



ZnO/ZnS/Carbon Nanocomposite-Derived Sulfur-Doped carbon nanosheets using a layered nanoreactor: Towards advanced supercapacitor electrodes and devices

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ABSTRACT

Various approaches have been applied to increase the capacity of electric double layer capacitors (EDLC) by increasing the accessible surface area of the electrode material (mainly carbon) for electrolyte ions. One method is to make the active material particles smaller or use graphite-based carbon with less thickness. Another method involves doping carbon materials with some group III and V elements to create pseudo-capacitive properties. And finally, hybridization/combination of carbon with some metal compounds due to the inductive synergistic effect. Using the idea of layered nanoreactors, we prepared a ZnO/ZnS/S-doped carbon nanocomposite, *i.e.* producing a metal oxide/sulfide with a heteroatom-doped carbon material, simultaneously. ZnO/ZnS/carbon nanocomposite was acid washed to remove ZnO and obtain ZnS/C; ZnS/carbon nanocomposite was again acid washed to remove ZnS and obtain S-doped carbon material. ZnO/ZnS/S-doped carbon, ZnS/S-doped carbon nanocomposites and S-doped carbon materials showed the specific capacitance (C_s) values of 119, 1048 and 454F/g, respectively, when used as the active material in the three-electrode system. In addition, the S-doped carbon material showed a C_s value of 57F/g when used as the active material in the fabrication of a symmetric commercial-like supercapacitor device.

1. Introduction

Metal compound/carbon, nanohybrid/nanocomposites have been reported as good candidates as electrode materials in supercapacitors (SCs) [1–3]. This is due to the low specific capacitance (C_s) of electric double-layer capacitors (EDLC) with carbon-based active materials, which may be due to the limited access of electrolyte ions to the carbon surface. Along with the pseudo-capacitance property resulting from reversible faradic charge transfer reactions, a synergistic effect between carbon and metallic compounds has been reported, leading to increased charge storage efficiency [3]. Low specific surface area and low conductivity limit the performance of supercapacitors based on metal compounds such as oxides. To overcome these issues, hybrid/composite

materials have been prepared using carbon as a conductive material and metal compounds [4]. This results in a synergistic effect between metal compound and carbon, improves electron and ion conductivity and widens the potential window to increase chemical and mechanical stabilities as well as pseudo-capacitive behavior [3,4]. In addition to metal oxides, researchers have also focused on metal sulfides due to their high pseudo-capacitive performance [5–7].

Due to high theoretical energy density, high thermal stability, environmentally friendly, and low cost, zinc oxide is recognized as a metal compound with pseudo-capacitive behavior for production of a carbon/hybrid/composite as the active material for use in SC electrodes [6]. In addition, zinc sulfide as a metal sulfide has attracted much attention due to its excellent performance as an electrode material [5,7].

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In the case of SCs with carbon electrode materials used in EDLCs, another way to increase the capacity is to introduce heteroatoms such as N, S, B, etc. into the carbon structure [8–10]. This leads to higher electron mobility and thus higher electrical conductivity, better surface wettability, and also affects on the pseudo-capacitance property because the heteroatom acts as an n-type (or p-type) dopant.

In our previous works, we used the idea of layered nanoreactors to prepare highly porous 3D spongy-like non-doped and N, P, B and N/Fe-doped carbon nano plates to be used as the efficient electrocatalysts for oxygen reduction reaction (ORR) and also as the active material in supercapacitor electrodes [9,11]. Herein, we want to show how our layered nanoreactors can be used as a precursor to produce ZnO/ZnS/S-doped carbon and ZnS/S-doped carbon nanocomposites as well as S-doped carbon nano plates. By removing the ZnO, we show the role of ZnS in obtaining high C_S value in ZnS/S-doped carbon nanocomposite as the electrode material. By removing the ZnS from the ZnS/S-doped carbon nanocomposite, the remaining S-doped carbon exhibits high C_S values as the active material in three-electrode system experiments, and in a commercial-like SC device.

2. Experimental section

2.1. Material synthesis/fabrication

The initial α -phase layered material, zinc hydroxide sulfate (ZHS) was synthesized via a precipitation method from 0.2 M $ZnSO_4$ solution. The solution was kept at pH 7.0 ± 0.05 by dropwise additions of 0.5 M NaOH solution with vigorous stirring. The precipitate was filtered, washed with water, ethanol and acetone, and dried in an oven, overnight at $80^\circ C$. Zinc hydroxide sulfate/gallate (ZHSG) nanoreactor (incompletely ion-exchange) was prepared by contacting 1 g of the ZHS into 200 ml aqueous solution containing gallate anion for one hour (1 g gallic acid was dissolved in distilled water and brought the solution to pH ≈ 6 by adding 2 M NaOH to obtain gallate anions). The ZHSG sample was thoroughly washed in distilled de-ionized water, ethanol and acetone, and finally dried at $80^\circ C$, overnight. For comparing, a complete ion-exchange process of gallate for sulfate anions was done (3 h ion-exchange time) and the sample was denoted as ZHG. The ZHSG was heat-treated at $700^\circ C$ in an electric tubular furnace under argon atmosphere at a flow rate of 50 ml/min for 1 h at a rate of $5^\circ C/min$ and then cooled down naturally under argon atmosphere. The heat-treated product (HZHSG) was a ZnO/ZnS/S-doped carbon nanocomposite. To remove the zinc oxide and zinc sulfide, the HZHSG was added in 1 M HCl (1 g solid/200 ml) for 4 h at around $50^\circ C$. This process could lead to the removal of only ZnO and the remaining material including zinc sulfide and carbon was named as ZSG. To remove the zinc sulfide from ZSG, the ZSG powder was dispersed in 1 M HCl (1 g solid/200 ml) at around $50^\circ C$ for 4 h. The resulting S-doped carbon nanosheet material was obtained and denoted as CSG.

2.2. Physical characterization

X-ray diffraction patterns were collected on a Unisantis XMD300 powder diffractometer unit using $CuK\alpha$ ($\lambda = 1.5418 \text{ \AA}$) at 45 kV and 0.8 mA. FTIR spectra were recorded using a Perkin-Elmer RXI spectrophotometer in the range of $400\text{--}2000 \text{ cm}^{-1}$. Inductively coupled plasma-atomic emission spectrophotometer (ICP-AES), a Labtest Equipment Co. Model 710 Plasmascan, was used to determine the zinc mass fraction values in the resulting ZnO/ZnS/S-doped carbon nanocomposite. The field emission scanning electron microscopes (ZEISS Supra 55VP and TESCAN, MIRA3) and the energy-dispersive X-ray spectroscopy (EDS, XFlash 6130 detector-Bruker) were used to determine material morphologies, the elemental composition and mapping of the materials. The texture of the S-doped carbon material was characterized by a transmission electron microscope (TEM, Zeiss Libra 200FE). X-ray photoelectron spectroscopic (XPS) measurements were performed on a

Thermo Scientific K-Alpha X-ray photoelectron spectroscopy using Al $K\alpha$ and spot size $400 \mu m$. The surface area and pore size distribution of the materials were determined by a BELSORP measuring instrument (BELSORP-mini, JAPAN, INC) using nitrogen gas adsorption-desorption technique at 77 K. Thermal properties of the as-prepared ZHS and the ZHSG nanoreactor were determined using a simultaneous thermal analyzer instrument (STA), Polymer Laboratories PL-STA1640, conducted under argon atmosphere at a flow rate of 50 ml/min from 25 to $700^\circ C$ at a rate of $5^\circ C/min$.

2.3. Electrochemical tests

A three-electrode system was used to explore the electrochemical properties of the materials as the supercapacitor electrodes in half-cell tests. Each sample was ultrasonically dispersed in a mixture of polyvinylidene difluoride (PVDF), acetylene black and N-Methyl-2-pyrrolidone (NMP) solution (100 mg carbon material, 10 mg acetylene black and 10 mg PVDF binder) and then transferred onto a glassy carbon electrode (GCE) and dried at $70^\circ C$. A very thin layer of the Nafion solution (5 %) was applied onto the dried active material on the GC electrode to obtain the working electrode. A platinum wire electrode (Metrohm) as a counter and an Ag/AgCl (3 M KCl) electrode (Metrohm) as a reference electrode were used. A fresh 1 M Na_2SO_4 solution was prepared as the electrolyte. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) cycles and electrochemical impedance spectroscopy (EIS) analyses were measured using a Potentiostat/Galvanostat (Autolab PGSTAT204) instrument. For comparison, an electrode composed of exactly the same materials as the electrodes (with the same percentage of binder, acetylene black, and Nafion), except for the presence of synthesized active materials, was fabricated and denoted as Substrate. The C_S value of the carbon electrodes was calculated from their discharge curves according to the following equation [9]:

$$C_S = It/m\Delta V \quad (1)$$

where, I is the discharge current, t is the discharge time, ΔV is the potential window, and m is the mass of each active material used for preparing the working electrode in three-electrode system.

Due to make a symmetric commercial-like SC device, a paste was made by mixing the CSG as the active material, PVDF and acetylene black in NMP (100 mg CSG, 10 mg acetylene black and 10 mg PVDF binder) and the paste was coated onto an aluminum foil (as current collector). After coating the paste onto the foil, the electrode was dried on a heater plate at $85^\circ C$. The dried electrode was pressed with a pressure of 100 MPa for 30 s. The electrode material thickness onto the aluminum foil was $\approx 50 \mu m$ and mass loading of the active electrode material was $\approx 3\text{--}4 \text{ mg/cm}^2$. Two pieces of the prepared electrodes were assembled with a nonwoven polyolefin as the separator. A solution of 1 M sodium sulfate in water was used as electrolyte. It should be noted that in order to increase the conductivity of CSG carbon material, CSG was subjected to heat treatment again at $1000^\circ C$ before being used as the active material in making SC device electrodes [12]. The C_S value of the device was calculated from its discharge curves according to the following equation [13]:

$$C_S = 4It/m\Delta V \quad (2)$$

where, I is the discharge current, t is the discharge time, ΔV is the potential window, and m is the mass of the active material for both electrodes used in fabricating the SC device. The energy density (E_{SC} , in Wh/kg) and power density (P_{SC} , in W/kg) of the symmetric supercapacitor was determined using the following equations (3) and (4) [12,13] by using the charge-discharge curves measured at different current densities of 0.25 to 2 A/g.

$$E_{SC} = C_S \cdot \Delta V^2 / 2 \times 3.6 \quad (3)$$