



Redox-active organic molecules functionalized nitrogen-doped porous carbon derived from metal-organic framework as electrode materials for supercapacitor



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ABSTRACT

Metal-organic frameworks (MOFs) have been turned out to be an excellently self-sacrificing template for preparing porous carbon. Herein, we synthesized a nitrogen-doped porous carbon materials (NPCs) by direct thermolysis of zinc-based MOFs (ZIF-8). Fortunately, the NPCs with high specific surface area and abundant pore structure was suitable for using as conductive substrate to anchor organic molecules. Anthraquinone (AQ), 1, 4-naphthoquinone (NQ) and tetrachlorobenzoquinone (TCBQ) were selected to functionalize NPCs *via* noncovalent interactions, respectively. As a consequence, the multielectron redox centers possessed by AQ, NQ and TCBQ were implanted in the NPCs. More interestingly, the electrochemical rate-determining step for the functionalized NPCs was surface process rather than diffusion, which is similar to capacitive behavior of the electrical double layer. The functionalized NPCs revealed an enhanced overall capacitance (about 1.4 times higher than NPCs) because the electrochemical capacitance was superposed on the electrical double layer capacitance. Furthermore, the as-assembled asymmetrical supercapacitor (ASC) exhibited excellent energy storage performance. The topological structure of MOFs skeleton and the potential self-matching behavior between the positive and negative electrodes were responsible for high energy density (23.5 Wh kg⁻¹ at 0.7 kW kg⁻¹, which is 1.54 times higher than that of NPCs symmetrical supercapacitor) of the device.

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1. Introduction

The fossil energy such as coal, oil and gas, which is once used to support the rapid development of human civilization in the 20th century, is undergoing an unprecedented crisis in recent years. Except for reserves dwindles, the emissions coming from burning those fossil fuels lead to global warming, hazy weather and a series of environmental problems. Therefore, developing environmentally friendly, inexpensive and trustworthy energy storage systems is a foundation of global sustainable development [1–3]. Supercapacitors, which have also been called as electrochemical capacitors or ultracapacitors, are emerging energy storage devices. In general, supercapacitors possess higher power density (*ca.* 5–15 kW kg⁻¹), superior cycle stability (over 10⁶ cycles) and rapid charge-discharge rate. But their drawback is limited energy density

(*ca.* 5–10 Wh kg⁻¹) comparing with lithium-ion batteries (*ca.* 120–170 Wh kg⁻¹) and lead acid batteries (*ca.* 20–35 Wh kg⁻¹) [4,5]. Thus, the researchers have to face an unavoidable problem: how to improve the energy density of the supercapacitor to meet the growing power supply demand of a variety of applications such as portable devices, electric/hybrid vehicles, stand-by power systems, and so on. As is known to all, the energy density (*E*) of a supercapacitor is expressed as $E = 0.5 C \cdot \Delta V^2$, where *C* is the total specific capacitance and ΔV is the cell voltage of a device [6]. Apparently, increasing *C* or broadening ΔV of the supercapacitor is an effective and feasible method to enhance the energy density.

According to the calculation formula of the capacitance ($C_c = \epsilon A/d$), C_c is a function that depends on the specific surface area (*A*) of electrode [7]. Thus, nanoporous materials with optimal pore size and pore distribution naturally become a class of promising electrode to improve the energy density of the supercapacitor [8]. Recently, metal-organic frameworks (MOFs) or porous coordination polymers have been investigated in the field of supercapacitors because of tremendous specific surface area, abundant

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topological structure, tunable pore distribution and high ordered crystalline state [9–11]. They are usually applied in following ways: firstly, pristine MOFs crystals can be directly used as electrode materials due to their essential porous structures and exposed metal centers, which store charges by absorbing electrolyte ions or corresponding reversible redox reactions, respectively; secondly, converting MOFs into porous metal oxides in an air atmosphere to store charges by taking place fast Faradaic reactions; thirdly, pyrolyzing MOFs to achieve porous carbons that store charges through electrostatic accumulation of charges [12]. Amongst these ways, each approach has their own merits and shortcomings in supercapacitor applications. Pristine MOFs always show poor conductivity, while the metal oxides are non-renewable resources. However, MOFs derived nanoporous carbons are not only able to inherit the structural characteristics of the precursors but also environmentally friendly. Comparing with other methods to prepare nanoporous carbons, this method not need to remove template from the resultant and the experimental procedures are simple and suitable for wholesale production. To a certain extent, the MOFs derived porous carbon has embodied its superiority in the construct of supercapacitors with high performances. For example, Yusuke Yamauchi et al. obtained nanoporous carbon and cobalt oxide (Co_3O_4) electrode materials from cobalt based MOFs (ZIF-67) by controlling the annealing conditions. The asymmetric supercapacitor (ASC), which is constructed by nanoporous carbon and Co_3O_4 , exhibited high specific energy (36 Wh kg^{-1} , 1600 W kg^{-1}) and excellent rate capability [13]. Gao Qiuming et al. also fabricated an ASC by using MOF-5 derived porous carbon as negative electrode and Ni-Zn-Co oxide/hydroxides as positive electrode. The device delivered a high energy density of 41.65 Wh kg^{-1} and displayed a good cycle stability [14]. Salunkhe R. et al. prepared a high specific surface area ($1523 \text{ m}^2 \text{ g}^{-1}$) nanoporous carbon materials *via* direct carbonization of ZIF-8 for assembling symmetric supercapacitors (SSC). The SSC could deliver a high energy density of 10.86 Wh kg^{-1} with a power density of 225 W kg^{-1} in $1 \text{ M H}_2\text{SO}_4$ electrolyte [15]. Besides, Torad N.L. et al. were also synthesis another nanoporous carbon materials by using cobalt based MOFs as sacrificial templates. When the as-prepared nanoporous carbon materials were used as electrode materials for a symmetric supercapacitor, the energy density could reach to 19.6 Wh kg^{-1} at a power density of 700 W kg^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte [16].

But no matter how to adjust and control the pore structure and size, the electrical double-layer energy storage mechanism of the MOFs-derived porous carbon, as a kind of carbon-based materials, is always not involved in Faradaic charge reactions and results in limited specific capacitance of $100\text{--}300 \text{ F g}^{-1}$ in an aqueous electrolyte [12]. Against this background, the functionalization of the MOFs-derived porous carbon becomes particularly important. Namely, redox-active organic molecules can be used to improve the surface properties of them. As a result, the electrochemical capacitance originated from the anchored redox-active organic molecules is superposed on the electrical double-layer capacitance of the MOFs-derived porous carbon [17]. As well-known, there are a great number and various sorts of redox-active organic molecules in the available chemical resources, which can meet the selection needs for researchers [18,19]. More importantly, the electrochemical properties of the organic molecules can be selectively tuned by adjusting the organic functional groups or molecular scaffolds [20]. However, the solubility of the selected organic molecules should be not be too high in the applied electrolyte, or else the active species will migrate between the positive and negative electrode and generate shuttle effect, which always leads to capacitive fading. Based on above analysis, it is believed that the functionalized MOFs-derived porous carbon can collect many merits at once. On the one hand, it

has the feature of tunable pore size and plentiful topological structures. On the other hand, it can acquire the desired surface properties which are regulated and controlled by organic molecule functionalization. Based on our previous reports [21], the electrochemical kinetics of the organic molecules modified carbon-based materials have following characteristics: firstly, the peak currents (i_p) are linear to the applied sweep rates (ν); besides, the cyclic voltammetry (CV) curves have small peak separations between oxidation and reduction peaks. This implies that surface redox reactions of anchored organic molecules will not be controlled by diffusion, which is similar to the behaviors of electrical double layer capacitance [22].

In this work, we attempted to provide a new strategy for preparing electrode materials of supercapacitors, in which the MOFs were employed as a self-sacrificing template to derive porous carbon with high specific surface area, tunable pore distribution and controllable pore size while the redox-active organic molecules were used to realize the surface functionalization. The monodispersed ZIF-8 crystals with well-defined and regular polyhedral morphologies were synthesized by means of typical coordination chemistry method. Then, the as-obtained ZIF-8 crystals as precursors were converted into nitrogen-doped porous carbon, which could retain their original morphologies and possess large specific surface area ($1140 \text{ m}^2 \text{ g}^{-1}$) and appropriate porosity after the pyrolysis treatment. Subsequently, the AQ was selected to functionalize NPCs to gain negative electrode material (AQ-NPCs) while NQ and TCBQ collectively decorated NPCs to obtain positive electrode material (TN-NPCs). The resultant positive and negative electrodes generated a potential self-matching behaviour because the electrochemical response of AQ, NQ and TCBQ molecules were located at about -0.09 , $+0.28$ and $+0.53 \text{ V}$. More importantly, the asymmetric supercapacitor fabricated by AQ-NPCs and TN-NPCs with homologous pore structures can deliver an energy density of 23.5 Wh kg^{-1} (along with the power density of 0.7 kW kg^{-1}) in $1 \text{ M H}_2\text{SO}_4$ aqueous electrolyte. It is pointed out that the above-mentioned strategy is promising for constructing a supercapacitor in term of green, all-carbon and excellent supercapacitive performances.

2. Experimental

2.1. Synthesis of ZIF-8 derived nitrogen-doped porous carbon

Firstly, according to the common method [23], the ZIF-8 crystals were prepared as following: 0.988 g of zinc acetate dehydrate and 2.956 g of 2-methylimidazole (Melm) were dissolved in the 270 mL anhydrous ethanol, respectively. The above two solutions were mixed and vigorously stirring for 5 min , and then the resulting solution was aged at room temperature for 24 h . After that, the white precipitates were collected by filtration and washed carefully with ethanol for several times. Secondly, the as-obtained ZIF-8 crystals were directly carbonized at 800° C for 8 h under a N_2 atmosphere with the heating rate of $3^\circ \text{ C min}^{-1}$. After cooling down to room temperature, the black powders were washed by 1 M HCl to remove ZnO nanoparticles and washed with distilled water to neutral, then dried at 70° C and achieved NPCs.

2.2. Synthesis of organic molecules-functionalized NPCs

Based on our previous report [24], 0.04 g of pure organic compound (AQ) and mixed organic compound (0.024 g NQ and 0.016 g TCBQ) were dissolved in 40 mL acetone and then 0.05 g NPCs was added, respectively. The mixtures were sonicated for 30 min . By evaporating the acetone at 70° C , the organic compounds were anchored on the NPCs. After that, the samples

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