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Structure controllable carbon matrix derived from benzene-constructed porous organic polymers for high-performance Li-S batteries

Zhichang Xiao [a, b, 1], Debin Kong [a, c, 1], Jiaxu Liang [a, b], Bin Wang [a], Rashid Iqbal [a, b], Quan-Hong Yang [c, **], Linjie Zhi [a, b, c, *]

[a] *CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing, 100190, China*
[b] *University of Chinese Academy of Sciences, Beijing, 100049, China*
[c] *School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300350, China*

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A B S T R A C T

A kind of porous carbon material with tunable pore structure and morphology was successfully built up from a knitting based bottom-up method. This porous carbon material feature abundant porosity and remarkably high-efficiency restrain for the pore collapse after the pyrolysis process, namely, a specific surface area retention (SSRA) high up to 45% in the absence of pore forming agent. Based on this unique porous carbon material, further compositing with MWCNT can enhance its performance for Li-S batteries, specifically, 1 C for 631 mA h/g and 2 C for 574 mA h/g after 300 cycles, with capacity decay as low as only 0.104% and 0.07%, respectively, which may further open the opportunity for a new family of porous carbon materials with well-controlled structures and properties for high performance applications in energy conversion and storage fields.

1. Introduction

Porous carbon materials, with excellent chemical stability, good conductivity, high specific surface area and tunable pore size, have become one of the most attractive research topics towards varied applications [1–6], particularly for energy conversion and storage [7–11]. As electrode materials, these porous carbon have shown great potential in developing electrocatalysts [12–14], lithium-ion batteries [15], Zn-air batteries [16], supercapacitors [17,18], lithium-sulfur batteries [19,20] and Na-ion batteries [21]. There are many preparation processes for porous carbon materials. The conventional activated carbon is synthesized from pyrolysis and physical or chemical activation of pitch, coal or wood at elevated temperature [22]. To obtain new carbon materials with high porosity, several approaches were reported by using nanotechnology. One way is to pyrolyze proper precursors within suitable templates [19,23–25]; however this approach inevitably requires the removal of the template by environmentally hazardous reagents afterwards [26]. An alternative is the chemical activation method by using pore forming agent such as KOH or NaOH [27,28]; however, this method often makes the resultant pores with high uncertainty and some pore may collapse because of the critical corrosion of the pore forming agent [29]. To prevent the collapse, and also build carbon matrix with controllable porosity, constructing a porous carbon material from the molecular level rather than the “top-down” approach is attractive [26].

Porous organic polymers (POPs) formed by simple and cheap routes with various monomers, are attracting more attentions due to their large surface area, controllable pore size and high chemical stability [30–36]. They have already been successfully used as gas storage and separation materials, supports for catalysts and sensors, showing extremely high methane uptake [37] and high-performance catalytic support for liquid phase reaction [38]. More importantly, via simple pyrolysis process, the porous organic polymers can be further converted into carbonaceous materials

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* Corresponding author. CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing, 100190, China.

** Corresponding author. School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300350, China.

E-mail addresses: qhyangcn@tju.edu.cn (Q.-H. Yang), zhilj@nanoctr.cn (L. Zhi).

[1] These authors contribute equally to this work.

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with delicately designed structure. Such novel porous carbon materials possess high specific surface area and excellent conductivity attributed to the intrinsic porosity of the POP, imparting the related electrode with superhigh Li-ion storage capacity as well as outstanding supercapacitive behavior [39]. Additionally, thermalized triazine-based frameworks (TTFs) with excellent conductivity, tunable nitrogen configurations, and adjustable multi-heteroatom doping can be obtained by simply changing the reaction temperature, altering the reaction time or using heteroatom-containing reactants from porous organic network, which present detailed exploration of the electrochemical mechanisms of metal-free catalysis, as well as developing high performance catalysts for ORR [40]. However, the porosity of the POP is always easy to be destroyed during the pyrolysis process, leading to the resultant porous carbon materials with less porosity and reduced specific surface area. The 2D porous polymer sheets are found with obvious decrease in surface area along with the temperature being elevated, maybe attributed to the degradation of the polymers and the rearrangement of fragments under the carbonization conditions, resulting in a severe block of the ion- and electron-transportation in the framework ultimately by comparison with those treated with $ZnCl_2$. Therefore, developing efficient method to restrain the pore collapse during the pyrolysis process by the use of porous organic polymers is highly expected.

Herein, we develop a porous carbon with tunable pore structure and morphology derived from a knitting based bottom-up method as illustrated in Fig. 1. Benzene monomers are selected to be controllable knitted together by an external cross-linker (formaldehyde dimethyl acetal, FDA), resulting in the benzene-constructed porous organic polymers (denoted as KBF-x, where x represents the mole ratio between benzene and FDA, x = 1, 2, 3), which is then pyrolyzed to obtain the structure controllable carbon matrix (p-KBF-x). Interestingly, after carbonization the obtained carbon matrixes can fully inherit the intrinsic porosity as well as the morphology of the structure-controllable precursors. Besides, when the mole ratio of crosslinker to monomer was 3, the well cross-linked network can effectively restrain pore collapse and thus possess a specific surface area retention (SSRA) high up to 45% in the absence of pore forming agent. The unique pore-restraining ability in conjunction with the abundant conductive networks result in excellent electrical performance when used as electrodes for Li-S batteries: stable cycling performance over 300 cycles (with a discharge capacity decay as low as 0.07% per cycle), and rate capability with 574 mA h/g at 2 C was achieved, respectively.

2. Experimental

2.1. Sample preparation

Synthesis of KBF-1: *the synthesis of KBF-x is conducted by a modified knitting reaction* [41]. 0.02 mol (895 μL) benzene was added into the solution of $FeCl_3$ (1.6 g, 0.01 mol) and 0.02 mol FDA (900 μL) in 20 mL DCE. The solution was stirred in ice-bath to guarantee a uniform mix of the monomers. Afterwards, the mixture was stirred at 45 °C for 5 h to get the original network, and then treated at 80 °C for 19 h to complete the reaction. The precipitate was washed with ethanol for several times till the solution is colorless, and then washed with ethanol thoroughly in a Soxhlet for 24 h, followed by drying in an oven at 60 °C overnight.

Synthesis of KBF-2 and synthesis of KBF-3 are similar to that of KBF-1, except the amount of FDA is 0.04 mol (1800 μL) and 0.06 mol (2700 μL).

Synthesis of MWCNT@KBF-3: 120 mg MWCNT was first added into the 20 mL DCE solution, containing 1.6 g (0.01 mol) $FeCl_3$ and

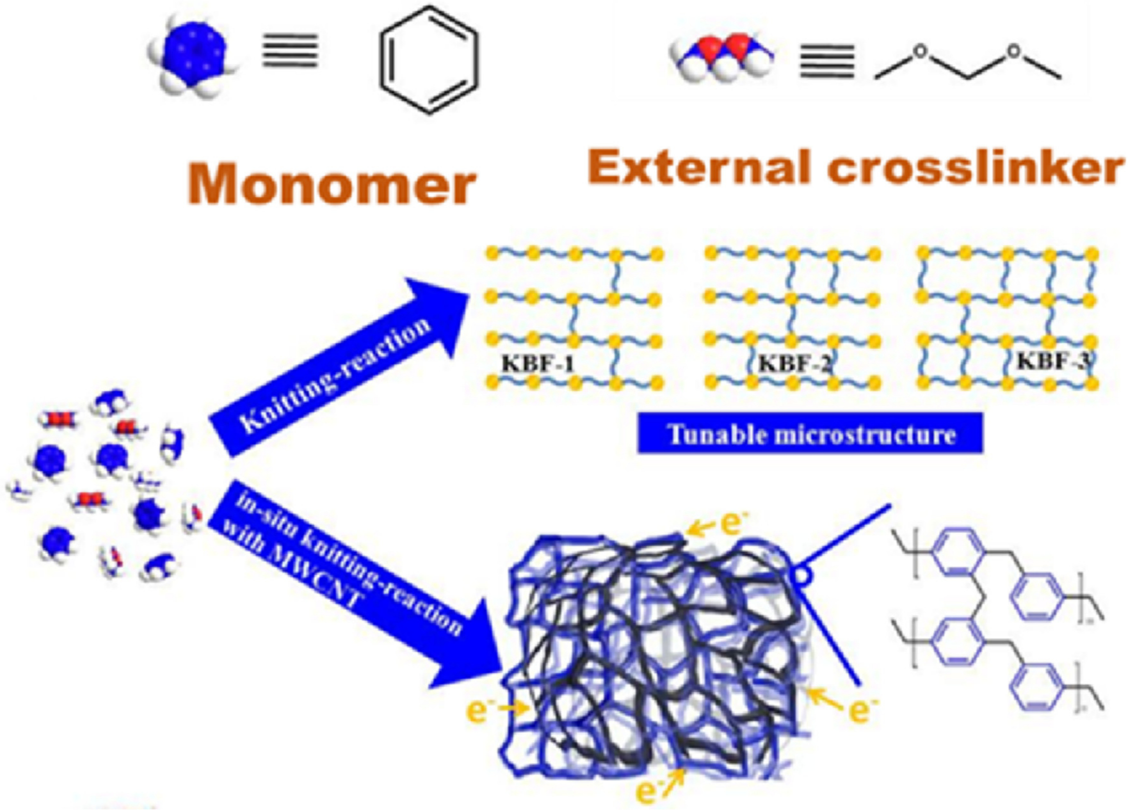

Fig. 1. Schematic illustration of the fabrication of KBF-x and MWCNT@KBF-3. (A colour version of this figure can be viewed online.)