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Highly activated porous carbon with 3D microspherical structure and hierarchical pores as greatly enhanced cathode material for high-performance supercapacitors

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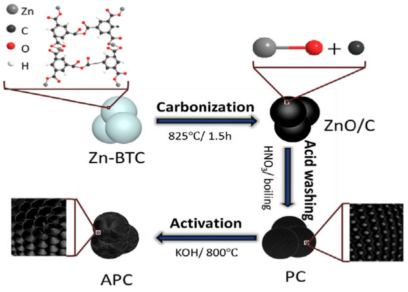
HIGHLIGHTS

- Highly activated porous carbon (APC) is derived from zinc based MOFs.
- The APC has uniform spherical shaped morphology with average size of 3–5 μm.
- The obtained APC also has a high specific surface area is up to 2314.9 m^2g^{-1}.
- The APC electrode showed a specific capacitance of 325 F g^{-1} at 1 A g^{-1}.
- The supercapacitor exhibits a remarkable stability for 150000 cycles at 50 A g^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

Highly activated porous carbon with attractive and promising electrochemical properties is employed as cathode material for high performance supercapacitors. The present paper proposes a novel activated porous carbon which is derived from zinc-based metal organic framworks as a source and template by carbonization at 825 °C and also further activation with KOH. The obtained activated porous carbon has uniform unique spherical morphology with an average size of 3–5 μm and has a specific surface area up to 2314.9 m^2g^{-1}. The activated porous carbon with superior mesoporous structure exhibits a high electrochemical performance and an excellent electrochemical stability in 6 M KOH solution. It provides a high specific capacitance and power density of 325 F g^{-1} and 71.2 W kg^{-1}, respectively, at a current density of 1 A g^{-1}. Additionally, the activated porous carbon retains its specific capacitance with very slight decay rate of 1.21% after 150,000 cycles at an ultrahigh current density of 50 A g^{-1}. Hence, the present investigation demonstrates that the as-prepared activated porous carbon is a promising candidate as a low-cost and highly efficient electrode material for high-performance supercapacitors.

1. Introduction

In recent years, increased research efforts have been devoted to the development of renewable energy storage devices for various power applications due to the global climate change and the rapid depletion of fossil fuel resources [1–4]. During the past decades, supercapacitors or electrochemical capacitors have received great attention as one of the most promising electrochemical energy storage devices due to their attractive properties such as high power density, fast charge-discharge rate, super durability, safety and reliability [5–11]. However, the recent

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reported supercapacitors have a certain practical limitation like low energy density, which ultimately affects their practical applications. Therefore, many researchers have focused on improving the energy density of supercapacitors via developing highly efficient electrode material. Recently, the porous carbon becomes one of the most efficient electrode materials for supercapacitors due to its excellent desired features, including high chemical stability, high electrical conductivity and resource abundance [12]. The surface area and pore size distribution of porous carbon have important effects on the electrochemical efficiency of supercapacitor devices [13]. Porous carbon materials (e.g. carbon molecular-sieves and activated carbon) are usually prepared by various methods such as template synthesis, activation, carbonization of polymers, etc [14]. Most carbon materials are prepared from carbon-rich sources by heat treatment in inert atmospheres. The essential properties of these carbons are influenced by several important factors such as carbon precursor, prevalent accumulating phases, preparation conditions and structural features of the product [15]. It can also be prepared through a pyrolysis process by using a suitable precursor [16].

Modernly, the metal organic frameworks (MOFs) have been authenticated as an important type of porous carbon starting material [17–19]. The MOFs have many applications such as separation for heterogeneous catalysis, gas storage, chemical sensors [20–23], luminescent material and drug delivery [24]. MOFs are considered as eligible precursors and templates to obtain porous carbon (templated porous carbon) with unique porous structure and high specific surface area because of their regular framework structures which are made from organic ligands and transition metals [25–28]. When the porous carbon material is prepared from MOFs by thermal-treatment at the temperature higher than 600 °C, and it exhibits an extra-high efficiency as supercapacitor material with high cyclic stability due to the ordered porous structure of carbon which is permeable for ions-diffusion [29,30]. Moreover, in order to enhance the electrochemical performance of porous carbon, the chemical or physical activation is widely adopted. However, chemical activation is more attractive than physical activation due to its high adequacy in pores creating, which is an appropriate way to achieve large specific surface area [31]. Generally, the chemical activation of carbon is carried out by mixing carbon with specific chemical agents such as KOH, NaOH, $ZnCl_2$, etc after the carbonization process of MOFs at high temperature to obtain porous carbon with higher specific surface area [32,33].

Recently, Huang et al. obtained N-doped porous carbon sheets from ZIF-8 by carbonization and KOH activation with a specific surface area of $1190\,m^2\,g^{-1}$ and a specific capacitance of $290\,F\,g^{-1}$ at a current density of $1\,A\,g^{-1}$ [34]. Zou et al. prepared N-doped nanoporous carbon using N-doped MOF that exhibits a high capacitance of $272\,F\,g^{-1}$ at $0.1\,A\,g^{-1}$ of current density [35]. Bao et al. reported a high performance 3D hybrid-porous carbon derived from zinc based MOF for supercapacitors with a specific capacitance of $215\,F\,g^{-1}$and a high cyclic stability for 10,000 cycles at a current density of $5\,A\,g^{-1}$ [36]. Liu et al. reported a porous carbon activated material for supercapacitors derived from MOF with large specific surface area of $2872\,m^2\,g^{-1}$ and specific capacitance of $258\,F\,g^{-1}$ at low current density of $250\,mA\,g^{-1}$ [37]. Besides, a N-doped porous carbon material derived from zeolitic imidazolate framework was reported by Zhong et al. and it revealed a specific capacitance of $258.5\,F\,g^{-1}$ at a relatively low current density of $0.1\,A\,g^{-1}$ with 97.8% specific capacitance retention at $10\,A\,g^{-1}$ after 1000 cycles [38]. The carbonnanospheres derived from MOF-5 were reported by Khan et al. and they exhibited a high electrochemical performance for supercapacitors by supplying a specific capacitance of $300\,F\,g^{-1}$ at a current density of $1.5\,A\,g^{-1}$ with capacitance retention of 91.5% after 3000 cycles [39]. In addition, Wang et al. have reported the hierarchical porous carbon from zinc based MOF for supercapacitors, which provided a specific capacitance of $283.4\,F\,g^{-1}$ at low current density of $0.2\,mA\,g^{-1}$ and the specific capacitance remains 92.8% after 10,000 cycles at $5\,A\,g^{-1}$ [40]. From these reports, it has been observed that the large specific surface area and pore volume of porous carbon are effective factors to increase the specific capacitance and power density of supercapacitors [41].

In this work, we prepared zinc based MOF with uniform unique structure by using zinc nitrate as a metal ion source and benzene organic ligand of tricarboxylic acid as organic source, denoted as Zn-BTC. Then, the Zn-MOF was directly carbonized in vacuum at high temperature and then dissolved with nitric acid to remove the zinc species played a role of a natural pore generator. The obtained porous carbon (PC) was further activated with KOH at 800 °C to improve its microstructure which is the important criteria for enhancement of electrochemical performance of supercapacitors. A three electrodes system was used to study the electrochemical properties of this material. The fabricated supercapacitor displays a superior specific capacitance of $325\,F\,g^{-1}$ in the electrolyte of 6 M KOH at current density of $1\,A\,g^{-1}$, and pretty high capacitance retention of 98.8% is also achieved after 150,000 cycles at high current density of $50\,A\,g^{-1}$. Therefore, it clearly shows that the prepared activated porous carbon (APC) exhibits a much higher supercapacitor performance as compared with the previously reported porous carbon derived from MOFs.

2. Experimental section

2.1. Chemicals and raw materials

All chemicals were analytical reagent grade and used without any further purification. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) was received from Beijing Yili fine chemicals Ltd, China. Benzene tricarboxylic acid ($C_9H_6O_6$, 99%) was purchased from Weng Jiang Reagent, China. Ethanol and nitric acid (HNO_3) were purchased from Beijing chemical works, China. Graphite powder was received from Shanghai Kumho Plastic Co. Ltd, China and polytetrafluoroethylene (PTFE, 60%) was received from Shanghai Micro-technology Co., Ltd. Potassium hydroxide (KOH, 95%) was purchased from Beijing Huarong Chemical factory, China.

2.2. Preparation of porous carbon

Porous carbon was prepared according to the methods reported in literature [42,43] as follows: 1.8 g of $Zn(NO_3)_2.6H_2O$ and 0.63 g of $C_9H_6O_6$ were dissolved in 60 mL of ethanol with constant stirring for 20 min. Then, the mixture was placed in a 100 mL Teflon-lined stainless steel autoclave in an oven and heated at 120 °C for 12 h. After that, the autoclave was cooled down to room temperature and the resulting white crystal of Zn-BTC precipitate was filtered and washed with ethanol and deionized (DI) water for several times until the filtrate presented neutral. Finally, the Zn-BTC was dried in a vacuum oven at 60 °C for 3 h.

The as-prepared Zn-BTC crystals were directly carbonized in a tube furnace in vacuum atmosphere and heated to 825 °C at a rate of $10\,°C\,min^{-1}$, and then kept for 1.5 h. Then, the obtained ZnO/C composite was mixed with 3 M HNO_3 solution and boiled to remove zinc oxide, and then the sample was filtered and dried at 60 °C for 4 h, which was denoted as porous carbon (PC).

2.3. Activation of porous carbon material

The as-prepared PC was activated using KOH. Briefly, the PC was gently mixed with KOH in a ratio of 1:3 and the attained mixture was heated in a vacuum tube oven in argon atmosphere at 800 °C for 1.5 h. After that, the resultant was cooled and added into 3 M HNO_3 and boiled, followed by filtration and washing with DI water to remove residual HNO_3 until presenting natural. Then, the obtained activated porous carbon (APC) was dried at 60 °C for 4 h and used as electrode material for supercapacitors The schematic illustration of the preparation of APC is displayed in Fig. 1 and Fig. S1.