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Template-free synthesis of nitrogen-doped hierarchical porous carbons for CO_2 adsorption and supercapacitor electrodes

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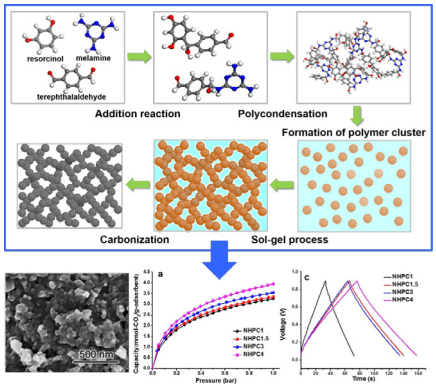
GRAPHICAL ABSTRACT

Nitrogen-doped hierarchical porous carbons with controllable nitrogen content are prepared via a template-free method by direct carbonization of mel amine-resorcinol-terephthaldehyde networks. This new nitrogen-doped hierarchical porous carbons with tunable hierarchical porosity and chemical composition have good potential applications in the gas separation and electrochemical energy storage.



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ABSTRACT

Nitrogen-doped hierarchical porous carbons (NHPCs) with controllable nitrogen content were prepared via a template-free method by direct carbonization of melamine-resorcinol-terephthaldehyde networks. The synthetic approach is facile and gentle, resulting in a hierarchical pore structure with modest micropores and well-developed meso-/macropores, and allowing the easy adjusting of the nitrogen content in the carbon framework. The micropore structure was generated within the highly cross-linked networks of polymer chains, while the mesopore and macropore structure were formed from the interconnected 3D gel network. The as-prepared NHPC has a large specific surface area of 1150 $m^2 \cdot g^{-1}$, and a high nitrogen content of 14.5 wt.%. CO_2 adsorption performances were measured between 0 °C and 75 °C, and a high adsorption capacity of 3.96 $mmol \cdot g^{-1}$ was achieved at 1 bar and 0 °C. Moreover, these nitrogen-doped hierarchical porous carbons exhibit a great potential to act as electrode materials for supercapacitors, which could deliver high specific capacitance of 214.0 $F \cdot g^{-1}$ with an excellent rate capability of 74.7% from 0.1 to 10 $A \cdot g^{-1}$. The appropriate nitrogen doping and well-developed hierarchical porosity could accelerate the ion diffusion and the frequency

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response for excellent capacitive performance. This kind of new nitrogen-doped hierarchical porous carbons with controllable hierarchical porosity and chemical composition may have a good potential in the future applications.

1. Introduction

Porous carbon materials are outstanding candidates in the field of modern technological applications, such as water and air purification [1,2], gas separation [3], catalyst supports [4], biological and chemical sensing [5], and energy storage and conversion [6,7], owing to their high surface area, thermal and chemical stability, high conductivity and excellent mechanical properties. Generally, the pore diameter distribution, surface area, channel connectivity, and architecture of the carbon materials usually affect their action in particular applications [8,9]. Therefore, synthesis of porous carbon materials with tailored structure and porosity has emerged as a promising field of research [10,11]. Nowadays, porous carbons with hierarchical architecture are among the most favorable materials for adsorption and electrochemical applications [12–14]. In the hierarchical porous structure, macropores provide a high volume to shorten the diffusion distance, mesopores are necessary for the fast mass diffusion and transport, and micropores contribute to size- and shape-selectivity and high surface area [15–18]. Up to date, methods employed to synthesize hierarchical porous carbons (HPCs) include templating strategy, a combination of template carbonization and post activation, bio-inspired methods, and chlorination of titanium-carbide-carbon composites [19–23]. Among them, the most applicable synthetic procedure is the templating approach using sacrificial templates to infiltrate with a suitable carbon source, followed by carbonization of the composite, and succedent removal of the template. However, the synthesis of hierarchical structure is usually quite complicated, time-consuming, and high-expense, due to preparation of templates, removal process of templates, and post activation. Thus, these disadvantages impart to HPCs an uncompetitive price-to-performance ratio and severely limit their large-scale commercial applications. Therefore, to solve these problems, developing an inexpensive template-free method for the preparation of HPCs materials is critical, however, it still exists a big challenge.

The performance of porous carbon materials depends not only on the structural characteristics but also on the surface chemical properties [24]. Having the ability to modify the porous carbon networks by the heteroatomic dopant, the interactions between the networks and guest molecules could be adjusted, making them increasingly controllable for specific applications [25,26]. Among diverse dopants (phosphorus, sulfur, boron, nitrogen), nitrogen is the most appealing and widely doped heteroatom which appears as basic nitrogen groups and is often directly incorporated into the carbon backbone [27]. Nitrogen atom with five valence electrons is superior because it could serve as an electron donor in the lattice, causing the shift of Fermi level position towards the valence band in carbon. Moreover, the doping of nitrogen into carbon materials could also significantly improve the carbon wettability, basic property, surface polarity, adsorptive ability and conductivity [28,29]. Nitrogen could be doped into carbon matrix by post-treatment of the carbon materials or by direct pyrolysis of nitrogen-rich carbon precursors [27–29]. For the former, the nitrogen-doped carbon materials could be obtained by introducing nitrogen into carbon networks through treating it with nitrogen-containing reagents such as ammonia, amine, urea and HNO_3 [30]. However, the nitrogen functional groups introduced by such a method are often on the surface of carbon rather than in the bulk to improve the properties of the carbon backbones [31,32]. Therefore, the nitrogen-containing functional groups are often unstable with only a limited surface doping of no more than 10 at.% [31,32]. The drawback can be overcome by the direct pyrolysis of nitrogen-containing polymers, or co-pyrolysis of an appropriate nitrogen carrier employing N-containing carbon precursors such as acrylonitrile, melamine, cyanamide, urea polymer and biomass containing nitrogen [10,33–40]. By this method, nitrogen can be preserved in the bulk carbon structure at a relatively high content by adjusting the N-containing carbon precursor and the carbonization temperature. Meanwhile, the nitrogen in the carbon frameworks can stay stable under a rigorous working condition. However, to create additional porosity, the most applicable synthetic techniques often require the use of a sacrificial template, such as mesoporous silica or zeolites, which involve harsh experimental conditions or costly synthetic procedures, or undergo a time-consuming activation [41,42]. Therefore, it still remains a great challenge to develop facile and feasible synthetic approaches for high-performance porous carbon materials with controllable nitrogen content.

Hierarchical porous carbons with nitrogen-containing functionalities possess excellent textural characteristics and surface basic groups, which enable them to be promising candidates for electrical energy storage, heterogeneous catalysts, gas and liquid separation and so on. Recently, utilizing nitrogen-doped hierarchical porous carbons as the electrode and adsorption materials has received much attention. Zhu et al. [43] prepared nitrogen-doped hierarchical porous carbon spheres by solvent-exchange method using acrylonitrile-*co*-acrylamide as carbon precursor. The results demonstrated that the outstanding CO_2 adsorption capacities are owing to the well-developed micropores and the relatively large pyridinic nitrogen content derived from the co-polymer precursor. Zhou et al. [44] synthesized nitrogen-doped hierarchical porous carbons by a two-stage method with the combination of a hard-templating process and KOH-activation treatment. They suggested that the outstanding capacitive performance may be attributed to the combined action of the hierarchical pore structure, large specific surface area and high heteroatom doping, leading to both double layer capacitance and Faradaic capacitance contributions. Hou et al. [45] prepared hierarchical porous nitrogen-enriched carbon nanosheets by an effective simultaneous activation/graphitization route from biomass-derived natural silk. The results indicated that high hierarchical porosity, large specific surface area, high N-doping content and defects have favorable multiple synergistic effects, beneficial for high-performance energy storage-related applications. Nevertheless, developing a facile and low-cost synthesis approach to synthesize nitrogen-doped hierarchical porous carbon materials with well controllable functionalities is still an urgent task for future development of applications.

In this work, we present an effective template-free synthesis of nitrogen-doped hierarchical porous carbons (NHPCs) with tunable nitrogen content by direct carbonization of polymer networks, expanded upon our previous work on the synthesis of nitrogen-doped hierarchical polymer networks [46]. The nitrogen-doped hierarchical polymer networks were prepared by a sol-gel polymerization of melamine, resorcinol and terephthaldehyde in dimethyl sulfoxide (DMSO). By removal of the residual solvent in the polymeric gel, the as-prepared polymer networks