Microporous and Mesoporous Materials 206 (2015) 127–135

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Controlled synthesis of tunable nanoporous carbons for gas storage and supercapacitor application

Kolleboyina Jayaramulu [a], Kasibhatta Kumara Ramanatha Datta [b], Konda Shiva [c], Aninda J. Bhattacharyya [c], Muthusamy Eswaramoorthy [b], Tapas Kumar Maji [a,*]

[a] Molecular Materials Laboratory, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, India
[b] Nanomaterials and Catalysis Laboratory, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, India
[c] Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India

ARTICLE INFO

Article history:
Received 26 March 2014
Received in revised form 17 October 2014
Accepted 7 December 2014
Available online 13 December 2014

Keywords:
Nanoporous carbon
Metal–organic framework
Hydrogen storage
Carbon dioxide storage
Supercapacitor

ABSTRACT

A simple methodology has been developed for the synthesis of functional nanoporous carbon (NPC) materials using a metal–organic framework (IRMOF-3) that can act as a template for external carbon precursor (viz. sucrose) and also a self-sacrificing carbon source. The resultant graphitic NPC samples (abbreviated as NPC-0, NPC-150, NPC-300, NPC-500 and NPC-1000 based on sucrose loading) obtained through loading different amounts of sucrose exhibit tunable textural parameters. Among these, NPC-300 shows very high surface area (BET ≈ 3119 m^2/g, Langmuir ≈ 4031 m^2/g) with a large pore volume of 1.93 cm^3/g. High degree of porosity coupled with polar surface functional groups, make NPC-300 remarkable candidate for the uptake of H_2 (2.54 wt% at 1 bar, and 5.1 wt% at 50 bar, 77 K) and CO_2 (64 wt% at 1 bar, 195 K and 16.9 wt% at 30 bar, 298 K). As a working electrode in a supercapacitor cell, NPC-300 shows excellent reversible charge storage thus, demonstrating multifunctional usage of the carbon materials.

1. Introduction

Over the past decade, porous carbon materials have attracted a great deal of attention due to their potential applications in the fields of gas storage/separation, catalysis, fuel cell and biology [1–10]. Nanoporous carbons have received special attention compared to other contemporary porous materials because of its low density, chemical inertness and high thermal stability [11–13]. Among various techniques (both physical and chemical) to prepare nanoporous carbons, nanocasting approach using sacrificial template is an advantageous method owing to its fine control over pore size, surface area and pore volume [14–20]. In the past mesostructured silica, zeolites and clays have been utilized as hard templates for synthesizing hierarchical (meso/micro) porous carbons respectively [21–29]. Microporous carbon materials possessing high surface area are potential candidates for the adsorption and storage of small molecules such as hydrogen and carbon dioxide [30]. Recent reports suggests that materials are required to have appropriate balance between ultra microporosity, pore volume and surface area for high density hydrogen storage because of small kinetic diameter and low polarizability of hydrogen molecule [30]. Therefore, the synthesis of nanoporous carbon materials with high surface area and micropore (ultra-micropores) volume is of paramount importance, although it is not straightforward.

Metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) are a novel class of crystalline materials and have various applications in gas storage, separation, catalysis, magnetism and drug delivery based on their structural topology, tunable pore size and environment [31–50]. MOFs with ordered functional porous environment combined with high crystallinity and thermal stability can also be utilized as templates for the preparation of high surface area porous carbons [51–56]. Using MOF as a template, Xu et al. first prepared porous carbons using furfuryl alcohol as an external carbon precursor [53]. Later, other research groups also reported porous carbons derived from MOF, with and without external carbon precursor [53]. Furthermore, porous carbon materials with tunable textural properties have received substantial attention, owing to their important industrial applications in catalysis, adsorption, chemical sensing and as a supercapacitor [27]. Therefore, the right choice of external carbon precursor and MOF is very critical to fabricate desired tunable nanoporous carbon sample. As MOFs offer ordered and tunable soft porous environment with various functional groups on organic linker, it is feasible to choose suitable carbon precursor which can be easily immobilized through an intermolecular host–guest interaction. Herein,

* Corresponding author. Tel.: +91 80 2208 2826; fax: +91 80 22082766.
E-mail address: tmaji@jncasr.ac.in (T.K. Maji).

http://dx.doi.org/10.1016/j.micromeso.2014.12.008
1387-1811/

we report a simple route for the synthesis of nanoporous carbon materials from IRMOF-3 {[$Zn_4O(NH_2\text{-}BDC)_3$]·xDMF}, (NH_2BDC = 2-amino-1,4-benzenedicarboxylate) which acts as a template for external carbon source (sucrose) and a self-sacrificing carbon precursor [60]. Although the synthesis of porous carbon from MOFs and external carbon precursor are well studied, their tunable textural property based on the loading of the external carbon precursor is yet to be accounted. This work reports synthesis, characterization, tunable surface area and pore volume (high ratio of micropore to mesopore) of various nanoporous carbon samples (NPCs) (NPC-0, NPC-150, NPC-300, NPC-500 and NPC-1000) obtained based on different loadings of sucrose in IRMOF-3. The beneficial influence of external carbon precursor to obtain high surface area NPC samples with high micro pore volume has been discussed in the context of gas storage and electrochemical supercapacitors. Among the NPC samples, NPC-300 shows high BET surface area of (3119 m^2/g) with a large pore volume (1.93 cm^3/g) which has been exploited for hydrogen and carbon dioxide storage and electrochemical double layer super capacitors.

2. Experimental section

2.1. Materials

All the reagents and solvents employed were commercially available and used as supplied without further purification. $Zn(NO_3)_2{\cdot}6H_2O$, 2-aminobenzenedicarboxylic acid, sucrose, were obtained from Aldrich Chemical Co.

2.2. Preparation of nanoporous carbon using IRMOF-3

IRMOF-3 was prepared according to the literature as reported by Yaghi et al. [57] using $Zn(NO_3)_2{\cdot}6H_2O$ (4.8 g, 16 mmol) and 2-aminoterephthalic acid (1.32 g, 8 mmol) in 30 mL of dimethylformamide (DMF) at 120 °C for 6 h. The resultant compound was filtered, thoroughly washed with DMF and then activated by guest exchange with ethanol (20 mL) for 7 days. The sample was then filtered and dried in vacuum at 130 °C. For the synthesis of porous carbon, we took desolvated IRMOF-3, different amounts of sucrose (X = 0, 150, 300, 500, 1000 mg), 8 μL of H_2SO_4 and then mixed together in 2 mL of water to form light yellow colored paste. This mixture was then kept in an oven for successive temperatures 100 °C for 6 h and 160 °C for 6 h. The resulting composites were then pyrolyzed in a nitrogen flow at 900 °C and kept under these conditions for 6 h to carbonize the composite. The NPCs were obtained after removal of ZnO species using 20% hydrochloric acid by filtration, washed several times with water–ethanol mixture followed by drying at 100 °C. The resultant carbons obtained by variation in sucrose content are denoted by "NPC-X", where X indicates that amount of sucrose used. The obtained samples were designated as NPCs (NPC-0, NPC-150, NPC-300, NPC-500 and NPC-1000) based on the different amount of sucrose loading. All the resultant NPCs were characterized by FT-IR, elemental analysis, thermogravimetric analysis, powder X-ray diffraction (PXRD), Energy dispersive X-ray analysis (EDS) and different microscopic techniques.

3. Characterization techniques

3.1. Physical measurements

The resultant NPC samples were characterized through different techniques. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Discover instrument using Cu-Kα radiation. The morphology and porous nature of NPCs examined with field emission scanning electron microscope (FESEM, FEI Nova-Nano SEM-600, Netherlands) and transmission electron microscope (TEM) (JEOL JEM-3010 with an accelerating voltage at 300 kV). The Raman spectra were recorded in backscattering arrangement, using 532 nm laser excitation using 6 mW laser power. Elemental analyses were carried out using a Thermo Scientific Flash 2000 CHN analyzer. FT-IR spectra were recorded using KBr pellets in the range 4000–400 cm^{-1} on a Bruker IFS-66v spectrophotometer. Thermogravimetric analysis (TGA) were carried out under nitrogen (flow rate of 50 mL/min) with Metler Toledo TGA-850 TG analyzer in the temperature range between 25 and 600 °C at a heating rate 3 °C/min.

3.2. Adsorption measurements

Adsorption studies of N_2 (77 K), CO_2 (195 K for NPC-300) and H_2 (77 K for NPC-300) for NPC samples prepared at 423 K under high vacuum, were carried out using QUANTACHROME AUTOSORB-1C analyzer. The adsorption isotherm of different solvents (like H_2O and C_6H_6, at 298 K) for NPC 300 was measured in the vapor state by using BELSORP-aqua-3 volumetric adsorption instrument from BEL, Japan. In the sample chamber (~12 mL) maintained at T ± 0.03 K was placed the adsorbent sample (100–150 mg), which had been prepared at 423 K in 10^{-1} Pa for 18 h prior to measurement of the isotherms. The adsorbate was charged into the sample tube, and then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure in the equilibrium state. All operations were computer-controlled and automatic. High-pressure H_2 (77 K) and CO_2 (298 K) sorption measurements for NPC-300 was carried out on a fully computer controlled volumetric BELSORP-HP, BEL JAPAN high pressure instrument. All the gases used for high pressure measurements are scientific/research grade with 99.999% purity. For the measurements, approximately 300 mg sample was taken in a stainless-steel sample holder and degassed at 493 K for a period of 18 h under 0.1 Pa vacuum. The dead volume of the sample cell was measured with helium gas of 99.999% purity. Non-ideal correction for H_2 and CO_2 gases were made by applying virial coefficients at the respective measurement temperature.

3.3. Supercapacitor cell measurements

Investigations were carried out using NPC-300 as a working electrode in a cell containing 1.0 M aqueous H_2SO_4 solution as electrolyte, platinum wire as counter electrode and a saturated calomel electrode (SCE) as a reference electrode. All electrochemical characterizations were performed at room temperature. The composite working electrode was prepared by dispersing a mixture of NPC-300, polyvinyldifluoride (PVdF) binder and acetylene black in N-methyl-pyrrolidone (NMP) solvent. The three components were in the ratio 85:05:10 (w/w) in NMP and processed to form homogeneous slurry. The homogeneous mixture is pasted onto stainless steel (SS) current collector (0.5 × 0.5 cm^2) and electrodes were dried at 120 °C for 12 h under vacuum.

4. Results and discussion

4.1. Synthesis and characterization NPCs

The step-wise synthesis of various nanoporous carbons obtained from sucrose and IRMOF-3 is illustrated in Fig. 1. IRMOF-3 {$Zn_4O(NH_2\text{-}BDC)_3$} has a three dimensional structure consist of an oxo-centred {$Zn_4O(CO_2)_6$} secondary building units connected by NH_2-BDC linkers. Framework has 3D channels (dimensions of 18 × 18 $Å^2$) decorated with basic –NH_2 functional