

Molten salt assisted synthesis of microporous polyaniline nanosheets with superior gas sorption properties

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ABSTRACT

Porous polyaniline (PANI) nanosheet has unique structure and properties that can be applied in gas separation, gas storage, and energy storage and conversion devices. To date, it is still a great challenge to construct microporous PANI nanosheet materials. Here, we present an inorganic salt template pyrolysis route for the direct synthesis of ultrathin PANI nanosheets with well-defined microporous structure from hexaaminobenzene monomer. The obtained PANI nanosheets give an ultrathin thickness of 1.6 nm, high surface area ($\sim 395 \text{ m}^2 \text{ g}^{-1}$), and well-defined microporous structure (centered at $\sim 0.54 \text{ nm}$). The PANI nanosheets with plenty of micropores exhibit superior gas sorption property for CO_2 and CH_4 at room temperature, which is also expected to improve the performances of PANI nanosheets in other application fields.

1. Introduction

Polyaniline (PANI), the primary oxidation polymerization product of aniline, was firstly discovered in the mid-19th century [1]. The PANI material has high environmental stability, interesting redox chemistry and unique doping/de-doping properties, and therefore, has attracted broad research interests in the last three decades. As a polymer with intrinsically conducting nature, PANI material has been widely used in the energy storage systems, sensors, electronic devices, fuel cells and solar cells [2–5]. Previous studies reveal that the electrical properties of PANI material can be tailored via nanostructuring. To enhance the performances of PANI materials in different fields, various 0D (nanospheres) [6], 1D (nanofibers, nanowires, nanorods, and nanotubes) [7–9], 2D (nanobelts and nanosheets) [10,11], 3D [5,12] nanostructured PANI materials have been designed and synthesized.

Among the different PANI nanostructures, porous PANI nanosheets which feature plenty of accessible active sites exposed on surface and in the pores of nanosheets are especially attractive in adsorption and catalysis [13]. With amphipathic perfluorinated carboxylic acids and block co-polymer as dual templates, mesoporous PANI nanosheets were successfully synthesized by solution-based super-molecular assembly of aniline [14,15]. The porous PANI nanosheets can not only provide more active sites but also facilitate the diffusion and adsorption process of guest molecules in the nanosheets, and has the great potential to

improve the performances of porous PANI nanosheets [13]. In comparison with PANI nanosheets with mesopores, PANI nanosheets with microporous structure are suitable for the adsorption and separation of small guest molecules such as gas, small organic molecules and coordination complexes. Although soft-template methods have been well established for the preparation of mesoporous PANI nanosheets, precise design of 2D PANI nanosheets with well-defined microporous structure (pore diameter smaller than 2 nm) still remains a great challenge to date.

Recently, the advantages of inorganic salts with low melting points have received increasing attention as solvents in inorganic synthesis, and a wide range of nanostructured materials have been synthesized mediated by molten inorganic salts [16]. In this study, we propose an inorganic salt template pyrolysis route for the direct synthesis of free-standing ultrathin PANI nanosheets with well-defined microporous structure by pyrolysis and polymerization of hexaaminobenzene (HAB) monomer in a eutectic inorganic salt of LiCl/KCl (59:41 mol %, melting point of 353 °C). This novel bottom-up strategy relies on the control of monomer/inorganic salt (LiCl/KCl) ratios. The morphology, structure, surface area, and pore size of the PANI nanosheets were systematically studied by various characterization techniques. By our method, uniform PANI nanosheets with a lateral size of tens of micrometers, an ultrathin thickness of only 1–2 nm well-defined micropore sizes (0.54 nm) as well as high surface area ($395 \text{ m}^2/\text{g}$) can be successfully obtained.

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Additionally, sorption experiments reveal that the microporous PANI nanosheets have superior gas sorption capability for CO₂ and CH₄ at room temperature.

2. Experimental section

2.1. Materials

10%Pd/C and 4-aminotriazole were purchased from Sigma. NaOMe, p-nitroaniline, and LiCl were purchased from Alfa Aser. The 10%Pd/C and NaOMe samples were stored in a glove box filled with purified argon. H₂SO₄, DMSO, HCl, HNO₃, EtOAc, KNO₃ and KCl were purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Synthesis of C₃N nanosheets

2,4,6-Trinitroaniline (TNA), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and hexaaminobenzene trihydrochloride (HAB) was synthesized according to the previous report [17], 50 mg HAB, 4.5 g LiCl and 5.5 g KCl (the weight ratio of reactant and molten salt was 1/200) were mechanically milled in a Retsch PM 400 planetary ball mill. The ball milling was carried out at a rate of 100 rpm for 1 h with 8 steel balls (6 of 1 cm in diameter and 2 of 1.3 cm in diameter), and then the mixture was transferred into in an aluminum oxide boat. All the manipulations were conducted inside a glove box filled with purified argon. The aluminum oxide boat was put in the tube furnace and heated in a relatively low pressure (10⁻³ torr). The temperature was increased to 500 °C (5 °C/min) under vacuum for 2 h. After the reaction, the products were cooled down to room temperature and washed thoroughly with water for three times to remove the LiCl and KCl in the products. In comparison with the weight of PANI products with that of the theoretical yield of PANI product, the yields of PANI products with different reactant/salt weight ratios were also above 95%.

2.3. Characterization

Powder X-ray diffraction (XRD) pattern was recorded on an X'Pert Pro (PANalytical) diffractometer with Cu K α radiation at 40 kV and 40 mA. Scanning electron microscopy (SEM) images were performed on a JSM-7800F scanning electron microscope. Thermogravimetric-Differential Thermal Analysis (TG-DTA) measurements were carried out on a Netzsch STA449C thermal analysis system. A heating rate of 2 °C/min was applied to 5 mg sample. Volumetric release measurements were performed on a commercial gas reaction controller (Advanced materials Co. USA). Ca. 100 mg sample was firstly purged in vacuum for 5 min and then heated to a desired temperature at a ramping rate of 2 °C/min. Transmission electron microscopy (TEM) images were obtained with JEM 2100 Transmission Electron Microscope operating at 200 kV. Atomic force microscopy (AFM) analysis was conducted in veeco multimode 3D. N₂ adsorption-desorption experiments were undertake isothermally at 77 K on a Micromeritics ASAP 2010 volumetric adsorption analyzer. The sample was degassed at 473 K and 10⁻³ Pa for 6 h prior to the adsorption measurements. Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and micropore size distribution curve was calculated by the Non Local Density Functional Theory (NLDFT) model. X-ray photoelectron spectroscopy (XPS) measurements were performed using an Escalab 250 Xi X-ray photoelectron spectrometer (Thermo Scientific) with nonmonochromatic AlK α radiation. Elemental analysis (C, N, H) was performed on an Elemental Analyzer EA 1110. ¹³C cross polarization magic angle spinning NMR (CPMAS NMR) measurements were performed on a Bruker Advance III 500 NMR spectrometer working at a frequency of 128.28 MHz and owning a 4 mm MAS NMR probe. The chemical shift of ¹³C resonance was referenced to Glycine at 176 ppm.

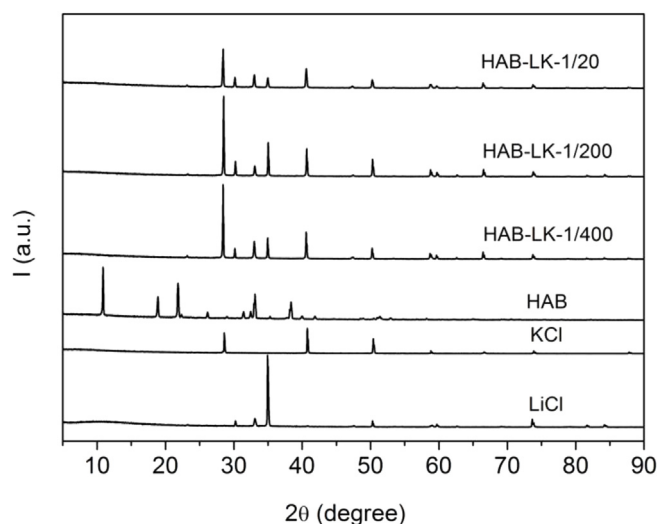


Fig. 1. XRD patterns of LiCl, KCl, HAB, and mixed HAB-LK samples with different HAB/salt weight ratios.

2.4. CO₂, CH₄ and N₂ adsorption measurements

The CO₂, CH₄ and N₂ adsorption isotherms were measured by using a Hiden Isochema intelligent gravimetric analyzer (IGA-100) at 25 °C. In this instrument, an ultrasensitive microbalance of resolution 0.2 μg is mounted in a thermostatted heat sink with high-precision temperature controls. The IGA-100 system can operate up to a pressure of 20 bar, and it is equipped with a high vacuum turbomolecular pump with a dry (membrane) backing pump to ensure minimal contamination of the sample and microbalance chamber. Prior to the measurement, 30 mg of sample was loaded into the IGA-100 and degassed at about 10³ Pa at 200 °C for 24 h. The measurements were then carried out under a water bath. The buoyancy corrections were carried out following our previous publications.

3. Results and discussion

3.1. Preparation and characterization of PANI nanosheets

As depicted in Fig. 1, HAB trihydrochloride, a molecule with six NH₂ functional groups, was employed as the monomer for the synthesis of ultrathin microporous PANI nanosheets [18]. Recent result demonstrates that 2D layered PANI material based on stacked C₃N network layers can be prepared by direct pyrolysis of HAB at 500 °C for 2 h [19,20]. Different from this direct pyrolysis route, we developed a salt template pyrolysis route to synthesize microporous PANI nanosheets from pyrolysis of HAB monomer in the presence of inorganic salt. By take advantage of a eutectic mixture of LiCl/KCl (45:55 wt %), microporous PANI nanosheets have been successfully synthesized for the first time. In a typical experiment, HAB solid was mechanically ball milled with LiCl/KCl (59:41 mol %) at 100 rpm for 1 h firstly. XRD patterns of post milled samples with different HAB/salt weight ratios can be fully indexed into LiCl and KCl (Fig. 1), indicating that no structure changes occurred during solid ball milling process. Additionally, none of peaks corresponding to the HAB crystal can be observed for the post milled samples with HAB/salt weight ratios of 1/20, 1/100 and 1/200.

The pyrolysis and polymerization of HAB in presence of LiCl/KCl was performed at 500 °C for 2 h. The PANI products obtained from the mixtures with different HAB/salt weight ratios were denoted as PANI-LK-x, where x represents the weight ratios of HAB/salt. After polymerization, the LiCl and KCl salts in the products can be facily removed by extensive washing with water.

Thermogravimetric-Differential Thermal Analysis (TG-DTA) was

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