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Research article

Wrinkled porous carbon nanosheets from methylnaphthalene oil for high-performance supercapacitors

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ABSTRACT

Long and tortuous pores in granular porous carbons for supercapacitors result in inferior rate capability and low capacitance. Sheet-like porous carbons with short pore length show potential applications as supercapacitor electrode materials. Herein, wrinkled porous carbon nanosheets (WPCNSs) were prepared from methylnaphthalene oil using $CaCO_3$ template coupled with in-situ KOH activation strategy. The WPCNS features wrinkled sheet-like architecture with abundant short pores. The WPCNS electrode shows a high capacitance of 286 F g^{-1} at 0.05 A g^{-1}, a good rate capability of 201 F g^{-1} at 20 A g^{-1}, and an outstanding cycle stability with 98.4% initial capacitance after 7000 cycles in KOH electrolyte. This work provides a feasible method to prepare WPCNSs from aromatic liquid carbon precursors using low-cost $CaCO_3$ as template for high-performance supercapacitors.

1. Introduction

Supercapacitors have received considerable attention due to their reliable cycle life, short charge time, and high power density [1–3]. The special characteristics of supercapacitors impel them to be applied in electric vehicles, wearable electronic devices, and smart grids [4–7]. As known, the energy storage mechanism of supercapacitors is based on the ion adsorption/desorption at the electrolyte/electrode interface and Faradaic reactions. The electrode materials play a key role for the overall properties of supercapacitor [8]. The electrode materials include metal oxides [9,10], carbon materials [11–13] and conducting polymers [14,15], of which, carbon materials are the main ones used in commercial supercapacitors, especially granular porous carbons. Yet, the long and tortuous pores in granular porous carbons are inaccessible to the electrolyte ions, resulting in poor rate performance and low capacitance [16–20]. Recently, two dimensional carbon-based materials and other two dimensional graphene analogues emerge as novel materials for supercapacitors [21,22]. Among them, two dimensional carbon nanosheets, including graphene and graphene oxide have been considered as the next-generation electrode materials of supercapacitors because of its good conductivity and large theoretical surface area [23–26]. Yet, carbon nanosheets tend to agglomerate together in the fabrication process of electrode, resulting in the reduced surface area and specific capacitance [27]. It is necessary to prepare carbon nanosheets with wrinkles to prevent their agglomeration from low-cost carbon sources for commercial supercapacitors.

There are plenty of industrial by-products with high carbon content, e.g. coal tar, coal tar pitch, petroleum asphalt, methylbenzene. These by-products can be used as carbon sources for advanced electrode materials to solve the ever-increasing environmental issues [28–32]. In general, the template strategies have been widely used to prepare porous carbons and carbon nanosheets, of which the used templates include nano-MgO, $Mg(OH)_2$, ZnO, etc. [33–38]. However, these templates are relatively expensive, limiting their commercial applications. Therefore, it is necessary to seek cheap template to reduce the production cost of porous carbon and carbon nanosheets. As we all know, $CaCO_3$ is cheap and abundant, which can be used as the template candidate to prepare porous carbons and carbon nanosheets. Huang et al. synthesized graphene film by using $CaCO_3$ as template, showing high rate capability [39]. Kim et al. designed interconnected hierarchical porous carbon by using $CaCO_3$ as template, exhibiting good cycle performance [40]. The above results demonstrate that $CaCO_3$ is

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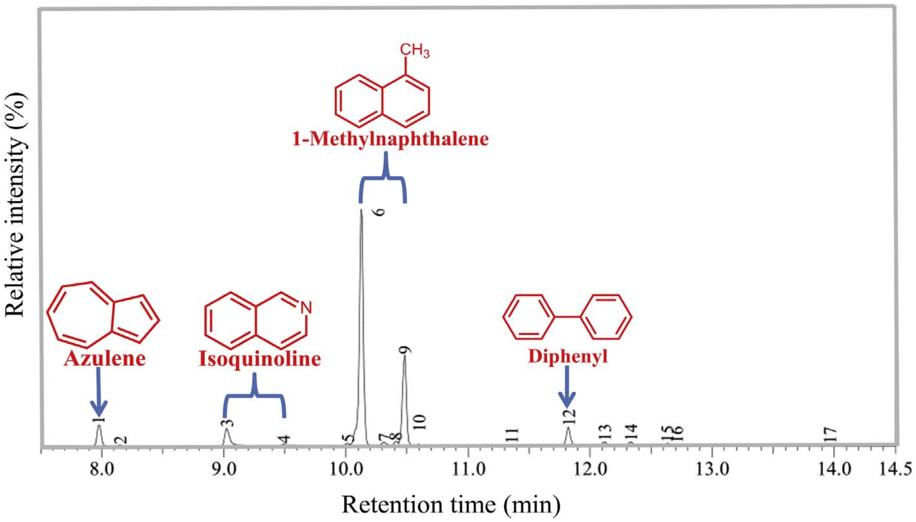

Fig. 1. GC-MS chromatogram of methylnaphthalene oil.

one of the good template candidates for the preparation of carbon nanosheets as the advanced electrode materials for high-performance supercapacitors.

Herein, a feasible method is suggested for the first time to prepare wrinkled porous carbon nanosheets (WPCNSs) from methylnaphthalene oil by coupling $CaCO_3$ template with in-situ KOH activation. The as-prepared WPCNSs possess abundant micropores and some small mesopores with short pore lengths. These short pores are favorable for ion transport and the large nanosheets are beneficial for electron conduction, resulting in outstanding rate capability and high capacitance. So far, works on the synthesis of such unique WPCNSs directly from methylnaphthalene oil have not been reported.

2. Experimental

2.1. Material preparation

Methylnaphthalene oil was received from Maanshan Iron & Steel Co. Ltd. of China. $CaCO_3$ and KOH were purchased from Ruicheng Xintai Nano-Materials Technology Co. Ltd. and Sinopharm Co. Ltd., respectively. Typically, 12 g KOH was ground in a mortar and mixed with 6 g $CaCO_3$. The resultant mixture was poured into a beaker containing 6 g methylnaphthalene oil, and the mixture was homogenized to obtain the reactants. The reactants were evenly spread in a corundum boat, followed by being heated to 550 °C at 5 °C min^{-1} in the tubular furnace, and held for 30 min in Ar atmosphere, then heated to 900 °C for 60 min. The product was washed with 2 M HCl solution and distilled water to remove the impurities. After being dried, the as-prepared sample is named as $WPCNS_{12}$, where the subscript 12 stands for the mass of KOH (g). Similarly, when the mass of KOH is 8 g, 10 g and 14 g, the as-prepared sample is termed as $WPCNS_8$, $WPCNS_{10}$ and $WPCNS_{14}$, respectively, with other conditions remaining constant. The yield of $WPCNS_8$, $WPCNS_{10}$, $WPCNS_{12}$ and $WPCNS_{14}$ is 1.004 g, 0.997 g, 0.984 g and 0.873 g, respectively.

2.2. Material characterization

The components of methylnaphthalene oil were investigated on a gas chromatography-mass spectrometer (GC-MS). The WPCNSs were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffractometer (XRD), fourier transformed infrared spectrometer (FTIR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, thermal gravimetric analysis (TGA), N_2 adsorption-desorption technique. Please see Characterization Section in Supporting information for details.

2.3. Electrochemical measurement

A slurry with 88.0 wt% WPCNSs and 12.0 wt% polytetrafluoroethylene was made into round carbon films (12 mm in diameter), and then dried at 110 °C for 2 h under vacuum. The mass loading of active materials in the WPCNS electrodes is ca. 2.5 mg cm^{-2}. The round carbon films were pressed onto nickel foam to make the electrodes. Then, the electrodes were soaked in 6 M KOH solution for 2 h under vacuum condition. The symmetric supercapacitor was fabricated using the soaked electrodes. The tests of cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impendence spectroscopy (EIS) was conducted on the electrochemical workstation (CHI760C, China), supercapacitance test system (SCTs, Arbin Instruments, USA) and solartron impedance analyzer (Solartron Analytical, SI 1260, UK), respectively.

The gravimetric capacitance (C, F g^{-1}) of the single WPCNS electrode was obtained based on Eq. (1).

$$C = \frac{4I}{m\frac{\Delta V}{\Delta t}} \tag{1}$$

where I (A) is the discharge current, $\frac{\Delta V}{\Delta t}$ (V s^{-1}) represents the slope of discharge curve, and m (g) is the total mass of the WPCNSs in both electrodes.

The energy density (E, Wh kg^{-1}) of WPCNS electrodes was obtained based on Eq. (2).

$$E = \frac{1}{2 \times 4 \times 3.6} CV^2 \tag{2}$$

where V (V) means the usable voltage.

The power density (P, W kg^{-1}) of WPCNS electrodes was obtained based on Eq. (3).

$$P = \frac{E}{\Delta t_d} \tag{3}$$

where Δt_d (h) stands for the discharge time.

3. Results and discussion

Methylnaphthalene oil is employed as carbon source to synthesize WPCNSs and its components were identified by GC-MS. As shown in Fig. 1, there are four main compounds in methylnaphthalene oil, e.g. 1-methylnaphthalene (79.45%), isoquinoline (5.10%), azulene (4.93%)