Chemical Engineering Journal 297 (2016) 121–127

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

A layered-template-nanospace-confinement strategy for production of corrugated graphene nanosheets from petroleum pitch for supercapacitors

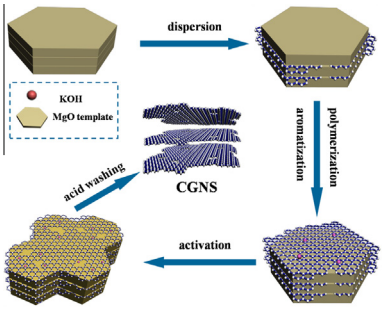
Xiaojun He [a,*], Nan Zhang [a], Xiaolong Shao [a], Mingbo Wu [b], Moxin Yu [a], Jieshan Qiu [c,*]

[a] School of Chemistry and Chemical Engineering, Anhui Key Lab of Coal Clean Conversion and Utilization, Anhui University of Technology, No. 59 Hudong Road, Maanshan 243002, China
[b] State Key Lab of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, China
[c] Carbon Research Lab, Liaoning Key Lab for Energy Materials and Chemical Engineering, State Key Lab of Fine Chemicals, Dalian University of Technology, Dalian 116024, China

HIGHLIGHTS

- Corrugated graphene nanosheets (CGNSs) were firstly synthesized from petroleum pitch.
- The specific surface area of CGNSs ranges from 2095 to 2216 $m^2 g^{-1}$.
- The CGNS electrode shows high capacitance, good rate performance and cycle stability.
- This work provides a new way for fabricating low-cost CGNSs for supercapacitors.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 January 2016
Received in revised form 30 March 2016
Accepted 31 March 2016
Available online 7 April 2016

Keywords:
Corrugated graphene nanosheets
Petroleum pitch
Layered-template-nanospace-confinement strategy
Supercapacitor

ABSTRACT

Corrugated graphene nanosheets (CGNSs) with abundant short pores for ion transport are highly demanded as one of the most promising electrode materials for high-performance supercapacitors. However, the efficient production of CGNSs remains a big challenge. Herein, a layered-template-nano space-confinement strategy coupled with *in situ* chemical activation is reported to synthesize CGNSs from petroleum pitch. Firstly, petroleum pitch was mixed with potassium hydroxide (KOH) particles, and the mixture was dispersed between and onto the sheet-like nano-MgO templates. Secondly, the nano-MgO templates coated with petroleum pitch and KOH mixture were heated, in which the petroleum pitch was polymerized, leading to interconnected film in the layered-template-confinement-nano space. At the same time, the thin films were activated *in situ* by KOH in the nanospace, and yielding CGNSs after removing the template by acid washing. The thin sheet-like CGNSs feature many wrinkles and hierarchical short pores, and have a high specific surface area up to 2132 $m^2 g^{-1}$ and a big lateral size/thickness aspect ratio. As electrodes for supercapacitors, the CGNSs show a high capacitance of 280 $F g^{-1}$ at 0.05 $A g^{-1}$ in 6 M KOH electrolyte, an excellent rate performance with capacitance remaining at 233 $F g^{-1}$ at 20 $A g^{-1}$ and a superior cycle stability with over 96.8% capacitance retention after 1000 charge–discharge cycles at 1 $A g^{-1}$. This layered-template-nanospace-confinement strategy may pave an efficient way for large scale production of electrode materials from cheap petroleum pitch for high-performance supercapacitors.

* Corresponding authors. Tel.: +86 555 2312355; fax: +86 555 2311822 (X. He).
Tel.: +86 411 84986080; fax: +86 411 84986015 (J. Qiu).
E-mail addresses: agdxjhe@126.com (X. He), jqiu@dlut.edu.cn (J. Qiu).

http://dx.doi.org/10.1016/j.cej.2016.03.153
1385-8947/

1. Introduction

The limited availability of fossil fuels in the long run has prompted the exploration and utilization of sustainable energy resources such as solar energy and wind energy. For the sake of efficient utilization of these resources, energy storage devices that can effectively store and release the electrical energy on demand are highly required. Among the energy storage devices, supercapacitors have attracted increasing attention in recent years in view of their rapid charge–discharge rate, high power density and long cycle life. The electrochemical performance of supercapacitors depends on the electrode materials largely [1]. Various carbon materials, such as activated carbons [2], carbon fibers [3], carbon nanotubes/activated carbons [4], mesoporous carbons [5], carbon nanocages/nanospheres [6], carbon nanotubes [7], and graphene [8,9] have been widely investigated as electrode materials for supercapacitors. Among them, graphene, a two-dimensional carbon material, is one of the most promising electrode candidates for supercapacitors owing to its high theoretical surface area, good electric conduction and electrochemical stability [10]. However, graphene nanosheets tend to agglomerate in an irreversible way or restack due to van der Waals interactions between the sheets, resulting in the loss of the specific surface area and lowered specific capacitance thereafter. Therefore, efforts have been made to tackle this problem, such as the design of sandwich-like structures with metal oxides or carbon nanomaterials as "spacers" between the sheets [11,12], the development of graphene foams [13], and three-dimensional porous graphene [14]. Nevertheless, the methods available now for the synthesis of less-stacked graphene nanosheets are time- and energy-consuming, leading to the high-cost of the graphene materials. Therefore, it is necessary to develop an efficient method for production of corrugated graphene nanosheets (CGNSs) with abundant short pores that are easily accessible to ions, which is helpful for fast ion transport and for delivering excellent supercapacitance.

Petroleum pitch, a residue from the distillation of crude oils in petrochemical industry, is cheap and abundant. The aromatic hydrocarbons are abundant in petroleum pitch, featuring sp^2-hybridized carbon atoms, and are highly similar to the hexagonally ranged carbon atoms in graphene. These aromatic hydrocarbon molecules in petroleum pitch may be polymerized and further aromatized to large interconnected thin polymeric films in the layered-template-confinement-nanospace, and the thin polymer films can be further transformed into graphene nanosheets in the nanospace at high temperatures.

Herein, we report a layered-template-nanospace-confinement strategy coupled with *in situ* chemical activation to synthesize CGNS from petroleum pitch. Petroleum pitch mixed with KOH particles was firstly dispersed between the sheet-like MgO templates, where the aromatic hydrocarbon molecules in petroleum pitch undergo a polymerization step to thin films in the layere d-template-confinement-nanospace. The resultant thin films were then converted into CGNSs by high temperature annealing. The CGNS materials were finally obtained after removing the template via acid washing. The thin CGNS materials are found to have abundant hierarchical short pores and large sheets. This kind of pores are favorable for ion adsorption, and for fast ion transport, and the large sheets favor the fast electron conduction, which combine to result in improved supercapacitance. To the best of our knowledge, reports on the high-efficiency synthesis of such unique CGNSs from petroleum pitch for supercapacitors have not been reported.

2. Experimental

2.1. Synthesis of CGNSs

Petroleum pitch was obtained from CNOOC (China National Offshore Oil Corp.) with 87.39 wt% of carbon, 7.93 wt% of hydrogen, 3.30 wt% of sulfur, 1.30 wt% of nitrogen and 0.07 wt% of oxygen. Other chemicals were purchased from Aladdin without further purification. In a typical run, petroleum pitch with a particle size below 100 μm (3.0 g), sheet-like nano-MgO (18.0 g) and KOH (6.0 g) were ground, respectively, and mixed in solid state. The resultant mixtures were transferred to a corundum boat, which was put into a tube furnace and heated to 473 K at 5 K min^{-1}, and kept for 30 min in flowing argon of 60 mL min^{-1}, then heated to 1073 K at 5 K min^{-1} and kept for 1 h to make CGNSs. The CGNSs were obtained by acid washing with 2 M HCl solution and distilled water repeatedly to remove the template and inorganic impurities. The as-made CGNS is termed as $CGNS_{3\text{-}1073}$, where the subscript 3 refers to the mass of petroleum pitch, and 1073 is the heat treatment temperature. Similarly, CGNS made at 1073 K for 1 h with 2.0 g petroleum pitch, 19.0 g MgO, 6.0 g KOH is termed as $CGNS_{2\text{-}1073}$, and CGNS made at 1173 K for 1 h with the mass of petroleum pitch, MgO, KOH at 3.0 g, 18.0 g, 6.0 g is termed as $CGNS_{3\text{-}1173}$ with other conditions remaining unchanged.

2.2. Characterization of CGNS

The CGNS materials and MgO were examined by transmission electron microscopy (TEM, JEOL-2100), scanning electron microscopy (SEM, S-4800), and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB250, USA) to reveal the chemical bonding states of carbon and oxygen elements in CGNSs. The Raman spectra of CGNSs were recorded on a Raman spectroscopy (JYLab−Ram HR800, excited by a 532 nm laser). The water contact angle of the samples was measured by the contact angle measurement system (OCA15Pro, DataPhysics Instruments, Germany). The electrical conductivity of the CGNS materials was measured on a GM-II multifunction automatic measuring instrument. The CGNS materials were pressed into a thin disk at 30 MPa cm^{-2}. Nitrogen adsorption–desorption isotherms were obtained at 77 K with an Autosorb-IQ system (Quantachrome, USA). The surface area (S_{BET}) of CGNSs was calculated by the BET method. The pore size distribution was calculated by the density functional theory (DFT) method from the adsorption branches of the isotherms. The total pore volume (V_t) was estimated at $P/P_0 = 0.99$, and the micropore volume (V_{mic}) was estimated using the *t*-plot method. The non-V_{mic} was calculated from the difference of V_t and V_{mic}. The average pore size (D_{ap}) of CGNSs was obtained by the equation of $D_{ap} = 4V_t/S_{BET}$.

2.3. Preparation and electrochemical test of CGNS electrodes

The electrochemical properties of the as-obtained CGNS materials were investigated using two-electrode cell at room temperature. The electrodes were prepared by mixing 88.0 wt% of CGNSs and 12.0 wt% of polytetrafluoroethylene (PTFE), and then rolled into carbon film and cut into a round film with a diameter of 12 mm, which was further dried at 383 K for 2 h under vacuum. The resultant carbon film was pressed onto nickel foam to make supercapacitor electrodes. Before the electrochemical test, the electrodes was soaked overnight in 6 M KOH aqueous electrolyte. The button-type supercapacitor was assembled with two similar electrodes (about 2.1 mg cm^{-2}) separated by a polypropylene