



High power supercapacitors based on hierarchically porous sheet-like nanocarbons with ionic liquid electrolytes



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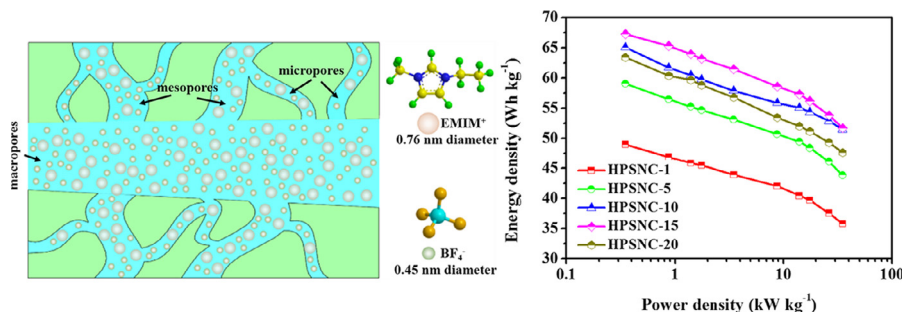
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HIGHLIGHTS

- HPSNCs were obtained by a simply large-scale preparing method.
- Hierarchically porous structure from micro-to-macro-pores are obtained.
- High power density along with high energy density are achieved.
- The HPSNC-based EDLCs show superior cycling stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Supercapacitors with ionic liquid (IL) electrolytes can reach high work voltage and accompanied high energy density, which are the critical parameters for supercapacitors' rapid development. However, supercapacitors with IL electrolytes usually suffer from low power density due to low conductivity, large ionic size and high viscosity of the electrolytes. Herein we reported hierarchically porous sheet-like nanocarbons (HPSNCs) prepared by direct activation of graphene oxide and polytetrafluoroethylene (PTFE) polymer are promising electrode materials for high power supercapacitors with also high energy density. During the activation process, the PTFE particles as a spacer that can effectively hinder the restack of graphene oxide and simultaneously transformed into sheet-like nanocarbons at high temperatures. As a result, the as-prepared samples exhibit highest surface area of $\sim 2000 \text{ m}^2 \text{ g}^{-1}$ and largest pore volume of $1.90 \text{ cm}^3 \text{ g}^{-1}$. Benefit from hierarchically porous structure from micro-to-macro-pores, which largely shorten the diffusion distance of electrolyte ions, the HPSNC electrodes show a high energy density of 51.7 Wh kg^{-1} at a power density of 35 kW kg^{-1} in symmetric supercapacitors with IL electrolyte. In addition, the HPSNC-based supercapacitors also possess an excellent cycling stability with 88% capacitance retention after 5000 cycles. Unambiguously, this work demonstrated the potential of HPSNCs for high power supercapacitors with high energy density and application in integrated energy management electronics.

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1. Introduction

Electrochemical double layer capacitors (EDLCs), one kind of supercapacitors, are new energy storage devices that store charge by electrostatic interaction between electrode/electrolyte

interfaces. Benefit from unique reversible ion adsorption, they possess high power density ($>10 \text{ kW kg}^{-1}$), fast charge/discharge rate (within seconds) and long cycle life ($>10^5$ cycles). Unfortunately, they usually suffer from relatively low energy density ($\sim 6 \text{ Wh kg}^{-1}$), which cannot meet the increasing requirements in portable electronic devices and electric vehicles [1–7]. Therefore, many strategies have been developed to improve its energy density, including (i) enhancing the physicochemical properties like specific surface area (SSA), pore structure, and the electrical conductivity, etc. of a single electrode material [8–11], (ii) structural design and chemical composite of electrode materials with multi-dimensional or micro/nano-structures [12–14], (iii) using the electrolyte with higher work voltage like ionic liquid electrolytes [15–17], and (iv) improving the manufacturing technology of the whole device [18].

Ascribing to much more electrochemical stability of IL electrolytes, the energy density of EDLCs has been considerably improved. For examples, hierarchical porous nitrogen-doped carbon in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) electrolyte possess a high energy density of 59.8 Wh kg^{-1} at a power density of 875 W kg^{-1} , while in 6 M KOH aqueous electrolyte, only exhibits an energy density of 10.3 Wh kg^{-1} at a power density 1.3 kW kg^{-1} [19]. Ma's group demonstrated that the graphene-activated carbon composite had an energy density of 6.1 Wh kg^{-1} in KOH aqueous electrolyte, while in EMIMBF₄ electrolyte, the energy density reached up to 52.2 Wh kg^{-1} [20]. Moreover, Tian et al. had reported that a renewable graphene-like nitrogen-doped carbon displayed a maximum energy density of 51 Wh kg^{-1} in the IL mixture of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI) and EMIMBF₄ electrolyte [21]. However, due to their low electrical conductivity, larger ionic size and high viscosity in nature, one typical IL electrolyte EMIMBF₄ shows $\sim 1/10$ in electrical conductivity comparing to commercial organic electrolyte tetraethylammonium tetrafluoroborate dissolved into acetonitrile solution (TEABF₄/AN), the supercapacitors with IL electrolytes usually suffer from low power density, meaning high equivalent series resistance (ESR) and rapid capacitance decline at a high current. Even through incorporating single-walled carbon nanotube with high electrical conductivity into graphene aerogel, the composited carbon aerogel electrodes in EMIMBF₄ electrolyte showed a high energy density of 65.6 Wh kg^{-1} along with a low power density of 9.1 kW kg^{-1} [22]. Since the energy density of EDLCs is far from lower than the secondary batteries like Li-ion batteries, the intrinsic advantages of high power and rapid charge-discharge must be maintained.

The power density, to some extent, is limited by the resistance to electronic transmission in porous electrodes and especially by the resistance to ionic current flow in the electrolyte [23]. There will be a confine to the small size of the pores that is related to the accessible pores to the ion from the electrolyte solution. As the average pore size becomes closer to the ion size, the electroadsorption kinetics slows down [24–25]. And the increasing resistance is another factor that is responsible for the commonly observed decline in rate-capability as the total surface area is increased, particularly at large surface area. Hence, it is very important to meet the balance between the pore size and the ion size of the electrolyte that are suitable for EDLCs. Alternatively, developing one kind of electrode material with hierarchical pore structure and high ion-accessible surface area that is helpful to ion transportation is probably to meet the demands of both high energy and high power for EDLCs. The previous works implied that hierarchical porosity design, large pore volume and wide pore size distribution could efficiently improve the ion-accessible surface area and hence leading to high capacitance [8,26–27]. However, these EDLCs in IL electrolytes greatly improve energy density at the sacrifice of high power density. And increasing energy without com-

promising power is still the topical challenge for supercapacitors [28].

Herein, we present a simply scalable approach to prepare hierarchically porous sheet-like nanocarbons based on direct KOH activation of graphene oxide and PTFE polymer. The obtained hierarchical porous carbon exhibits relatively high SSA ($\sim 2000 \text{ m}^2 \text{ g}^{-1}$), good electric conductivity and excellent electrochemical performance. Moreover, the optimized HPSNCs show abundant of micropores, mesopores and macropores that are beneficial to realize both high energy density and power density. The energy density reaches up to 51.7 Wh kg^{-1} with an extremely high power density of 35 kW kg^{-1} for HPSNC-based symmetric EDLCs with EMIMBF₄ electrolyte. In addition, the symmetrical EDLCs also possess long-term cycling stability with 88% retention after 5000 cycles. These observations unambiguously demonstrate the capability of simply large-scale processed HPSNCs as high-performance electrode materials for EDLCs with IL electrolytes, which opens up a new approach for high-performance energy storage.

2. Experimental section

2.1. Materials

Graphite powders (8000 mesh) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) ionic liquid electrolyte were purchased from Aladdin Industrial Corporation (Shanghai, China). Concentrated sulfuric acid (H₂SO₄), sodium nitrate (NaNO₃), potassium permanganate (KMnO₄) and hydrogen peroxide (H₂O₂, 30 wt %), hydrochloric acid (HCl) and potassium hydroxide (KOH) were analytical pure grade, which were purchased from Kelong Chemical Reagents Company (Chengdu, China) without further purification. Polytetrafluoroethylene (PTFE, 60 wt% dispersion in water) was purchased from Dakin (Japan). The polypropylene paper separator with a thickness of $20 \mu\text{m}$ was purchased from NKK Corporation.

2.2. Synthesis of HPSNCs

GO was synthesized by a modified Hummers method [29] and the detailed process is given in Supporting information (SI, Experimental S1). For preparing HPSNCs, in a typical procedure, 50 mg GO was uniformly dispersed into 50 ml deionized water by ultrasonic vibration for 2 h. And then, PTFE emulsion with a mass ratio of 60 wt% was weighed based on the weight ratio of GO to PTFE (from 1:1 to 1:20) and mixed with 20 ml deionized water under magnetic stirred for 5 min. Then, a certain amount of KOH with a weight ratio of 1:6 (KOH to GO and PTFE) was added into the above-obtained solutions and magnetic stirred for 15 min. After GO solution was added, the mixed solution was further agitated for 2 h. Afterwards, the plastic breaker with the solutions was transferred to a water bath kept at $60 \text{ }^\circ\text{C}$ under continually stirring until obtained solid mixture. After that, the solid mixtures were transferred into the tube furnace ($\Phi 80 \times 1000 \text{ mm}$, BTF-1400C, Anhui BEQ Technology CO., LTD, China) and firstly kept constant at $400 \text{ }^\circ\text{C}$ for 2 h and followed by reacted at $800 \text{ }^\circ\text{C}$ for 2 h under Ar atmosphere, and then immerse into enough 2 M HCl aqueous solution for 12 h. Finally, the mixture was washed with deionized water under vacuum filtration and desiccation at $80 \text{ }^\circ\text{C}$ for 12 h and the obtained samples were denoted as HPSNC-1, HPSNC-5, HPSNC-10, HPSNC-15, and HPSNC-20, respectively.

2.3. Sample characterizations

The morphologies of the as-prepared samples were characterized by a FEI QUANTA FEG 250 scanning electron microscopy

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