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Full Length Article

Three-dimensional sulphur/nitrogen co-doped reduced graphene oxide as high-performance supercapacitor binder-free electrodes

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ABSTRACT

Sulphur/nitrogen co-doped reduced graphene oxide (SNG) aerogels were prepared by a simple solvothermal method with l-cysteine-assisted in ethylene glycol. The morphology and composition tests showed that the S/N heteroatoms were evenly distributed on SNG microsheets, and these microsheets were further composed of SNG aerogels with three-dimensional (3D) porous structure. The cyclic voltammetry and galvanostatic charge/discharge tests illustrated the SNG bind-free electrode possessed electric double-layer capacitance and pseudocapacitance, and had a capacitance of 254 F g^{-1} at a current density of 1 A g^{-1}. After the 5000 cycles tests, the capacitance retained 83.54% at a current density of 2 A g^{-1}. Meanwhile, the electrochemical impedance spectroscopy data shown the electrode materials had excellent capacity and good conductivity. Hence, the SNG aerogel prepared by l-cysteine-assisted solvothermal method is a great material for high-performance supercapacitors.

1. Introduction

Electrochemical energy storage devices are more and more important with the economic development and the people's attention to environmental protection. Supercapacitor (SC) is a quick charge-discharge device with the advantage of easy fabrication, high power density and long life [1–3]. Generally, two electrodes and electrolyte between them associate a SC device, hence the electrode materials research is an important research direction for improving the SCs performance. Many electrode materials are employed in SCs, including electric double-layer capacitance (EDLC) materials (activated carbon [4,5], carbon nanotubes [6,7]), conducting polymers [8], faradaic pseudocapacitance materials (oxide [9,10], sulfide [11,12], selenide [13,14], etc.) and composite materials. Furthermore, the structure of SCs also has a development with symmetric capacitors and asymmetric hybrid capacitors.

Graphene is widely used in catalysts, energy conversion and storage fields own to its excellent electrical, thermal and mechanical properties [15,16]. The preparation methods of graphene include micromechanical exfoliation, liquid phase exfoliation, chemical vapor deposition, chemical oxidation reduction method and so on [16]. Among these methods, chemical oxidation reduction method is a commonly used method to prepare few-layers and functional graphene and graphene-based composites. And usually, the solvents of ethylene glycol (EG), ethanol, N,N-dimethylformamide and so on were used to reduce the graphene oxide (GO) to graphene oxide (rGO) [17]. In recent years, researchers build three-dimension (3D) structure by 2D graphene to obtaining larger specific surface area and better performance [18]. Furthermore, heteroatoms-doped carbon also is an effective method to improve the performance of carbon materials [19–21]. Wei et al. [20] take advantage of formamide to control the pore structure and surface property of nitrogen (N)-doped 3D graphene hydrogel. And this hydrogel showed an excellent electrochemical performance of SCs. Park and collaborators [21] used sulfur (S) and phosphorus (P) atoms to codope in 3D graphene aerogel. The C—S and C—P═O functional groups efficiently enhanced the electronic and chemical properties and made SCs have a high power and energy density. L-cysteine is a common amino acid with —NH_2 and -SH groups and is usually employed as a reagent to provide heteroatoms (S and N) for rGO [22–24]. L-cysteine can efficiently adjust the porous structure and surface functional groups of rGO, and improve the electric conductivity and chemical property of rGO.

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In this paper, we used a simple solvothermal method to prepare S/N co-doped rGO (SNG) hydrogels and control the 3D structure and surface functional groups. This SNG was employed as a binder-free electrode on nickel foam for SCs, and showed good electrochemical performance and cycling stability, indicating that solvothermal method combined with l-cysteine adjuvant is favourable to fabricate 3D SNG hydrogel, and is valuable for preparing 3D graphene-based composite materials.

2. Experimental

2.1. Preparation of SNG electrodes

Fig. 1 is a schematic diagram of fabricating 3D SNG hydrogels with GO, which was prepared by a modified Hummers' method. Firstly, GO powder was dispersed in EG with an ultrasonic processing to form an uniform 2 mg mL^{-1} solution. After that, 2 mmol l-cysteine was added into mixture solution and was stirred 0.5 h under 70 °C. Then the mixture was transferred into hydrothermal reactor and reacted 12 h at 180 °C. After the temperature was down to room temperature, the S/N co-doped rGO (SNG) hydrogels were washed 500 mL mixed solution of deionized water and ethanol (volume ratio is 9:1). With freeze drying for 48 h, the SNG aerogels were formed. The SNG aerogel was cut into pieces and one of pieces was pressured on the nickel foam (1 × 1 cm^2) with pressure of 2 MPa to form the binder-free SNG electrode.

2.2. Material characterizations

The morphology of SNG was performed by field emission scanning electron microscopy (SEM, SU4800, HITACHI) and high resolution transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-TWIN, America). And elements distribution was tested by TEM-energy dispersive X-ray Spectroscopy (EDX). The crystallographic structures of GO and SNG were measured by X-ray Diffraction (XRD, D/max2200PC, Cu Ka, λ = 1.54178 Å). Raman spectroscopy (Renishaw-invia, England) was used to study the micro structures of GO and SNG. Element types and valence states of SNG were tested by X-ray photoelectron spectroscopy (XPS, Axis Supra, England).

2.3. Electrochemical measurements

The electrochemical properties of cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), cycle performance and electrochemical impedance spectroscopy (EIS) for SNG electrode were measure by working station (CHI660E, CH Instrument, China) at room temperature. A three-electrode cell was employed to study the electrochemical properties for electrodes, which a prepared electrode was work electrode, a Pt sheet was counter electrode and a Hg/HgO electrode was reference electrode. The electrolyte aqueous solution insisted of 1.0 M potassium hydroxide and 0.5 M potassium chloride. Corresponding amplitude of 5 mV were employed in all EIS tests. Meanwhile all EIS data were recorded from 100 kHz to 0.01 Hz.

3. Results and discussion

3.1. The fabrication of SNG aerogels

Because of —NH_2, —SH and O—C=O groups, l-cysteine is usually used as a reducing agent for GO with many —OH, O—C=O, C=O oxygen-containing functional groups. With heating and stirring, the l-cysteine and GO sheets were uniformly dispersed in EG solution. During the solvothermal process, the l-cysteine anchored the surface of SNG sheets by —C—S—C—, —C=S— and C—N bonds. And the l-cysteine served as a bridge for SNG sheets to form SNG hydrogels. At the same time, the l-cysteine decorated on SNG surface would increase the hydrophilicity and result in SNG hydrogels swelling in the mixed solution with deionized water and ethanol [25]. After freeze drying, it was easy to fabricate the SNG aerogels with porous channel in 3D structure.

3.2. The morphology and composition

Fig. 2a and b are the SEM images of SNG aerogels, and the insert in Fig. 2a is the digital photo of SNG aerogel. As shown in Fig. 2a, SNG aerogel is made up with many SNG sheets, and some holes existed among the sheets. The Fig. 2b further describes the SNG aerogel with large pieces of SNG sheets and porous and interconnected structure. Fig. 2c is the TEM image of SNG sheets, which are micron size and include the elements of C, O, S and N in EDX data. Furthermore, the EDX data shown the atomic ratios of S (3.54%) and N (2.13%) in SNG aerogel, respectively. From Fig. 2d–g, the elemental mapping verified the uniform distribution of C, O, S, and N in SNG sheets. Hence, the SNG aerogel prepared by a simple solvothermal method and the additive of l-cysteine possesses the SNG microsheets to build the 3D porous structure, meanwhile, the S and N evenly distributed in the SNG sheets to efficiently improve the electrochemical property of SNG aerogels.

Fig. 3a shown the XRD diffraction peak spectra of GO and SNG aerogels, respectively. GO has an obvious peak in ~10° and a small peak during 20–30° due to GO interlayer spacing of oxygen containing functional groups and graphite (002) plane. After solventhermal process, the oxygen containing functional groups decreased and the diffraction peak of SNG aerogels in ~10° disappeared [26]. In Fig. 3b of Raman spectra for GO and SNG

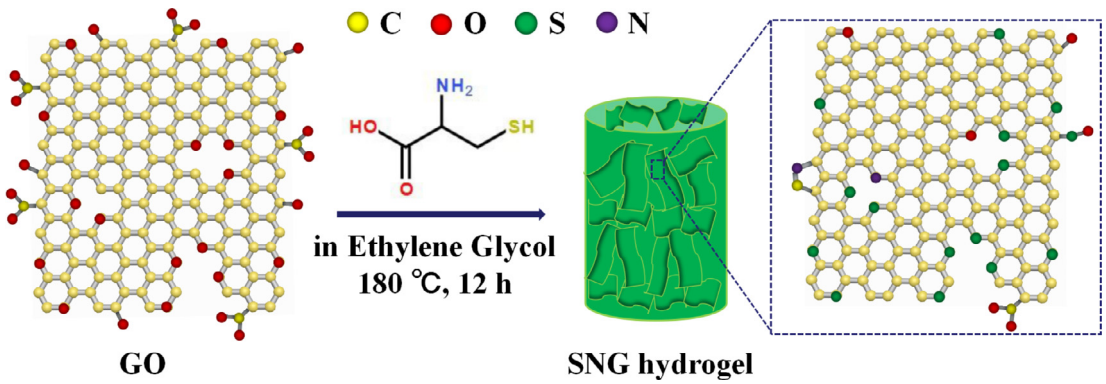

Fig. 1. Schematic diagram of solvothermal process of SNG hydrogel.