



Tuning the morphology and structure of nanocarbons with activating agents for ultrafast ionic liquid-based supercapacitors



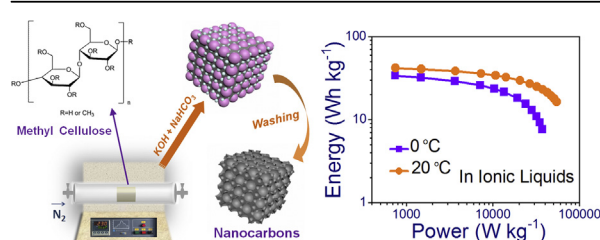
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HIGHLIGHTS

- The morphology and structure of nanocarbons can be tuned by activating agents.
- The nanocarbons with sheet-like morphology has a thickness down to ~4 nm.
- Nanocarbons are able to get extreme rate capability in ionic liquid at 0 and 20 °C.
- The facile precursor-synthesis route is promising for large-scale energy storage.

GRAPHICAL ABSTRACT



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ABSTRACT

The increasing demand for supercapacitors with high energy and power density has attracted extensive attention in designing advanced carbon materials with high accessible surface area, hierarchical porosity, and 2D/3D morphology. Here, we report a new approach to tune the morphology and structure of the nanocarbons by using methyl cellulose as the precursor. Due to the varying effect of different activating agents, the interconnected sheet-like carbon with a high surface area of up to 2285 m² g⁻¹ and a thickness down to ~4 nm can be obtained. These important characteristics make the nanocarbons demonstrate a high capacitance of 144 F g⁻¹ at 1 A g⁻¹ and 20 °C, and an excellent capacitance retention ratio of 64% at 100 A g⁻¹ in ionic liquid. Because of the high fraction of meso/macropores for nanocarbons, an outstanding capacitance of 116 F g⁻¹ can be achieved at 0 °C, with a high capacitance retention ratio of 39% at 100 A g⁻¹. A high energy of 16–17 and 9–10 W h kg⁻¹ can be maintained at 20 and 0 °C when the supercapacitor is charged in less than 1s. The excellent electrochemical response of nanocarbons suggests that the proposed preparation process is promising for developing advanced carbon electrodes.

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1. Introduction

Energy storage and conversion is one of the great challenges in

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modern society, which can solve the environmental issue and energy security [1,2]. Among them, electrochemical double layer capacitors, also known as supercapacitors, have attracted extensive attention due to their greater power density and longer life spans, which can be applied in the high power situations [3–6]. Compared with batteries, the energy density of supercapacitors is much lower [7,8]. However, more and more occasions require energy to be

stored efficiently, quickly, and inexpensive with a high energy density [6]. Therefore, substantial improvements in the energy of supercapacitors should be made to satisfy modern requirements. Carbon material is the dominant electrode for supercapacitors [9], and the capacitance mainly arises from the charge accumulation at the electrode-electrolyte interface [9,10]. It is suggested that the use of ionic liquid can extend the potential window of supercapacitors [11], giving a pathway to increase the energy density, since the energy density is proportional to the square of voltage [12,13]. In the case of ionic liquid media, the surface area and porous structure of carbons are the key parameters to affect the capacitance due to the viscosity of ionic liquid and the large size of ion [9,14,15]. Therefore, there is a critical demand for designing advanced nanocarbon electrodes for highly efficient energy storage in ionic liquid electrolyte.

Current technologies allow for synthesis of various types of carbon materials, including activated carbons [16], template carbons [17,18], carbide derived carbons [19,20], carbon nanotubes [21], and graphene [4,22,23], with different morphologies, porosities, and structures. Template carbonization is an efficient route to control the surface area and pore structure, however, the complicated synthesis process and rigorous washing procedure limited the large-scale production [24]. By removing the non-carbon elements in the carbide, the remaining carbon architecture (named as carbide derived carbon) possesses high surface area with tuned pore sizes. The main drawback for carbide derived carbon is the use of toxic gases, such as chlorine [19]. Some carbon nanotube, graphene, and their hybrids exhibit good pore connectivity and high surface area, but they need either special designed strategy or high-cost fabrication [4,21–23]. The traditional activation method is widely used for the production of activated carbons, which has been well-established for large-scale production [13]. However, the obtained activated carbons are dominant microporosity with tortuous structure, hindering smooth ion transport, and leading to moderate specific capacitance and poor rate capability [25]. Therefore, to overcome the drawbacks of activated carbons is one of the effective ways to get low-cost and high-performance electrodes.

As pointed out above, synthesis of carbons by using activation method is promising for large-scale production. The main challenge is to find suitable precursor and activating agent. Activation technique, including physical and chemical activations, is widely used to prepare activated carbons [26–29]. The chemical activation involves the mixing of the precursors and reactive chemicals (such as KOH, ZnCl₂, H₃PO₄) [30–33], and the heating of the mixtures in an inert environment. Compared with physical activation, which involves the gasification of carbons with the aid of oxidizing gasifying agents (H₂O, CO₂, etc.), the chemical activation needs lower reaction temperature and shorter processing time, but more washing procedures [28,29]. Different activating agents and carbon sources would play different roles in the activation process, leading to different porosity and morphology. In order to control the porosity and morphology of nanocarbons, we select methyl cellulose as the precursor, and three approaches have been used to solve this problem. One approach is based on the fabrication of carbon nanosheets by KOH activation, which can create a 2D layer structure with high surface area (up to 2285 m² g⁻¹) and rich micro/mesopores. However, the carbon yield is usually low for KOH activation. An alternative approach is adopted to fabricate 3D interconnected sheet-like carbons with higher carbon yield by NaHCO₃ activation. Unfortunately, the as-prepared sheet-like carbons have a relatively lower surface area (~1100 m² g⁻¹). To combine the advantages of these two approaches, the activation was carried out by using both KOH and NaHCO₃, leading to the fabrication of highly sheet-like carbons with high surface area (up

to 2182 m² g⁻¹) and moderate carbon yield. For conventional, the Methyl Cellulose derived Carbons were designated as MCC-x-y, where x indicates the mass ratio of sodium bicarbonate to methyl cellulose, and y represents the mass ratio of potassium hydroxide to methyl cellulose. We envisage that the nanocarbon materials with these characteristics are expected to give multiple synergistic effects on enhancing the electrochemical performance in a conventional ionic liquid electrolyte at near or below room temperature. The maximum energy and power density is as high as 44 Wh kg⁻¹/26 Wh L⁻¹ and 282 kW kg⁻¹/141 kW L⁻¹ at room temperature, while the maximum energy and power density is 35 Wh kg⁻¹/18 Wh L⁻¹ and 159 kW kg⁻¹/80 kW L⁻¹ at 0 °C.

2. Experimental

2.1. Material synthesis

The methyl cellulose was thoroughly mixed with sodium bicarbonate and/or potassium hydroxide in different mass ratios. The mixture was heated to 200 °C for 2 h, and then heated up to 800 °C for 4 h under nitrogen atmosphere with a heating rate of 3 °C min⁻¹. The MCC material was liberated by washing with diluted hydrochloric acid and/or deionized water to neutrality.

2.2. Material characterization

X-ray diffraction (XRD) data were collected by using a Bruker D8 Advance powder diffractometer with Cu-K α radiation operated from 2 θ = 10–60°. Scanning electron microscope (SEM) and transmission electron microscope (TEM) tests were performed using Hitachi S-4800 operated at 10 kV and Tecnai G2 F20 operated at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was obtained on a Thermo ESCALAB 250 XI spectrometer. The Raman spectroscopy was recorded on a microscopic confocal Raman spectrometer (Lab RAM HR800) with an excitation laser wavelength of 532 nm, an effective laser power on the sample of 5 mW, and a spot size of 1 μ m. Nitrogen adsorption-desorption analysis was investigated with a Micromeritics 3 FlexTM surface characterization analyzer at 77 K using nitrogen as the adsorbate. Thermogravimetric analysis was performed using Mettler TG/DSC 2 HT/1600 from 20 °C to 1000 °C with a heating rate of 5 °C min⁻¹ under N₂ atmosphere. The packing densities of the carbon materials were evaluated by pressing a given amount of sample in a mold at a pressure of 10 MPa using a cylindrical rod. The measurements were repeated three times with an error smaller than 3%.

2.3. Electrochemical evaluation

The electrochemical evaluation of the MCCs was performed in ionic liquid electrolyte using a two-electrode configuration. 80 wt% carbon material, 10 wt% super P, 10 wt% poly(vinylidene difluoride) (PVDF) was mixed in *N*-methyl-2-pyrrolidinone. The slurry was coated on stainless steel foil and then dried at 100 °C overnight in a vacuum oven. The mass loading of carbon in the electrode was ~2 mg cm⁻². The electrode thickness is in the range of 100–200 μ m. CR2032 coin cells with two symmetrical carbon electrodes separated by a Celgard 3501 separator were assembled inside an Ar-filled glovebox (<0.1 ppm of both O₂ and H₂O). 1-ethyl-3-methylimidazolium bis [(trifluoromethyl) sulfonyl] imide (EMIM TFSI, Aladdin, 97%) was selected as the electrolyte. The viscosity of the used ionic liquid is about 40 mPa s at 20 °C [34]. In order to test the electrochemical stability of the used ionic liquid, the voltage hold test was carried out. In brief, the cell was applied to a constant voltage of 3 V for up to 500 h. Every 10 h, three galvanostatic charge-discharge cycles were performed between 0 and 3 V using a

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