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Highly flexible pseudocapacitors of phosphorus-incorporated porous reduced graphene oxide films

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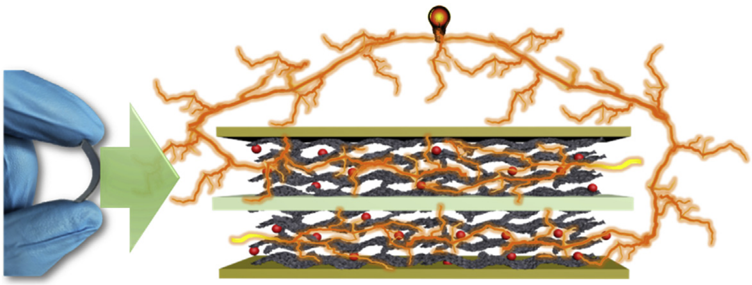
HIGHLIGHTS

- A hierarchical structure of P-incorporated graphene film was synthesized.
- A flexible pseudocapacitor was fabricated with gel electrolyte.
- The HPG films exhibited excellent electrochemical performances.
- The redox charge storage was investigated by in-situ and ex-situ analyses.

GRAPHICAL ABSTRACT



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ABSTRACT

We demonstrate hierarchically structured, phosphorous (P)-incorporated reduced graphene oxide (HPG) films prepared by a vacuum-filtrated and ice-frozen assembly, freeze-drying and thermal treatment for all solid-state flexible pseudocapacitors. The porous morphology is originated from the interconnected networks of graphene layers and the surface roughness is reduced by the P doping, which results in improving the electrochemical performances. The P=O sites of C-P=O bonding acting as electro-active sites of HPG film are identified by XPS spectra and their charge storage behavior is monitored by *in-situ* and *ex-situ* spectrochemical analyses. The HPG film achieves the specific capacitance of 149 F g^{-1}, the capacitance retention of 90.8% from 1 to 30 A g^{-1}, and the cyclic stability of 94.2% over 1000 charging/discharging cycles. Moreover, the pseudocapacitive performances of the HPG films are preserved at the bending state of 120° angle. These excellent electrochemical behaviors are attributed to the unique hierarchical structure and the formation of electro-active of P=O sites by heteroatom doping.

1. Introduction

With the fast boost of flexible and wearable electronics, carbonaceous nanomaterials have attracted a significant attention as supercapacitor electrodes due to the high electrical conductivity, large surface area, chemical and mechanical stabilities, and light weight. Along with activated carbons and carbon nanotubes [1,2], graphene-based materials have been extensively investigated to improve electrochemical performances of flexible supercapacitors due to their remarkable physical and chemical properties and various surface chemistries [3–9]. Since supercapacitor stores charges at the electrode/electrolyte interface, a chemical approach to improve energy density at a small form factor while preserving high power density and long term cyclability is the control in the surface chemistry of graphenes.

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Among various surface modifications, heteroatom doped into graphene lattices and edges is considered a promising surface chemistry to tailor and improve electronic structure and properties [10,11]. On a basis of the different electronegativities and bond lengths and angles of heteroatoms from carbon atoms [12–15], the electrochemical active sites were created to act as charge storage sites, which disrupted the electric neutrality and crystallinity structure of graphitic materials and generated strong covalent bonding configurations [16–19]. Moreover, the heteroatom configurations could decrease the charge transfer resistance between the electrode and electrolyte and provide electrochemical activity. Thus, the surface modifications of graphene such as single or dual heteroatoms (i.e. N, O, S, and P) have been applied for electrocatalysis [20–23], lithium-ion batteries [24–27], and supercapacitors [10,14,28–31]. For instance, three-dimensional N-doped graphene nanoarchitectures demonstrated a high specific capacitance of 320 F g^{-1} in KOH aqueous electrolyte and 96% of capacitance retention after 10000 cycles [31]. B and N co-doped graphene also showed improved electrochemical properties [28]. Although phosphorus (P)-modified carbon materials have been intensively investigated for electrochemical applications [32–34], there were very few reports about their flexible supercapacitor application. Park and coworkers reported surface redox charge storage mechanism of three-dimensional porous graphene aerogels for a supercapacitor application [35]. Moreover, other groups demonstrated P-incorporated or N, P co-doped graphenes for improved performances of supercapacitors [36]. Meanwhile, other heteroatom (B, N, or S)-doped graphenes were solely applied in the field of flexible supercapacitors [37].

Herein, we demonstrate P-incorporated porous reduced graphene oxide (RGO) films for the fabrication of symmetric flexible supercapacitor integrating with the PVA-H_2SO_4 gel as an electrolyte. The as-fabricated supercapacitor achieved a high specific capacitance, excellent rate capability and cyclic stability, which were associated with the synergistic effects of hierarchical structure for fast ion diffusion and pseudocapacitive behavior arising from the formation of electro-active P sites. Furthermore, flexibility test was carried out to demonstrate the mechanical integrity of HPG. These results indicate that a surface modification of porous graphene film provides a rational design of flexible graphene-based electrodes for high performance flexible energy storage devices.

2. Experimental

2.1. Synthesis of HPG film

Graphene oxides (GOs) were prepared from natural graphite powder using a modified Hummers method through the acidification, oxidation, and exfoliation [38] and their dispersion quality was obtained as previously demonstrated [39]. The flexible HPG films were prepared combining self-assembly, freeze-drying and thermal activation of phytic acid functionalized GOs. In a typical procedure, a 20 mL of GOs dispersion (0.5 wt%) was mixed with 0.3 mg of phytic acid and then, the resulting dispersion was diluted by 150 mL of DI water followed by bath-sonication for 30 min. The homogeneous dispersion was filtrated under vacuum for 2 days to fabricate the wet film. Subsequently, the wet film was ice-templated immerging into liquid nitrogen in the course of a phase transition of DI water from liquid to ice, and freeze-dried for 3 days to achieve the phytic acid-functionalized porous GO film. The as-prepared film was transferred into the center of furnace, and heated at 900 °C with argon atmosphere at the flow rate of 200 cc min^{-1} and the heating rate of 10 °C min^{-1}. After thermal treatment for 1 h, the furnace was cooled down to room temperature at the same flow rate to get the HPG film. Meanwhile, the hierarchically porous RGO film was prepared following the same method without phytic acid, and noted as HP. The non-porous restacked P-incorporated RGO film was prepared using the same method without an ice-templating process.

2.2. Characterization

Scanning electron microscope (SEM) images were obtained using a field emission scanning electron microscope (Philips SEM 535 M) equipped with a Schottky-based field emission gun. Transmission electron microscope (TEM) images were collected on a JEM-3010 HR TEM (300 kV). Elemental mapping in STEM mode was performed using a probe focused to 0.2 nm and a camera length of 20 cm. The scan raster was 512 × 512 points with a dwell time of 8.5 s per scan. Raman spectra were measured by a Jasco-Raman spectrometer with excitation by 520 nm laser light. The Brunauer–Emmett–Teller (BET) surface areas and nitrogen adsorption–desorption isotherms were measured at 78 K using BELSORP-mini analysis program. XPS data were obtained using a Thermo MultiLab 2000 system with an Al-Mg α X-ray source. Cyclic voltammetry (CV) curves were obtained using a CHI 760D electrochemical workstation. GCD measurements were performed using a Solartron 1260.

2.3. Electrochemical measurement

CV measurements were carried out using a symmetric two-electrode configuration. The as-obtained HPG film was used as the working electrode, and PVA/H_2SO_4 gel as the electrolyte and separator; the detailed preparation process of electrode material and gel electrolyte was as follows. Firstly, the gel electrolyte was prepared by mixing 5 g of PVA and 5 g of H_2SO_4 in 50 mL of DI water. The mixture was stirred at 80 °C for 2 h and degassed at bath-sonication for 10 min to remove the possible existence of bubbles. Secondly, the HPG film was cut into a rectangular shape with the size of 2 cm*1 cm. The resulting HPG film was placed onto the surface of Au-coated PET. Finally, the two solid HPG pieces were symmetrically integrated into one piece by hot pressing at 70 °C, and then connected with Au-coated PET as current collector. Galvanostatic charge/discharge (GCD) curves were measured at a specific current from 1 A g^{-1} to 30 A g^{-1} using CHI 760 electrochemical work station. The electrochemical impendence spectroscopy was evaluated with a frequency range from 10^6 to 10^{-2} Hz at the amplitude of 10 mV. The specific capacitances (C_s) was calculated using the following equation:

$$C_s = I/M\left(\frac{\Delta V}{\Delta t}\right)$$

where I is the applied current density, M is the total weight of two electrodes and $\frac{\Delta V}{\Delta t}$ is the discharge slope after IR drop, respectively.

2.4. In-situ and ex-situ measurement

To demonstrate the surface charge storage mechanism of HPG film, a specific solid-state cell was constructed for *in-situ* FT-IR measurement. Firstly, two electrodes was cut into a small pieces with a size of 1 cm*0.5 cm, and PVA/H_2SO_4 gel applied as electrolyte and separator. Then, the two electrodes were constructed into a symmetric solid-state cell with partially exposing the electrode material to contact with the laser beam. To collect *ex-situ* XPS data, the single electrode was fully charged for 30 min using a three-electrode configuration, and then the electrode wan fully discharged for 40 min. Subsequently, the sample was directly used to check the XPS after being fully charged and discharged.

3. Result and discussion

A synthetic process was schematically described in Fig. 1a to fabricate the flexible HPG films through vacuum-filtrated and ice-templating assembly, freeze-drying and thermal activation. The homogeneous mixture of phytic acid and GO is a crucial factor to make a well-defined hierarchical structure. During a vacuum filtration process, the phytic acid-functionalized GO film was fabricated via directionally