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Two dimensional holey carbon nanosheets assisted by calcium acetate for high performance supercapacitor

Chenglong Cai [a], Qingli Sui [a], Zhe She [b], Heinz-Bernhard Kraatz [b], Cuili Xiang [a, **], Pengru Huang [a], Hailiang Chu [a], Shujun Qiu [a], Fen Xu [a], Lixian Sun [a], Afzal Shah [c], Yongjin Zou [a, b, *]

[a] Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin, 541004, PR China
[b] Department of Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, M1C 1A4, Canada
[c] Department of Chemistry, Quaid-i-Azam University, 45320, Islamabad, Pakistan

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ABSTRACT

Nanostructured carbon materials are the first preference for fabricating electrodes as they have intrinsic conductivity, excellent chemical stability and high surface area. In this report, a novel two dimensional (2D) holey carbon nanosheet was prepared by pyrolysis of a composite of resorcinol–formaldehyde resin (RF) and calcium acetate (CA), followed by acid etching and base activation. The results reveal that CA plays a crucial role in the formation of the 2D holey carbon nanosheet. The CaO originated from the decomposition of CA was found not only to act a template for the holes, but a catalyst for the graphitic carbon. The obtained carbon nanosheet exhibited uniformly distributed holes with an average diameter of 60 nm. The hierarchical micro/mesoporous structure has a high surface area of 1258.2 $m^2 g^{-1}$, which is great for the fabrication of electrode materials in supercapacitor. It delivered a specific capacitance of 360.1 $F g^{-1}$ at the current density of 1.0 $A g^{-1}$ in 6.0 M KOH solution. Furthermore, a two-electrode symmetric supercapacitor based on the carbon material displayed an energy density of 13.3 $Wh kg^{-1}$ at a high power density of 7125 Wkg^{-1}. The supercapacitor also showed superior rate capability, cycle stability and great potential for use in practical applications.

1. Introduction

As a new energy storage device, supercapacitors have drawn much attention in recent years owing to their fast charging-discharging rate and good cycling stability, in addition to high safety and being light-weight [1,2]. They have potential applications in many commercial fields such as portable electronic devices, memory back-up systems and even electrical-powered vehicles [3]. The core component of the supercapacitor is the electrode material, which determines most of its performance [4]. Supercapacitors need electrode materials a high surface area, which exposes more of the active sites to the electrolyte and accumulates a large amount of charges. It should possess high conductivity, which enables efficient transfer of electrons to the outer circuit. Furthermore, rapid ion migration inside the material is highly desirable. A number of materials have been explored for the fabrication of supercapacitors, including carbon-based nanomaterials [5–7], transition metal oxides [8–10], and conducting polymers [11–14].

Porous carbon-based nanomaterials such as graphene, carbon nanotubes, carbon nanosheets and carbon nanosphere are superior choices for electrode materials in supercapacitors due to their excellent stability, good conductivity, and large surface area [15–17]. Generally, the pore size and structure of carbon-based nanomaterials are the primary factors that influence their supercapacitive performance [18]. For instance, activated carbon has super high surface area (as high as 3000 $m^2 g^{-1}$). However, a large number of irregular and isolated micropores with a diameter in the range of 0.5–1.5 nm are present in activated carbon, which greatly limits the transport of bulky electrolyte ions within the pore channels, resulting in increased inner resistance at high current density [19]. Supposedly, macroporous carbon may facilitate the rapid transport of electrolyte ions in electrodes, whereas usually

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* Corresponding author. Material Science and Engineering, Guilin University of Electronic Technology, 1# Jinji Road, Guilin, 541004, PR China.
** Corresponding author. Material Science and Engineering, Guilin University of Electronic Technology, 1# Jinji Road, Guilin, 541004, PR China.
E-mail addresses: xiangcuili@guet.edu.cn (C. Xiang), zouy@guet.edu.cn (Y. Zou).

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the surface area is limited in bulk states [20]. Graphene, being a single layer carbon material, is expected to have a high surface area. However, irreversible aggregation or re-stacking of graphene nanosheets lowers the surface area to a level much below the theoretically predicted value [21]. In addition, large flakes (several microns) of graphene block the pathway of the electrolyte ions during the charge/discharge processes [12]. To overcome these problems, carbon materials with a hierarchical porous structure combining macropores (>50 nm), mesopores (2–50 nm) and micropores (<2 nm) have been explored as electrode materials for supercapacitors, because they offer effective diffusion paths [19,22]. In this porous structure, macropores act as ion-buffering reservoirs, while mesopores play the role of channels for accelerating the rapid transport of ions within the carbon materials. Meanwhile, the micropores are involved in charge accommodation. For example, Wang and coworkers prepared hollow porous carbon spheres with micro/mesoporous combination shell and macroporous core that exhibited a larger specific surface area of 1290 $m^2\ g^{-1}$, providing a large amount of “ion-adsorption sites” for the formation of electric double layer [7]. However, designing of carbon materials with hierarchical porous structure is still a challenge. For the most part, it involves the use of toxic reagents and harsh reaction conditions and tends to result in metal contamination and poor control over the porous micro- and mesoporous structure of the resulting material [23,24]. On the other hand, it is widely accepted that graphitic carbon possesses higher conductivity than disordered carbon [25,26]. However, graphitic carbons are usually produced under harsh conditions, such as arc discharge, laser evaporation and thermal chemical vapor deposition. This results in products that exhibit low specific surface areas and are obtained in poor yields [27]. Though catalytic graphitization can be done at moderate temperatures without destroying the pore structure of the carbon using a transition metal catalyst (namely, Fe, Co, or Ni) [27,28], the removal of the catalyst is difficult. Therefore, a simple fabrication method of carbon materials with a graphitized structure is highly desirable [29].

In this study, we have investigated the preparation of a novel 2D holey graphitized carbon nanosheet with a hierarchical porous structure using a simple method involving the pyrolysis of a composite of resorcinol–formaldehyde resin (RF) and calcium acetate (CA), followed by acid etching and KOH activation. The CaO originated from the decomposition of CA catalyzed the formation of graphitized carbon and templated the holes on the two dimensional carbon. Macropores, which can facilitate ion migration and improve the electrochemical performance, were effectively formed when CaO was removed by acid etching. The unique porous structure renders the materials having excellent supercapacitive properties. The resulting porous 2D carbon electrode was found to show good long-term electrochemical stability and excellent rate performance (83.4% retention of the capacitance from 1 to 10 $A\ g^{-1}$). These features are superior to previous reported carbon based supercapacitor electrodes, offering useful approach for the design of nanostructured carbons.

2. Experimental section

2.1. Preparation of precursors

All chemicals were analytical grade and purchased from Aldrich chemical Co. The RF-CA composite was prepared using resorcinol, formaldehyde and calcium acetate ($Ca(CH_3COO)_2\cdot H_2O$) as starting materials. To a stirring solution of resorcinol (2.2 g) in 50 mL of deionized water, 8 mL of formaldehyde (37 wt%) was added in a dropwise manner. The mixture was vigorous stirred for 3 h and then 0.22 g of $Ca(CH_3COO)_2\cdot H_2O$ was added. The mass ratio of resorcinol/$Ca(CH_3COO)_2\cdot H_2O$ is 10 unless otherwise noted. Then, the acidity of the solution was adjusted to pH~8 using aqueous ammonia (25 wt%). The mixture was reacted for 24 h under vigorous stirring. Finally, the suspension was dehydrated for 24 h in a freeze-dryer. For comparison, the RF was prepared under identical conditions without the addition of $Ca(CH_3COO)_2\cdot H_2O$. All the precursors were synthesized at 25 °C.

2.2. Preparation of 2D holey carbon nanosheets

The RF-CA powder in a vessel was placed in a tube furnace and heated to 800 °C with a heating rate of 10 °C min^{-1} under in a nitrogen flow (15 mL min^{-1}). The sample was kept at 800 °C for 3 h, the furnace was then switched off then allowed to cool down to room temperature. The resulting black powder was washed thoroughly with 2 M HCl solution to remove any residual calcium adducts. Next, the sample was thoroughly rinsed with deionized water and dried at 80 °C for 12 h. The black powder was dispersed in 8 wt% KOH solution to activate the carbon. The mass ratio of black powder/KOH was kept at 1:2. Next, the solution was transferred into a 200 mL Teflon-lined autoclave and heated at 120 °C for 24 h. Then, the mixture was evaporated to dryness at 100 °C for 4 h under vacuum before placing it in a tube furnace at 750 °C a nitrogen flow for 4 h. Finally, the black powder was rinsed with deionized water until the filtrate was neutral and dried at 80 °C in a vacuum oven for 24 h, giving RF-CA-HC. The control sample lacking calcium acetate was treated identically and thus RF was carbonized and activated with same procedure and denoted as RF-C.

2.3. Characterization of prepared carbon nanostructure

A Quanta 200 scanning electron microscope (SEM) and a Tecnai G2 F20 S-TWIN electron microscope (TEM) were used for morphological characterizations. The Fourier transform infrared (FTIR) spectra of the samples were recorded using an IR Nicolet 6700 spectrometer. The crystallographic information of the samples was examined by Powder X-ray diffraction (XRD) (1820, Philips, The Netherlands) with Cu K_α radiation ($\lambda = 1.5418$ Å). The Raman spectra were recorded by a Renishaw Invia Raman microscope system (Renishaw, Britain). Thermogravimetric (TG) analysis was carried out on a thermal analyzer (Q600, TA Instruments, USA) at a heating rate of 5 °C min^{-1} in an air flow of 80 mL min^{-1}; the temperature was varied from room temperature to 900 °C. The chemical composition was studied by X-ray photoelectron spectroscopy (XPS; ESCA 250) with an Al K_α excitation source. The N_2 adsorption–desorption isotherms were measured by a Quantachrome Autosorb-iQ2 Automated gas sorption system at 77 K. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method, while the pore size distributions were obtained by Density functional Theory (DFT).

2.4. Electrochemical tests

All the electrochemical tests including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were performed on an IM6e potentiostat (Zahner-Elektrik, Kronach, Germany) using a three-electrode configuration in a 6 M KOH solution. A saturated calomel electrode (SCE) and a platinum electrode ($1 \times 1\ cm^2$) were used as the reference and counter electrodes, respectively. The working electrodes were fabricated by mixing the carbon samples (90 wt%) with 10 wt% of polyvinylidene fluoride and grinding it into slurry using alcohol as solvent. The slurry was then pressed onto nickel-foam current collectors ($1 \times 1\ cm^2$) and dried at 80 °C for 2 h. The mass of the active material in working electrode was about 9 mg. All