Porous carbons derived from hypercrosslinked porous polymers for gas adsorption and energy storage

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ABSTRACT

Porous carbon materials with high surface areas were prepared using a hypercrosslinked porous organic polymer as porous precursor with potassium hydroxide activation. Nitrogen adsorption analysis revealed that the porous carbon materials have high surface area of up to 3101 m^2 g^{-1} and high pore volume of 1.84 cm^3 g^{-1}, which can provide more accessible surface and sites for gas adsorption and electrochemical energy storage. The porous carbons with high surface area show high H_2 uptake ability of up to 3.25 wt% at 77 K and 1.13 bar and CO_2 uptake ability of 6.69 mmol g^{-1} at 273 K and 1.13 bar. The lithium ion battery fabricated from CHCPB-K-600 shows a high specific discharge capacity of 1221 mA h g^{-1} at 100 mA g^{-1}, which could still retain 833 mA h g^{-1} after 50 cycles at 100 mA g^{-1}. CHCPB-K-600 also exhibits a high capacitance of 379 F g^{-1} at 0.5 A g^{-1} for supercapacitor, and the capacitance retains 91.2% after 3000 cycles at 2 A g^{-1}. Considering the high gas uptake ability, the excellent electrochemical performance, and the facile preparation strategy, these porous carbons hold a great potential for gas adsorption and energy storage.

1. Introduction

The rapid growing energy demand with serious environment issue has attracted enormous attention to develop clean energy sources that can replace fossil fuels. Among various clean energy systems, gas energy (e. g. H_2) and electric energy are the most potential energy sources. For the gas energy carrier, hydrogen with high gravimetric energy density of 120 kJ g^{-1} generates only water after combustion, which is regarded as the perfect clean energy [1]. In addition, the high hydrogen-to-carbon ratio endows methane with higher gravimetric energy density and lower carbon dioxide release, compared with other fossil fuels. However, the efficient storage of these energy gases remains a significant challenge. Meanwhile, CO_2 capture is regarded as a short-term solution to solve global warming until the fossil fuels can be absolutely replaced by clean energy [2–4]. In either case, the key element of gas storage is to develop advanced storage media, and most studies are focused on porous solid adsorbents, which physisorption gas molecules through relatively weak van der Waals forces, making regeneration of the materials energy efficient. To date, a wide range of microporous solid adsorbents including zeolites [5], metal—organic frameworks (MOFs) [6], porous organic molecules (POMs) [7,8], microporous organic polymers (MOPs) [9,10], and microporous carbons [11,12] have been proposed for the adsorption and storage of energy gases and/or CO_2.

Lithium ion batteries (LIBs) and supercapacitors (SCs) are undoubtedly two of the most popular and promising energy storage devices because of their high energy/power density and cyclability. It's known that graphite is the traditional anode materials for LIBs and the fully intercalated graphite exhibits a stoichiometry of LiC_6, which determines a theoretical capacity of 372 mA h g^{-1} [13]. SCs fabricated from commercial activated carbons normally show low electrochemical capacitance (<180 F g^{-1}) because of the low conductivity and limited surface area of electrode materials [14–16]. To meet the demand of rapid growing commercial electrical device, it

is desirable to develop new type of carbon materials with high energy storage.

Porous carbon show some advantages, such as high surface area, low cost, high conductivity, fast kinetics, diverse availability, and facile preparation strategies. These could make porous carbons promising candidates for catalysis [17], pollutant removal [18], gas adsorption [19,20], and electrochemical energy storage [21–23]. The precursors for carbon materials mainly include small organic molecules [24–27], biomass [21,28], metal-organic frameworks (MOFs) [29–34], and organic polymers [35–38]. Among variant of synthetic precursors, microporous organic polymers (MOPs) with intrinsic micropores have attracted a special interest as pyrolysis precursors for porous carbons [19,23,38]. Besides the structural diversity and controllability, tunable composition and resource renewability [12], the most significant feature of MOPs is their inherent microporous nature with high surface area, which benefits to further evolve carbon materials with abundant porous structure and high surface area [39–41]. Microporous carbons derived from MOPs have shown outstanding capability of gas adsorption and electrochemical energy storage and been the subject of intense recent interest. For example, the nitrogen-doped porous carbon of CPC-550 derived from benzimidazole-linked porous polymers exhibited respectively high CO_2 and CH_4 uptake of 8.3 and 2.7 mmol g^{-1} at 1 bar and 273 K [39], the microporous carbon nanotube of Py-CPN3 carbonized from a conjugated microporous polymer (CMP) exhibited a specific capacitance of 115 F g^{-1} at 1 mV s^{-1} [23], the carbonized CMP based on triazine-thiophene-benzene, NS-G@800, displayed a specific capacitance of 211 F g^{-1} at 0.5 A g^{-1} [42], the KOH-activated carbonized graphene-templated CMPs, aG-PTEPETBPE-C, gave a specific capacitance of 179 F g^{-1} at 0.2 A g^{-1} [43], the KOH-activated carbonized porous aromatic framework, K-PAF-1, showed a 280 F g^{-1} at 1 A g^{-1} [22], and the porous carbon of PHC-1 from CMPs delivered a reversible specific capacity of 519.6 mA h g^{-1} at about 74 mA g^{-1} for LIBs [38].

Hypercrosslinked porous polymers (HCPs) [44] are cost-effective and mainly prepared by Friedel-Crafts alkylation reaction [45]. Tan's group developed a facile and versatile strategy for preparing HCPs by one-step Friedel-Crafts reaction of formaldehyde dimethyl acetal (FDA), an external cross linker, with various aromatic monomers [46]. Applying this strategy, HCPs could be facilely prepared on a large scale using a wide range of aromatic monomers in low cost. Most previous work on HCPs were focused on exploring new building blocks for the improving surface area and varying pore size of the resulting polymers with the applications for gas adsorption and catalysis [45]. Recent studies revealed that porous carbon derived from HCPs show great potential in gas adsorption and electrochemical energy storage [16,19,47–49]. For instance, FCDTPA-K-700 carbonized from the nitrogen-rich hypercrosslinked porous organic polymers showed a hydrogen uptake ability of 2.61 wt% at 1 bar and 77 K [19], KCOP-M-700 porous carbon derived from a hypercrosslinked porous organic polymer exhibited a hydrogen uptake capability of 2.6 wt% at 1 bar and 77 K [49], microporous carbon, CNN-PMMA$_{191}$-b-PS$_{312}$, carbonized from hypercrosslinked poly(methyl methacrylate)-b-polystyrene gave a CO_2 uptake capability of 5.4 mmol g^{-1} at 273 K and 1.05 bar and a specific capacitance of 195 F g^{-1} at 0.2 A g^{-1} [16], carbonized HCP of phloroglucinol and α, α'-dichloro-p-xylen held a specific capacitance of 89 F g^{-1} at 0.1 A g^{-1} [48], microporous carbon, GHCP-1-900, derived from graphene-templated HCPs displayed a specific capacitance 144 F g^{-1} at 0.5 A g^{-1} [47].

In this work, a hypercrosslinked organic porous polymer (HCPB) with high surface area was synthesized by Friedel-Crafts reaction of FDA and phenyltrimethylsilane. Then, a series of porous carbon materials has been obtained by high-temperature treatment the HCPB precursor with potassium hydroxide activation. These porous carbons show ultrahigh surface area of 2739–3101 m^2 g^{-1} with large pore volume of 1.65–1.84 cm^3 g^{-1}, which allow for high hydrogen uptake ability (2.81–3.25 wt%, at 77 K and 1.13 bar) and methane adsorption (2.2–2.76 mmol g^{-1}, at 273 K and 1.13 bar). More importantly, the porous carbons show a high reversible specific capacity as high as 1220 mA h g^{-1} for LIBs and a high specific capacitance up to 379 F g^{-1} for SCs. These results demonstrated that these porous carbons are promising for gas adsorption and energy storage.

2. Experimental section

2.1. Materials

Phenyltrimethylsilane was purchased from TCI. Formaldehyde dimethyl acetal (FDA) was obtained from J&K Scientific Ltd. Ferric chloride ($FeCl_3$), potassium hydroxide (KOH), 1,2-dichloroethane (DCE), methanol, dichloromethane, acetone, and N-methyl-pyrrolidone (NMP, analytical grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. Polytetrafluoroethylene (PTFE) was purchased from Sigma-Aldrich Co. Ltd. Both acetylene black and polyvinylidenefluoride (PVDF) are commercially available. All chemicals were used as received.

2.2. Synthesis of the hypercrosslinked organic porous polymer of HCPB

To the mixture of phenyltrimethylsilane (0.9 g, 6.0 mmol) and FDA (1.404 g, 18.0 mmol) in 20 mL 1,2-dichloroethane, anhydrous $FeCl_3$ (2.925 g, 18.0 mmol) was added at room temperature. The mixture was then heated to 80 °C and stirred for 18 h. The mixture was then cooled to room temperature, and the precipitated polymer network was filtered and washed with methanol, distilled water, acetone and dichloromethane, successively, until the filtrate was nearly colorless. The product HCPB was dried in vacuum for 24 h at 80 °C to give deep brown powder (yield: 85.6%).

2.3. Synthesis of porous carbon materials

The precursor of HCPB (0.5 g) and KOH (2 g) were dispersed in 200 mL mixture solution of ethanol and water (95/5, v/v) and stirred overnight at room temperature. The resulting mixture was distilled to remove the solvents, and the brown residue was dried in vacuum for 24 h at 70 °C. Carbonization of the HCPB-KOH mixture was carried out in a nickel crucible placed within a tube furnace by heating the sample to the target temperatures of 600, 700 and 800 °C with a heating rate of 5 °C min^{-1} and held for 2 h at the desired temperature under nitrogen gas flow. After cooling down to room temperature, the black residue was washed with 2 M HCl to remove excess KOH. Further purification of the activated carbon was carried out by washing with distilled water and acetone, respectively. The resulting activated carbons were dried in vacuum for 24 h at 80 °C and denoted as CHCPB-K-600, CHCPB-K-700 and CHCPB-K-800 according to the target temperature.

2.4. Characterization

Elemental analysis was carried out on EURO EA30000 Elemental Analyzer. The microscopic features of the samples were carried out on a field-emission scanning electron microscopy (SEM) (SU8020, Hitachi, Tokyo, Japan) and a high-resolution transmission electron microscopy (HRTEM) (JEM-2100F, JEOL, Tokyo, Japan). Powder X-ray diffraction