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Superior supercapacitive performance of hollow activated carbon nanomesh with hierarchical structure derived from poplar catkins

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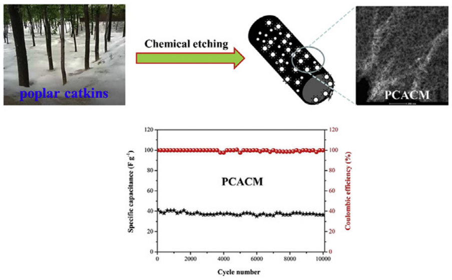
HIGHLIGHTS

- Hollow active carbon nanomesh (PCACM) is derived from biowaste-poplar catkins.
- Hierarchical porous structure is constructed in PCACM architecture.
- PCACM achieves excellent supercapacitive performances.

GRAPHICAL ABSTRACT



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ABSTRACT

The hollow activated carbon nanomesh (PCACM) with a hierarchical porous structure is derived from biowaste-poplar catkins by in-situ calcination etching with $Ni(NO_3)_2 \cdot 6H_2O$ and KOH in N_2 flow combined with an acid dissolution technique. This procedure not only inherits the natural tube morphology of poplar catkins, but also generates a fascinating nanomesh structure on the walls. PCACM possesses a large specific surface area ($S_{BET} = 1893.0$ m^2 g^{-1}) and high total pore volume ($V_p = 1.495$ cm^3 g^{-1}), and displays an exciting meso-macoporous structure with a concentrated pore size distribution of 4.53 nm. The specific capacitance of PCACM is as high as 314.6 F g^{-1} at 1.0 A g^{-1} when used as the electrode materials for supercapacitor. Furthermore, the symmetric supercapacitor of PCACM with 1.0 M Na_2SO_4 solution as the electrolyte displays a high energy density of 20.86 Wh kg^{-1} at a power density of 180.13 W kg^{-1} within a wide voltage rage of 0–1.8 V, which is comparable or even obviously higher than those of other biomass derived carbon reported. It is noteworthy that PCACM also exhibits superior cycling stability and coulombic efficiency. The excellent electrochemical behaviors enable PCACM to be a promising electrode material for supercapacitors.

1. Introduction

With the fast-growing energy demand in consumer electronics, electric vehicles, pulsing techniques as well as industrial power and energy management, great efforts have been made to exploit

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various energy-related devices and to improve the efficiency of conversion and storage. Among the various energy storage devices, supercapacitors are considered as one of the potential energy storage systems due to their outstanding advantages including high power density, long cycle life, rapid charging discharging rate, simple principles and fast dynamics of charge propagation [1–3]. Depending on the energy storage mechanism, there are two types of supercapacitors: 1) The most commonly known ones are originally called electrical double layer capacitors (EDLC), which store and release energy based on electrostatic charge diffusion and accumulation in the double layer formed at the surface of inert electrodes; and 2) The other category of capacitor materials are the ones which store energy through reversible surface Faradaic redox reactions at the electrode/electrolyte interface [3,4]. It is known that the active electrode material is one of the most important factors to affect the electrochemical performance of supercapacitor. So far, various materials have been used as supercapacitor electrode materials, such as metal or metal alloys [5–7], polymers [8], metal oxides [9–16], metal sulfides [17,18], carbon based materials [19–39], and their composites [40–45] reported recently. Among these materials, carbon based ones exhibit highly stable reversible electrical energy storage capacity and high power density in EDLC ascribed the high specific surface area, high conductivity, suitable pore size distribution, and chemical stability.

As for carbon based materials, biomass is an environmentally friendly and renewable resource with abundant availability to sever as a cost-effective carbon precursor. Till now, various natural biomass materials, such as cellulose [29], pomelo peel [31], cotton [21,46], kenaf [47], bamboo shells [48], seed shells [49], and poplar catkins [50–52] have been used to prepare porous carbon. This not only greatly reduces the cost, but also inherits both the structural flexibility and chemical diversity of the natural resources. Even so, the specific surface area of biomass carbon materials is much lower than that of the others owing to the deficiency of micropores and small-diameter mesopores. Therefore, some chemical activation strategies have been used to adjust their textural structures [53–55]. The resulting porous structures could effectively promote the contact between the electrolytes and electrode material, and shorten the diffusion pathway of ions through the porous sheets, resulting in an excellent specific capacitance and a low capacitance loss. However, single chemical activation is not easy to control the geometry and size of the pores. In addition, the pore numbers are also limited. Hence, it is urgent to form a hierarchical structure with abundant meso-macopores, which could provide a high density of ion diffusion channels, facilitate charge storage and transport at high rates for high-performance energy storage devices.

In 2014, Wei [52] prepared carbon microtubes from poplar catkins by chemical activation with $ZnCl_2$, which yield a specific capacitance of 206 F g^{-1} and an energy density of 7.5 W h kg^{-1} when used as electrode material for supercapacitor. In this work, the hollow activated carbon nanomesh (PCACM) is derived from poplar catkins using a two-steps chemical activation procedure for the first time. The inherited tube morphology of poplar catkins and the generated abundant pores construct an admirably hierarchical structure in PCACM, which enhances the electrochemical stability and ion transport network, and improves the electrochemical behaviors. Eventually, as a supercapacitor electrode, PCACM exhibits much more excellent electrochemical performance than carbon produced by carbonizing poplar catkins without etching (PCC) and the ones etched only with KOH (PCAC) or $Ni(NO_3)_2 \cdot 6H_2O$ ($PCAC^{\#}$). Furthermore, its specific energy density is comparable or even obviously higher than those of biomass derived carbon reported. This enables PCACM to be a promising electrode material for high-performance supercapacitors.

2. Experiments

2.1. Preparation of the samples

The pretreatment of poplar catkins which were collected from Zhengzhou city, P. R. China in April and May, was as follows: Firstly, a certain amount of poplar catkins were dispersed into absolute ethanol and stirred violently for about 3 h. Then, they were washed with DI water, and dealt with HNO_3 solution (1.0 mol L^{-1}) for 12 h to remove the seeds and impurities. Finally, the solid was filtered, washed with DI water and dried at 80 °C overnight.

Fig. 1 shows the schematic illustration for the preparation of hollow carbon nanomesh from poplar catkins (PCACM). Firstly, poplar catkins were calcined and in-situ etched with KOH and $Ni(NO_3)_2$ in nitrogen atmosphere. Some pores would be produced due to the release of the gases (NO_2, H_2, CO_2, and CO) produced in the reactions shown in Eqs. (1)–(5). Then, the resulting K and NiO reacted with hydrochloric acid shown in Eqs. (6)–(8) and left the nanomesh structure.

In brief, 2 g of dried poplar catkins was immersed with 10 wt% $Ni(NO_3)_2 \cdot 6H_2O$ ethanol solution at room temperature and followed by evaporating at 30 °C in an air oven. After such process was repeated three times, the obtained solid was calcined at 600 °C for 4 h with a ramp rate of 2 °C min^{-1} under nitrogen atmosphere in a tubular furnace. The products were immersed with KOH solution (2.0 mol L^{-1}) with the mass ratio of 4: 1 (KOH: the resulting solids) and dried at 80 °C. Then, it was activated at 800 °C for 1 h with a ramp rate of 3 °C min^{-1} under nitrogen atmosphere in a tubular furnace. The products were dispersed into HCl solution (1.0 mol L^{-1}) to consume K, NiO, and the residual KOH, washed with DI water and dried at 110 °C.

$$2Ni(NO_3)_2 \rightarrow 2NiO + 2NO_2 \tag{1}$$

$$C + 6KOH \rightarrow 2K_2CO_3 + 2K + 3H_2 \tag{2}$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \tag{3}$$

$$K_2CO_3 + 2C \rightarrow 2K + 3CO \tag{4}$$

$$K_2O + C \rightarrow 2K + 3CO \tag{5}$$

$$2K + 2H_2O \rightarrow 2KOH + H_2 \tag{6}$$

$$KOH + HCl \rightarrow KCl + H_2O \tag{7}$$

$$NiO + 2HCl \rightarrow NiCl_2 + H_2O \tag{8}$$

For comparison, the dried poplar catkins were carbonized at 600 °C for 4 h with a ramp rate of 2 °C min^{-1} under nitrogen atmosphere and the resulting material was denoted as PCC. Furthermore, PCC was only activated with KOH, which was similar to that for PCACM without the immersion process of $Ni(NO_3)_2 \cdot 6H_2O$. The obtained material was denoted as PCAC. In addition, the dried poplar catkins was immersed with $Ni(NO_3)_2 \cdot 6H_2O$ ethanol solution at room temperature, evaporated at 30 °C, calcined at 600 °C, treated with HCl solution, washed with DI water, and dried at 110 °C. This was same to that for PCACM without the immersion process of KOH and the further calcination at 800 °C. The obtained material was denoted as $PCAC^{\#}$.

2.2. Characterization

The textural parameters of the samples were obtained from nitrogen adsorption-desorption isotherms at −196 °C using a