Journal of Power Sources 345 (2017) 146–155

Contents lists available at ScienceDirect

Journal of Power Sources

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

Facile preparation of nitrogen/sulfur co-doped and hierarchical porous graphene hydrogel for high-performance electrochemical capacitor

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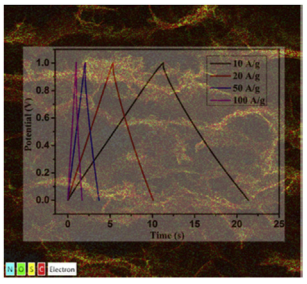
HIGHLIGHTS

- Nitrogen/sulfur co-doped and hierarchical porous graphene hydrogels were prepared.
- The pH values affected the microstructures and electrochemical properties.
- DHGHs were used as binder-free electrodes to assemble full-cell supercapacitors.
- The supercapacitors exhibited excellent performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 November 2016
Received in revised form
4 January 2017
Accepted 4 February 2017

Keywords:
Graphene hydrogels
Co-doped
Hierarchical porous
pH values
Binder-free
Supercapacitors

ABSTRACT

Nitrogen/sulfur co-doped and hierarchical porous graphene hydrogels (DHGHs) are prepared by facile self-assembly process. The results show that the pH values of preparation process significantly affect the microstructures and electrochemical properties of DHGHs and the mechanism has been discussed. The as-prepared DHGHs can be directly used as binder-free electrodes to assemble full-cell supercapacitor devices. It is surprising that the DHGHs prepared at basic condition (DHGH-12) delivers a specific capacitance of 251 F g^{-1} (0.5 A g^{-1}). Moreover, the DHGH-12 shows rectangular cyclic voltammetry shape at a high scan rate of 3000 mV s^{-1} and symmetrical galvanostatic charge/discharge curves at 100 A g^{-1} which exhibits a specific capacitance of 136.5 F g^{-1}, a high energy density of 4.74 Wh kg^{-1} and high power density of 25.47 kW kg^{-1}. Additionally, DHGH-12 presents superior cycling stability (96.8% retention after 2000 cycles at 20 A g^{-1}) in 6 M KOH solution. Therefore, the novel DHGHs can be considered as promising candidate for high energy density supercapacitors at high rates.

1. Introduction

Electrochemical capacitors (ECs, also called supercapacitors) with high power density, fast charging capabilities and long cycle life have attracted great research interests for wide applications,

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http://dx.doi.org/10.1016/j.jpowsour.2017.02.011
0378-7753/

such as electric vehicles, backup energy and other portable power supply. However, most of the present ECs are restricted by low gravimetric capacitance as well as energy density [1–5]. The most widely employed approach to increase the specific capacitance is to explore novel electrode materials. As well as known, microstructure and component are two main factors those affect the performance of electrode materials, for example the pore structure determines ion-accessible surface area, ionic transport rate [6], while the component mainly affects the electrical conductivity and electrochemical activity [7]. Therefore, preparation of high performance electrode materials with ideal porous structure and reasonable composition is desirable.

Graphene with three-dimensional (3D) structures i.e. aerogels and hydrogels have recently attracted extensive interests in ECs because of the combination of high electrical conductivity and excellent mechanical strength of graphene as well as the porous structure and high specific surface area (SSA) [8–11], thus resulting in excellently electrochemical performance [12,13]. In order to develop high performance graphene-based ECs, chemical vapor deposition (CVD) had been adopted to prepare high-quality graphene foam electrode with superior conductivity. However, the high exhaust, complexity and low productivity restrict practical application [14,15]. In the last few years, constructing 3D graphene hydrogels (GHs) and graphene aerogels (GAs) by self-assembly method have drawn much attention because of easy fabrication, porous structures and large SSA [16–19]. For example, GH prepared by a convenient one-step hydrothermal method was firstly reported by Shi's group [20] and the as-prepared GH electrodes were electrically conductive, mechanically strong, thermally stable, and exhibited a high specific capacitance of 160 F g^{-1} at a current density of 1 A g^{-1}. Additionally, the processes of reduction and self-assembly by various reducing agents [21,22] have been reported widely. However, the above mentioned 3D graphene only possess macropores (>50 nm) [23], while the ideal ECs electrode materials should possess a hierarchical porous structure: macropores for the ion-buffering reservoir, mesopores (2–50 nm) for ion transportation and micropores (<2 nm) for the enhancement of charge storage [24]. To address this problem, Xu et al. [6] prepared the holey graphene frameworks by the hydrothermal reaction of graphene oxide (GO) and H_2O_2 at 180 °C, the resultant holey GH delivers high gravimetric capacitance of 310 F g^{-1} at a current density of 1 A g^{-1}. However, the process required very harsh condition and the yield was very low which is unlikely to scale-up.

On the other hand, the components of graphene sheets can also largely affect the electrochemical property of supercapacitor as well. For example, doping heteroatom into graphene is an effective method to improve the electrochemical properties which benefits for energy storage and catalysts [25–33]. Feng's group [12] prepared nitrogen/boron co-doped graphene by a hydrothermal method for high-performance all-solid-state supercapacitors with high specific capacitance (62 F g^{-1}), good rate capability, and enhanced energy density (8.65 Wh kg^{-1}). Sui et al. [34] prepared nitrogen-doped graphene aerogel by hydrothermal method with GO and ammonia solution and exhibited superior capacitive behavior (223 F g^{-1} at 0.2 A g^{-1}) and long-term cycling performance. Besides, Shi's group [35] prepared sulfur doped graphene foam by Na_2S at 80 °C for oxygen reduction reactions. These progresses prompt us to believe that decorating promising characteristics of heteroatom-doping and hierarchical porous structure onto 3D graphene simultaneously would improve their supercapacitor performances significantly. To the best of our knowledge, no such study has been reported so far.

Herein, we presented a scalable approach to prepare nitrogen/sulfur co-doped and hierarchical porous graphene hydrogels (DHGHs) at extreme mild conditions. The DHGHs can be easily prepared using ammonium sulfide and GO as precursors through one-pot reduction and self-assembly process at different pH values. The as-prepared DHGHs were used directly as bind-free electrode without cut and pressed into the nickel foam to assemble full-cell supercapacitor devices. The pH values show great effect on the microstructure and the electrochemical properties of the obtained materials. Thereinto, the electrodes prepared at basic condition (DHGH-12) exhibited excellent supercapacitor performance (251 F g^{-1} at 0.5 A g^{-1}) and superior cycling stability (96.8% retention after 2000 cycles at 20 A g^{-1}) in 6 M KOH as well as high energy density of 4.74 Wh kg^{-1} and high power density of 25.47 kW kg^{-1} at 100 A g^{-1}.

2. Experimental section

2.1. Materials

Graphite powder (CP) and ammonium sulfide solution (20% w/w aq.) were supplied by Aladdin (Shanghai, China) and used as received. The chemicals including potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), concentrated sulfuric acid (H_2SO_4, 98%), hydrochloric acid (HCl) and potassium hydroxide (KOH) were all of reagent grade and were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. All reagents are used without further purification.

2.2. Synthesis of nitrogen and sulfur co-doped hierarchical porous graphene hydrogels (DHGHs)

GO was prepared by a modified Hummers' method [36] (See supporting information). DHGHs were prepared by reduction and self-assembly process with ammonium sulfide ($(NH_4)_2S$) solution as described in our previous report with some modification [37] and the process is scalable which is only limited by the volume of vessels. In a typical process, 4 mL of GO solution (1 mg mL^{-1}) was sealed in a 20-mL glass bottle with the addition of 0.2 mL ammonium sulfide solution. After standing at 95 °C for 3 h, the bottle was cooled freely and DHGH was obtained. The resulted DHGHs were termed as DHGH-2, DHGH-7 and DHGH-12 which were prepared at various pH values (pH = 2, pH = 7 and pH = 12, respectively). After carefully washing, the obtained DHGHs were pressed into the nickel foam to prepare the electrodes to assemble the full-cell supercapacitor devices.

2.3. Characterization

Scanning electron microscope (SEM) images were recorded with a Nova NanoSEM 450. Transmission electron microscope (TEM) images were taken by G2 F20, FEI Tecnai with an accelerating voltage of 200 kV. Raman spectra were obtained by LabRAM HR Raman Spectrometer (HORIBA Jobin-Yvon, France) with a laser at the excitation wavelength of 632.8 nm and 15.7 mW power irradiation. Scattered light was detected with a thermoelectric cooled (−70 °C) charge coupled device detector (CCD). All the measurements were carried out directly over the sample. Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku D/Max 2500) with monochromated Cu Kα radiation (λ = 1.54 Å) at a scanning rate of 4° min^{-1}. X-ray photoelectron spectroscopy (XPS) was conducted in a XSAM800 system, where Al Kα excitation source was used. Brunauere-Emmette-Teller (BET) measurement was performed in a Micromeritics ASAP 2020 Analyzer (Micromeritics, USA). Atomic Force Microscope (AFM) was recorded with Dimension Icon (Bruker, USA) and operated in air in tapping mode.