



Nitrogen and sulphur-functionalized multiple graphene aerogel for supercapacitors with excellent electrochemical performance



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ABSTRACT

Graphene aerogel has attracted increasing attention owing to its large specific surface area, high conductivity and electronic interaction. The paper reported the synthesis of nitrogen and sulphur-functionalized multiple graphene aerogel (N,S-MGA) through simple multiple gel method. The as-prepared N,S-MGA exhibits a much higher density and electronic conductivity compared with classical graphene aerogel. The density rapidly increases and resistance reduces with increasing number of the graphene oxide gelation. The unique architecture creates ultra fast electron transfer and electrolyte transport. The introduction of nitrogen and sulfur functional groups leads to additional pseudocapacitance. The N,S-MGA electrode provides high specific capacitance (486.8 F g^{-1} at the current density of 1 A g^{-1}), rate capability (261.8 F g^{-1} at the current density of 20 A g^{-1}) and cycling stability (lost of less 4% after 3000 cycles) in 1 M KOH electrolyte. The performance can be greatly improved by increasing number of the graphene oxide gelation. Interestingly, the addition of $\text{K}_3\text{Fe}(\text{CN})_6$ into the KOH electrolyte can enhance the pseudocapacitance via directly contributing pseudocapacitance to N,S-MGA electrode and promoting the electron gain and loss of nitrogen and sulfur functional groups. The specific capacitance is 4929.4 F g^{-1} at the current density of 2 A g^{-1} in the mixed 1 M KOH with 1 M $\text{K}_3\text{Fe}(\text{CN})_6$ electrolyte. The capacitance retention is more than 98.7% after 5000 continuous charge/discharge cycles, verifying good long-term cycling stability. The energy density reaches to $316.6 \text{ W h kg}^{-1}$ at the power density of 683.7 W kg^{-1} and $117.6 \text{ W h kg}^{-1}$ at the power density of 1020 W kg^{-1} . The study also opens an avenue for the design and synthesis of functional graphene aerogel-based materials to meet the needs of further applications in energy storages/conversion devices, biosensors and electrocatalysis.

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1. Introduction

The increasing popularity of portable electronic devices and automobiles has stimulated great interest in the development of advanced energy storage and management devices. Supercapacitor as a new-rising star has captured considerable interest in the past decades due to its fast charge/discharge process and long lifespan [1]. The supercapacitive performance mostly counts on its electrode. Thereby, developing rational electrode materials with porous nanostructure is important but meaningful to achieve large energy density, high-rate capability and outstanding cycle life for

supercapacitors. To date, a large amount of carbon-based materials of porous structures have widely been applied as the ideal electrode materials for supercapacitors due to its low cost, large specific surface, high conductivity and good chemical stability. Graphene aerogel-based material as a new type of carbon materials have attracted increasing attention owing to their large specific surface area, high conductivity and electronic interactions [2]. Graphene aerogel is the mesoporous structure formed by three-dimensional interconnected graphene sheets. Compared with the porous graphene materials constructed by physically and randomly stacked graphene sheets, graphene aerogel possesses a much higher electronic conductivity, because the constituent graphene sheets are chemically bonded, facilitating much faster charge transport across graphene sheet junctions, high specific surface area that offers abundant active sites for the catalytic reduction events, and large pore volume that provides fast mass transfer of the redox species [3]. However in reality, the discharge

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specific capacitance of pure graphene aerogel electrode is only 100–300 F g⁻¹ [4]. Such a low capacitance greatly limits its use in high-performance supercapacitors.

Great effort has been successfully attempted to enhance the discharge specific capacitance of graphene aerogel-based materials. The first strategy is to design new approach for the synthesis of graphene aerogel to further improve the porous nanostructure, mechanical property and electronic conductivity. For example, Liu et al. fabricated a highly porous graphene aerogels with excellent flexibility via simultaneous reduction and assembly of graphene oxides in various alcohols [5]. The resultant supercapacitors assembled by the graphene aerogels exhibited effective specific capacitance up to 287 F g⁻¹ at current density of 0.1 A g⁻¹ with excellent cycle stability. Wang et al. used in situ synthesis route for the fabrication of polypyrrole/graphene with an enhanced electronic conductivity. The resulted composite exhibits a remarkable performance as the electrode material of supercapacitors [6]. The specific capacitance reaches 564.1 F g⁻¹ at a current density of 1 A g⁻¹ and maintains 86.4% after 1000 charging/discharging cycles at a current density of 20 A g⁻¹. However, these graphene aerogel materials can only offer the electric double layer capacitors, the ability of the above method to enhance the capacity of the capacitor is very limited. The second strategy is to directly introduce pseudocapacitive materials into graphene aerogel to build on graphene aerogel hybrid, including Co(OH)₃ [7], Co₃O₄ [8], MnO₂ [9,10], MoO₃ [11], MoS₂ [12] and Fe₂O₃ [13]. Often, the hybridization can be an effective method to enhance the functionality of materials and the integration of nanomaterials on graphene nanosheets potentially paves a new way to improve their electronic, chemical and electrochemical properties, thus synthesis and application of the hybrid have become a hot research topic in material science. The investigations have confirmed that the introduction of pseudocapacitive materials is one of the most effective methods for improving the capacitance of graphene aerogel materials. However, the construction of hybrids requires a lot of steps. This often is complex and time-consuming. In addition, the use of metal salt may also reduce the chemical stability of the graphene material and produce a large number of wastewater containing heavy metals. The third strategy is to functionalize graphene aerogel with pseudocapacitive chemical moieties such as oxygen, nitrogen, and sulphur to introduce pseudocapacitance into the system [14]. The heteroatom functional groups are able to enhance the specific capacitance of the electrode due to their pseudocapacitive reactions [15,16]. The current research work is focused on the efficiency of electric double-layer capacitors-pseudocapacitors hybridization [17–20]. Despite many progresses were made, a great challenge for functionalized graphene electrode materials still remains to simultaneously achieve high specific capacitance, rate performance and cycle stability. On the one hand, the reported functionalized graphenes give a very low tap density, leading to a low volumetric capacitance. In fact, the present technologies can only get ultra light graphene aerogel, which is limited to low water-solubility of graphite oxide. However, the ultra light characteristic inevitably leads to a poor mechanical strength and electronic conductivity, because of sparse graphene sheets and fragile frame structure. On the other hand, the reported functionalized graphenes mostly offer poor electronic conductivity due to the existence of rich of hydrophilic groups. This will result in a poor rate performance and cycle stability.

In the study, we for the first time reported the synthesis of nitrogen and sulphur-functionalized multiple graphene aerogel (N, S-MGA) through simple multiple gel method. The as-prepared N,S-MGA exhibits a better electrochemical performance for supercapacitors compared with classical graphene aerogel. More importantly, the performance can be further improved by increasing number of the graphene oxide gelation. Because ideal

combination of the electric double-layer capacitors and pseudo-capacitors was achieved, the N,S-MGA electrode provides excellent supercapacitor performance.

2. Experimental

2.1. Synthesis of N,S-MGA

The synthesis of N,S-MGA includes three assembly processes. The first process is to disperse 0.25 g graphene oxide (GO) and 1.8 g of thiourea in 50 ml of ultrapure water under ultrasonic condition to form homogeneous GO dispersion. After added 30 mg of *p*-phenylenediamine, the GO dispersion was heated at 90 °C for 1 h to produce GO hydrogel. To obtain GO aerogel, the resulting GO hydrogel was treated by freeze-drying. The second process is to prick holes in the face of GO aerogel by fine steel needles ($\phi = 1$ mm). The GO aerogel was placed into another glass vial with a plug, which its inner volume consistent with volume of the GO aerogel. After that, the GO dispersion of 30 ml was added into the GO aerogel. Followed by heating at 90 °C for 1 h and freeze drying to obtain double GO aerogel. The above procedure was repeated in order to prepare a multiple GO aerogel until number of the GO gelation cycle reaches a desired value. The third process is to soak the multiple GO aerogel in 1.5 M phosphoric acid (H₃PO₄) for 24 h. Then, it was washed in water, dried and finally reduced by the thermal annealing at 200 °C in Ar/H₂ (95:5) for 2 h. Based on number (n) of the GO gelation cycle during the synthesis, corresponding product is designated as N,S-MGA-n.

2.2. General characterization

Scanning electron microscope (SEM) analysis was carried out in HITACHI S4800 field emission scanning electron microscope. SEM sample was prepared by placing a drop of dilute ethanol dispersion of N,S-MGA onto a copper plate attached to an aluminum sample holder, and the solvent was allowed to evaporate at room temperature. Transmission electron microscope (TEM) images were conducted on a JEOL 2010 transmission electron microscope at 200 keV. The sample was prepared by dispensing a small amount of dry powder in ethanol. Then, one drop of the suspension was dropped on 300 mesh copper. The TEM grid covered with thin amorphous carbon film. X-ray diffraction (XRD) patterns were measured on a X-ray D8 Advance Instrument operated at 40 kV and 20 mA and using Cu K α radiation source with $\lambda = 0.15406$ nm. X-ray photoelectron spectroscopy (XPS) measurement was performed by using a PHI 5700 ESCA spectrometer with monochromated Al K α radiation ($h\nu = 1486.6$ eV). The N₂ adsorption and desorption isotherms were measured at 77 K on a Quantachrome Nova 2000. Prior to the gas sorption measurements, all the samples were outgassed in vacuum at 120 °C for 24 h. The specific surface area and the pore size distribution were calculated using the Braunauer-Emmett-Teller (BET) method and the relative pressure range of p/p_0 from 0.1 to 0.3 was used for the multipoint BET calculations. Non-local density functional theory assuming the pores are slit/cylinder shaped was used to determine the pore size distribution and mesopore volume.

2.3. Electrochemical measurement

The electrochemical measurements were carried out at room temperature using a conventional three-electrode system with 1 M KOH aqueous solution or the mixed 1 M KOH with 1 M of K₃Fe(CN)₆ as the electrolyte. Herein, N,S-MGA-n electrode was used as working electrodes. Platinum foil (1 cm \times 1 cm) and saturated calomel electrode (SCE) were employed as the counter electrode and reference electrode, respectively. The working electrode was

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