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Nitrogen and sulfur co-doped porous graphene aerogel as an efficient electrode material for high performance supercapacitor in ionic liquid electrolyte

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HIGHLIGHTS

- A simple method is reported for synthesizing NS co-doped graphene aerogel.
- The NS co-doped graphene aerogel shows the hierarchical structures.
- The supercapacitors exhibit superior electrochemical performance.
- The supercapacitors deliver a maximum energy density of 100.7 Wh kg^{-1}.

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ABSTRACT

Nitrogen and sulfur co-doped graphene aerogel (NS-GA) is prepared by one-pot process. The as-prepared materials are investigated as supercapacitors electrodes in an ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate, $EMIMBF_4$) electrolyte. The NS-GA is characterized using X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy scanning electron microscopy. The results show that the NS-GA has hierarchical porous structure. Electrochemical performance is investigated by cycle voltammetry and galvanostatic charge-discharge. Notably, the supercapacitor based on the NS-GA-5 possesses a maximum energy density of 100.7 Wh kg^{-1} at power density of 0.94 kW kg^{-1}. The electrode materials also offer a large specific capacitance of 203.2 F g^{-1} at a current density of 1 A g^{-1} and the capacitance retention of NS-GA-5 is 90% after 3000 cycles at a scan rate of 2 A g^{-1}. The NS-GA-5 with numerous advantages including low cost and remarkable electrochemical behaviors can be a promising electrode material for the application of supercapacitors.

1. Introduction

With the development of economy, supercapacitors as novel energy storage devices have been exploited during the past decades. Owning to their fast charging and discharging rate, superior stability, high power density, and long cycle life, supercapacitors are recognized as a class of promising devices [1,2]. According to the energy storage mechanism, supercapacitors can be classified into electric double layer capacitors (EDLCs) and pseudocapacitors [3]. However, the supercapacitors store low energy density (typically 5–10 Wh kg^{-1}) when compared with the batteries (~20–170 Wh kg^{-1}), which limits their applications in high specific energy devices [4,5]. According to the energy density equation: $E = 1/2\ CV^2$, working voltage V and specific capacitance C are crucial parameters to extend the energy density.

Carbonaceous materials, including activated carbon, mesoporous carbon, carbon nanotubes and graphene, are good candidates for EDLCs [6,7]. Graphene, with a large specific surface, high electronic conductivity and stability, has been widely explored as electrode materials in supercapacitors [8–10]. In addition, the construction of 3D graphene hydrogels (GHs) and graphene aerogels (GAs) by using different methods have drawn much attention because of their porous structure and large specific surface area [11–14]. However, the specific capacitance of practical graphene electrodes is much lower than the theoretical value (550 F g^{-1}). Recently, porous graphene and heteroatom-doped graphene have been proposed as efficient electrode materials for supercapacitors [15]. The hierarchical porous structure of electrode materials can increase their surface area, while the incorporation of heteroatoms, such as boron, phosphorus, sulfur and nitrogen, is an

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effective method to enhance electrochemical performances of the electrode materials [16–20]. Theoretical and experimental studies have shown that doping graphene with heteroatoms can improve its electronic property and chemical reactivity, and may give rise to doped graphene with hitherto unreported properties [21,22]. Many researchers mentioned that introduction of heteroatom doping can change the electro-neutrality of graphene, and thus allow fast access of ions and electrolytes to the electrode resulting in an increased pseudocapacitance, fast charging-discharging rate and high charge storage capacity [23,24]. Furthermore, comparing with single doping, multiple doping is a versatile synthetic approach, which can further tune the properties of graphene. Normally, the electronic structure of carbon nano-materials can be modified with the incorporation of S-containing groups and hydrophilic group in order to generate the redox active sites [25]. The quaternary and pyridine nitrogen in graphene can enhance its capacitance [26].

On the other hand, non-aqueous electrolytes are more practical due to their high voltage windows. Ionic liquids (ILs) are ideal non-aqueous electrolytes for supercapacitors, and can improve the working temperature range and safety of supercapacitors [27]. Especially, the wide electrochemical windows of ILs can contribute greatly to the energy density for supercapacitors [28]. Jeon et al. [29] reported mesoporous reduced graphene oxide as supercapacitors electrode materials in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) electrolyte with a specific capacitance of 104.3 F g^{-1} at 1 A g^{-1}. Yu et al. [30] synthesized phosphorus and sulfur co-doped graphene aerogels as the electrode material and used $BMIMBF_4$ as the electrolyte to prepare the supercapacitors with an energy density as high as 88.5 Wh kg^{-1} at a power density of 5.3 kW kg^{-1}. However, N and S co-doped graphene with the hierarchical structure in ionic liquid electrolyte for supercapacitors have rarely explored.

Herein, we report a facile strategy for preparing N and S co-doped graphene aerogel with porous structure. The porous structure could provide a large accessible area, a fast ion diffusion and electrochemical stability. The electrode displays a high specific capacitance of 203.2 F g^{-1} at the current density of 1 A g^{-1}, and the as-prepared materials based supercapacitor, with ionic liquid ($EMIMBF_4$) as electrolyte, can provides a power density of 0.94 kW kg^{-1} and an energy density of 100.7 Wh kg^{-1}.

2. Experiment

2.1. Chemicals

Potassium permanganate (≥99.5%), hydrochloric acid were purchased from Luoyang Haohua Chemical Reagent Co., Ltd., potassium persulfate (≥99.0%), hydrogen peroxide (30.0%), graphite (325 m, 44 μm), and polytetrafluoroethylene (PTFE, 60%) were obtained from Aladdin Industrial Corporation, China. Hydrazine hydrate (≥85.0%) was purchased from Nanjing Chemical Reagent Co., Ltd., China. Sulfuric acid (95.98%) was gotten from Luoyang Chemical Reagent Factory, and phosphorus pentoxide (≥98%) was obtained from Tianjin Deen Chemical Reagent Co., Ltd. Sulfur was purchased by Tianjin Kemiou Chemical Reagent Co., Ltd., China. All the chemicals were used as received without further purification.

2.2. Synthesis of materials

Graphene oxide (GO) was prepared from nature graphite powder by the modified Hummers' method [31,32] (see Supporting Information). The NS-GA was prepared by a one-pot solvothermal route. Briefly, 80 mg of GO was added to 40 mL of deionized (DI) water, the mixture was stirred for 12 h, and then the sample was treated in a water bath by ultrasonication at 100 W to form GO suspension. 3 mL of hydrazine hydrate and 40 mL of GO solution (2 mg mL^{-1}) were added and sealed in a 100 mL Teflon-lined autoclave with addition of sulfur. The samples were heated to 200 °C for 12 h to obtain nitrogen and sulfur co-doped graphene hydrogels. The hydrogels were naturally cooled to room temperature, and then washed with DI water several times. Finally, the as-filtrated hydrogel was aged in DI water at room temperature for 72 h, where the water was changed every 24 h to wash out the residual agents. The final products were then freeze-dried for 48 h to obtain nitrogen and sulfur co-doping graphene aerogel (NS-GA). Three NS-GA with different sulfur content were obtained by adjusting the mass ratio of GO to sulfur (10:1, 5:1 and 1:1, denoted as NS-GA-10, NS-GA-5, and NS-GA-1, respectively). For comparison, the N doped graphene aerogel (N-GA) was prepared using the same amount of hydrazine hydrate by the above experiment procedure. We also attempted to prepare sulfur doped graphene using sulfur as reductant at a weight ratio of GO to sulfur (5:1) and the resultant was denoted as (S)-GA, because the results of XPS indicated that the sulfur element did not be doped in graphene (see Results and discussion).

2.3. Characterization

The morphologies of the samples were characterized by transmission electron microscopy (TEM, JEOL JEM-2100) and field-emission scanning electron microscopy (FESEM, Zeiss Supra 40). X-ray diffraction (XRD, Bruker D8 Advance) patterns were collected with Cu-Kα radiation (λ = 1.54 Å). X-ray photoelectron spectroscopy (XPS) measurements were performed in an ESCALab220i-XL system. Raman spectrum measurements were conducted in a Renishaw in Via unit with a 514 nm excitation laser. Nitrogen sorption isotherms were analyzed by means of nitrogen sorption at −196 °C using Micromeritics ASAP-2020 analyzer. The Brunauere-Emmette-Teller (BET) method was used to determine the total surface area. The pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method.

2.4. Electrochemical measurements

To prepare the working electrode, active materials were mixed with carbon black and polytetrafluoroethylene (PTFE) binder with a mass ratio of 85:10:5 in ethanol and sonicated to obtain homogeneous slurry. The thickness of the nickel foam sheet was 1.5 mm, and its diameter was 14 mm. Then the slurry was pasted on Ni foam and dried at 110 °C overnight in vacuum, and the material loaded on the electrode was 1.5–2 mg cm^{-2}. The symmetric supercapacitors in two-electrode configuration were performed using the cellulosic separator NKK TF 4030 in $EMIMBF_4$ ionic liquid (40 μL) as the electrolyte. And they were assembled in glove box under a dry argon atmosphere. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (Shanghai Chenhua instrument Co., Ltd., China). The cyclic stability tests were conducted on the CT2001A battery test system (Lanhe, Wuhan, China), the potential range was 0–3.8 V, and the current density was 2 A g^{-1}. The potential range of CV and GCD were evaluated from 0 to 3.8 V. EIS tests were carried out in the frequency range from 10^5 Hz to 10 Hz at a 5.0 mV amplitude referring to open circuit potential. The sheet resistance of the materials was measured by using a standard four-point probe method (4 Probes Tech, ST2253). The thickness of the tested samples for N-GA, (S)-GA, and NS-GA-5 was 0.8 mm, 0.6 mm, and 0.6 mm, respectively, with a same diameter of 13 mm. The specific capacitance (C_s) of single electrode material was calculated from equitation 1. The specific capacitance (C_{cell}), the energy density (E) and power density (P) of device were calculated from equations (2)–(4), respectively [33–35].

$$C_s = \frac{2I\Delta t}{m\Delta V} \tag{1}$$

$$C_{cell} = \frac{1}{4}C_s \tag{2}$$