



Synthesis of layered microporous carbons from coal tar by directing, space-confinement and self-sacrificed template strategy for supercapacitors



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ABSTRACT

It is a challenge to synthesize low-cost carbon materials with abundant pores by a simple route for supercapacitors. Herein, layered microporous carbons (LMPCs) with the specific surface area up to $1865 \text{ m}^2 \text{ g}^{-1}$ are fabricated from coal tar and melamine via a directing, space-confinement and self-sacrificed template strategy coupled with *in-situ* KOH activation. The button-type supercapacitor fabricated from LMPCs exhibits a high specific capacitance of 274 F g^{-1} at 0.05 A g^{-1} , a good rate performance of 191 F g^{-1} at 20 A g^{-1} and a superior cycle stability with 98.8% capacitance retention after 10000 cycles. This work presents a facile strategy for mass production of LMPCs from liquid polycyclic hydrocarbon molecules for supercapacitors.

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1. Introduction

Nowadays, more and more people are aware of the importance of renewable energy sources owing to the fast exhaustion of fossil sources. Conforming to this trend of development, there is an increased demand for energy storage device with advanced performance for the storage of renewable energy, such as wind power and solar energy. As a kind of promising energy storage device, supercapacitor with long life and rapid charge-discharge rates has attracted a lot of attention [1]. As the crucial contributors of energy storage device, the electrode materials of supercapacitors are drawing plenty of research interest [2–6]. In recent years, carbon materials with various kinds of nanostructures have been fabricated to enhance the overall performance of supercapacitors. The typical examples include carbon nanotubes/nanorods [7–10], nanofibers [11,12], graphene [13,14], nanosheets [15,16], nanospheres [17,18] and nanocages [19,20]. However, some of these carbon materials frequently suffer from high cost and complex synthesis process [21]. Alternatively, it is valuable to prepare porous carbon materials with low cost and good electrochemical performance for supercapacitor applications.

Porous carbons from fossil fuel including petroleum or coal, have been applied in supercapacitors due to low-cost carbon sources and simple synthesis methods, as well as their large surface area for abundant ion adsorption and desorption [22,23].

Coal tar is one of the cheap and abundant chemical by-products in coal coking industry. Over 20 million tons of coal tar is produced in China every year. Coal tar is a mixture of organic matters enriched with liquid polycyclic aromatic hydrocarbons. These liquid polycyclic aromatic hydrocarbons are active and easy to be polymerized and aromatized to form thin sheets during the heat treatment process [24]. These thin sheets are able to be transformed into high-performance carbon materials after being annealed at high temperature. Therefore, it is possible to develop a facile route to prepare high value-added carbon materials from coal tar for supercapacitor applications.

We herein report a directing, space-confinement and self-sacrificed template strategy coupled with *in-situ* KOH activation to synthesize layered microporous carbons (LMPCs) from coal tar and melamine. In the heating process, sheet-like melamine and graphitic carbon nitride ($g\text{-C}_3\text{N}_4$, intermediate product derived from the polymerization of melamine) functions as directing, space-confinement templates, respectively. Due to the sheet-like morphology of melamine and $g\text{-C}_3\text{N}_4$ [25–27], polymerization reactions of liquid polycyclic aromatic hydrocarbon molecules in coal tar are occurred on the surface of templates or in the layered

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space of the neighboring sheet-like templates. Finally, LMPCs are formed after high temperature annealing. Thanks to complete decomposition of $g\text{-C}_3\text{N}_4$ template at 670°C , this strategy reduces the dosage of hydrochloric acid used because there is no need to remove $g\text{-C}_3\text{N}_4$ template. The as-obtained LMPCs feature layered morphology with abundant micropores. The layered morphology with opened pores could not only shorten ion diffusion distance, but also favor good accessibility between electrolyte and carbon materials. And the abundant micropores provide large surface area for ion adsorption and desorption. Benefiting from the synergistic structural characteristics, LMPCs show enhanced electrochemical properties as supercapacitor electrode materials. To our knowledge, there is no report about the preparation of LMPCs from coal tar *via* the directing, space-confinement and self-sacrificed template strategy coupled with *in-situ* chemical activation for supercapacitors.

2. Experimental

2.1. Preparation of LMPCs

Coal tar was obtained from Maanshan Iron & Steel Co. Ltd. of China; melamine was from Aladdin Co. Ltd., and KOH was purchased from Sinopharm Co. Ltd. Typically, 3.0 g melamine and 12.0 g KOH were pulverized, respectively. Then, they were mixed with 6.0 g coal tar to obtain the mixture. Subsequently, the resultant mixture was put in a porcelain boat, which was placed in a horizontal tubular furnace. In 60 mL min^{-1} argon gas flow, the resultant mixture was heated to 800°C at 5°C min^{-1} and held for 60 min, followed by cooling to room temperature to obtain black solid. Next, the black solid was washed with 2 M hydrochloric acid and distilled water for several times to obtain LMPCs. Finally, LMPCs were dried in a drying oven at 110°C for 12 h. The as-made LMPCs were named as $\text{LMPC}_{800\text{-Ar}}$, where the subscript 800 represents the heat treatment temperature, and Ar is the shielding gas. Similarly, with other conditions remaining unchanged, the LMPCs made in nitrogen atmosphere at 800°C were called as $\text{LMPC}_{800\text{-N}_2}$, and that obtained in argon atmosphere at 900°C were called as $\text{LMPC}_{900\text{-Ar}}$. Besides, the LMPCs made from 6.0 g coal tar, 6.0 g melamine and 12.0 g KOH at 800°C in nitrogen atmosphere were called as $\text{LMPC}_{800\text{-N}_2}^*$. The carbon materials obtained from coal tar, $\text{Mg}(\text{OH})_2$ and KOH at 800°C in argon atmosphere was called as LMPC_R , in which the mass ratio of coal tar and KOH is the same as that in $\text{LMPC}_{800\text{-Ar}}$.

2.2. Characterization

The $g\text{-C}_3\text{N}_4$ and intermediate product were analyzed by an X-ray diffractometer (XRD, Ultima IV, Japan), Fourier transformed infrared spectrometer (FTIR, Nicolet 6700, USA) and thermogravimetric analyzer (TGA, DTG-60, Japan). The microstructures of LMPCs were investigated by scanning electron microscopy (SEM, NanoSEM 430, USA) and transmission electron microscopy (TEM, JEOL-2100, Japan). Nitrogen adsorption-desorption isotherms of LMPCs were collected at -196°C on an Autosorb-IQ system (Quantachrome, USA). The specific surface area (S_{BET}) of LMPCs was calculated by the traditional Brunauer-Emmett-Teller (BET) method. The pore diameter distribution was analyzed from the adsorption branches of the isotherms using the density functional theory (DFT) method. The total pore volume (V_t) was estimated at a relative pressure (P/P_0) of 0.99. The micropore volume (V_{mic}) was obtained using the t-plot method. The average pore diameter (D_{ap}) of LMPCs was calculated according to the equation of $D_{\text{ap}} = 4V_t/S_{\text{BET}}$. The atom binding states in LMPCs were examined by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB250, USA).

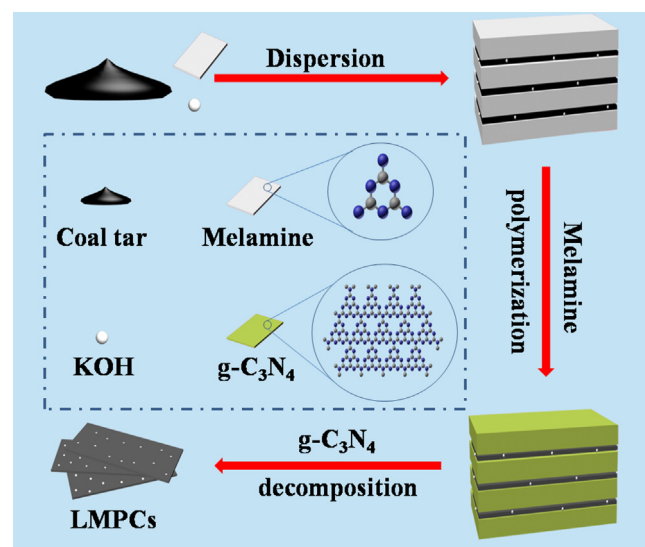


Fig. 1. Illustration of the preparation process for LMPCs.

2.3. Fabrication of supercapacitor electrodes

Firstly, LMPCs and polytetrafluoroethylene at mass ratio of 90–10 were mixed by adding deionized water as solvent. Then, the resultant mixture was rolled into thin film and further cut into several round films (12 mm in diameter, 0.12–0.14 mm in thickness). Subsequently, the round films were dried in vacuum oven at 110°C for 4 h. After that, they were pressed onto nickel foams to obtain supercapacitor electrodes, which were then soaked in 6 M KOH electrolyte under vacuum for 60 min. The button-type supercapacitor was made from a pair of electrodes separated by a polypropylene membrane. The carbon loading in a single $\text{LMPC}_{800\text{-N}_2}$ electrode, $\text{LMPC}_{800\text{-Ar}}$ electrode and $\text{LMPC}_{900\text{-Ar}}$ electrode is 7.94 mg cm^{-2} , 4.38 mg cm^{-2} and 2.85 mg cm^{-2} , respectively.

2.4. Electrochemical measurement

All the tests were performed in a two-electrode cell in 6 M KOH aqueous electrolyte. The cyclic voltammetry (CV) tests were measured on a CHI 760C electrochemical workstation (Shanghai Chenhua Instrument Company, China). The galvanostatic charge-discharge (GCD) measurements were conducted on a supercapacitance test system (SCTs, Arbin Instruments, USA) and the electrochemical impedance spectroscopy (EIS) measurement was carried out on a Solartron impedance analyzer (Solartron Analytical, SI 1260, UK).

The gravimetric capacitance of the single LMPC electrode (C , F g^{-1}) was calculated from the galvanostatic discharge profiles based on the following equation:

$$C = \frac{4I}{m \frac{\Delta V}{\Delta t}} \quad (1)$$

where I (A) stands for the discharge current, m (g) represents the total mass of the active material in two-electrode cell, and $\frac{\Delta V}{\Delta t}$ (V s^{-1}) means the average slope of discharge curve after IR drop.

The energy density (E , Wh kg^{-1}) and average power density (P , W kg^{-1}) of the supercapacitors were calculated based on the following equations:

$$E = \frac{1}{2 \times 4 \times 3.6} CV^2 \quad (2)$$

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