned to the ordered graphitic carbon, whereas *D* band at 1321 cm^{-1} is ascribed to the disordered carbon. The ratio of peak intensity (I_G/I_D) is 0.86. Such low value can be attributed to the disorder brought by nitrogen-doping and SiO_2 incorporation[13]. The peak at 2650 cm^{-1} could be assigned to *G′* band, further confirming the graphitic structure[14]. The XPS spectrum of N1s in Fig. 1c can be assigned to pyridinic nitrogen at 398.4 eV and pyrrolic nitrogen at 400.2 eV[15, 16]. The calculated nitrogen content is 2.65%, which proves the existence of N-containing functional groups in the materials.

Fig. 2 illustrates the morphology of N-CNC-Fe and N-CNC-Fe-Si. Carbon nanocapsules with an open-ended structure (outer diameter of 50 nm through a statistic calculation) are revealed for both N-CNC-Fe and N-CNC-Fe-Si (Fig. 2a, 2b), indicating that the incorporation of SiO_2 maintains the capsule morphology of the carbon materials. As shown in Fig. 2c, N-CNC-Fe-Si shows a capsule-like morphology with a wall thickness of 6 nm by a statistic calculation. Moreover, the high-resolution TEM image of N-CNC-Fe-Si (Fig. 2d) demonstrates the (002) d-spacing of 0.337 nm for the graphitic structure. It proves that SiO_2 doesn't disturb the graphitization of the carbon nanocapsules, which is in good agreement with the XRD result. The formation of the graphitic structure and macroscopic hollow architecture could be attributed to the catalytic graphitization and the removal of $K_3[Fe(CN)_6]$ catalyst[17].

Nitrogen adsorption isotherms and the corresponding pore size distributions of N-CNC-Fe and N-CNC-Fe-Si are presented in Fig. 3a. N-CNC-Fe presents a wide hysteresis loop at p/p_0=0.4-0.95, indicating a mesoporous structure with a wide pore size distribution[18,19]. In contrast, a distinct capillary condensation appears at p/p_0=0.40-0.80 for N-CNC-Fe-Si, suggesting its narrower pore size distribution than that of N-CNC-Fe. It is further confirmed by the pore