



Improving energy density of supercapacitors using heteroatom-incorporated three-dimensional macro-porous graphene electrodes and organic electrolytes



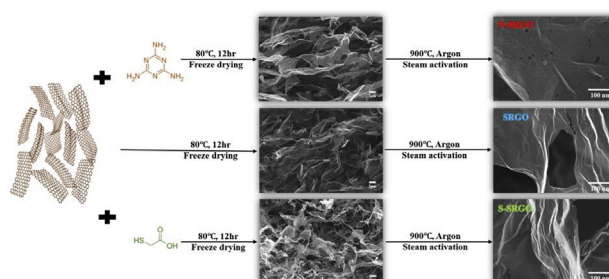
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HIGHLIGHTS

- The 3D hieratically porous doped graphene architecture is constructed.
- Heteroatoms are uniformly distributed onto the 3D graphene surface.
- A full cell supercapacitor is fabricated using organic electrolytes.
- Energy density of cell is enhanced improving specific capacitance and potential window.

GRAPHICAL ABSTRACT



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ABSTRACT

The synthesis of nitrogen- and sulfur-doped three-dimensional (3D) graphene architectures further treated by steam activation to increase surface area is reported in this study. Tetraethylammonium tetrafluoroborate (TEABF₄) in propylene carbonate as an organic electrolyte is used to enlarge the voltage range of a supercapacitor (SC) for high energy density. The 3D nitrogen- and sulfur-doped, steam activated, reduced graphene oxides (N-SRGO and S-SRGO) contained 7.84% and 6.93% of N and S heteroatoms and feature 497 m² g⁻¹ and 525 m² g⁻¹ of surface area due to hieratical porosity of the substance. As shown in the galvanic charge/discharge curves, a range of 0–2.5 V in the 3D N-SRGO architectures showed the highest capacitance of 23.1 F g⁻¹, delivering maximum energy and power densities of up to 20 Wh kg⁻¹ and 6190 W kg⁻¹. The rate capability and cycle stability over 5000 cycles were evaluated to be 63% and 68%, respectively, for N-SRGO. This study provides a systematic way to improve energy density of SCs by combining heteroatom-doped 3D graphene architecture with an organic TEABF₄/PC electrolyte.

1. Introduction

Supercapacitors (SC) can store electrical energy by accumulating positively and negatively charged ions in the electrochemical double layer (EDL) when the electrode is oppositely polarized. Such charge storage mechanism provides electrochemical double layer capacitor (EDLC) with several advantages, such as high power, fast rate

capability, and cyclic stability [1–3]. However, due to low energy densities of batteries, the application of SCs for high energy demanding electrical vehicle (EV) and energy storage system (ESS) has been limited [4,5]. Basically, energy density of SCs is determined by basic equation of $0.5 \times C \times V^2$, where C and V indicate specific capacitance and potential window, respectively [6]. In addition to the development of large surface area carbon nanomaterials for enhanced capacitance,

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broadening the potential window can improve energy density drastically. Since the electrochemical performance of SC cells can be determined by coupling electrolyte and electrode, researchers have investigated various combinations of the two to enhance energy density [7–10]. In particular, physical and chemical properties such as ionic conductivity, viscosity, and potential window of an electrolyte have been considered to increase energy densities and efficiencies [8–11]. In comparison with lower decomposition voltage of aqueous electrolytes, organic electrolytes are more electrochemically stable with considerable ionic conductivity and high potential window > 2.5 V [12].

Among various nano-structured electrodes, graphene-based materials are regarded as promising candidates owing to their high specific surface area, electronic conductivity, and electrochemical and mechanical stabilities [4,13,14]. To improve specific capacitance, various chemical approaches such as construction of three-dimensional (3-D) macroscopic structures, generation of micropores by physical or chemical activation, intercalation with other capacitive materials, and incorporation of heteroatoms or functional groups have been investigated. For instance, 3D macroporous graphene, curved graphene, rolled graphene, CNT or other metal oxide intercalated graphene, steam or chemically activated microporous graphene, and nitrogen (N), sulfur (S) or phosphorous doped graphene have been reported [15–20]. Despite intensive research on heteroatom-doped graphenes [15–20], there are very few systematic investigations at full-cell level that combine 3D hierarchically porous, heteroatom-doped graphene architectures with organic electrolytes.

In this work, we demonstrate a systematic approach to increase energy density by controlling 3D morphology, microporosity, and composition of graphene electrode and then combining the electrode with TEABF₄ in propylene carbonate (PC) electrolyte as follows. First, macro- and microporous structures of graphene are constructed via ice templating and steam activation. The 3D macroporous inter-networked continuity provides fast ion transport, large accessible area, and percolated electron conduction while the microporosity offers increased surface area. The microporosity arises from vacancies on the surface of graphene when activated oxygen in steam reacts with weakly bonded carbon in graphene to produce carbon monoxide or dioxide. Second, to provide excess charge density for the enhanced electronic conductivity and space charge capacitance [18,19], heteroatoms such as N and S are incorporated into the graphene surface. The reduced electronic conductivity caused by defect generation can be restored by the doping effect of heteroatoms. Third, TEABF₄ in PC is used to broaden the working voltage of our full cell SC. Despite a wide working voltage of TEABF₄, the high viscosity and cost of these electrolytes need to be resolved by using non-aqueous solvents such as acetonitrile and PC for more practical applications [21].

2. Experimental section

2.1. Synthesis

Graphene oxide (GO, from Graphene Supermarket) was dispersed in DI water at a concentration of 5 mg ml⁻¹. It was used as the starting material. Melamine and thioglycolic acid (from Sigma-Aldrich) were used as nitrogen and sulfur sources, respectively. For the synthesis of heteroatom-incorporated RGO samples, each doping source was added into GO solution (at a weight ratio of 1–4 for nitrogen source and 1 to 15 for sulfur source) and stirred at 80 °C for 12 h. The solution thus obtained was freeze-dried at 5 °C min⁻¹ and subjected to heat treatment in an argon rich atmosphere at 300 °C and 800 °C while maintaining the soaking time of 1 h. Moreover, 1 ml of steam was introduced into the furnace chamber of 800 °C at 0.16 ml min⁻¹.

2.2. Supercapacitor characterization and fabrication

A coin cell type full-cell supercapacitor was fabricated. Cyclic

voltammetry (CV) was performed in two-electrode system through an electrochemical workstation (Bio-Logic Science instrument-VSP). Symmetric full-cell SCs was fabricated by coating the slurry of sample and PVDF at a weight ratio of 8:2 with NMP as a solvent. The ground slurry was coated on the aluminum foil and dried in vacuum for 12 h at 60 °C. The coated dry sample was punched into circular discs (SCD) with punching machine. Full-cell was then fabricated by placing the SCD, separator, oaring, SCD, wavering, metal disc as depicted in Fig. S1 and sealed with another end disc of the coin cell. The fabricated electrodes and separator were soaked in the electrolyte overnight. Then 0.5 ml of electrolyte solution consisting TEABF₄/PC solution was dropped before and after placing the glass fiber separator (GF/F, Whatman) during coin cell fabrication. CV measurements for electrodes were made at various potential range and scan rates. Typically, the mass loading capacity of electrodes for the entire electrochemical test was 1 mg cm⁻². The device capacitance was calculated from the total mass of the electrode.

2.3. Characterization

Morphology and pore were analyzed through scanning electron microscopy (Philips SEM 535 M). For transmission electron microscopy, JEM-3010 HR-TEM was used for elemental mapping. Crystallography information was obtained using rigaku D/max IIIC (3 KW) with a θ/θ goniometer equipped with a Cu-K α radiation generator. The effect of steam activation in creating defects in graphitic sites was exploited through Raman spectra (Jasco-Raman spectrometer). Thermo multiLab 2000 system, an x-ray photoelectron spectroscopy analyzer, was employed to confirm the percentage of doping elements and effective reduction of graphene. A Belsorp-mini II BET analyzer was used to measure surface area and pore volume. This test was performed by degassing the sample at 200 °C for 3 h. Surface area was determined using N₂ adsorption/desorption. The BJH method helped us understand mesopore size distribution and total pore volume.

3. Results and discussion

The melamine/thioglycolic acid with DI water was stirred at 80 °C until it was completely dissolved followed by the addition of GO to the resulting solution. The protonated melamine/thioglycolic acid molecules spontaneously interacted with oxygen functional groups of GOs. The separation of the dispersed phase from the solution and color change indicated specific interaction between protonated molecules and GO. Samples were ice-templated by immersing in liquid nitrogen and thawed in a freeze dryer for 3–4 days. The resulting samples were freeze-dried to prevent restacking of graphene layers while preserving the 3-D macroporous structure created by the ice-templating process [22]. In order to retain exfoliated status of 3-D ice-templated architectures, freeze-dried samples obtained were subjected to a constant temperature of 300 °C for 1 h, thus converting it into reduced GO (RGO). The sample was then treated at 800 °C for 1 h to incorporate foreign elements onto RGO surface as illustrated in Fig. 1. Finally, the resulting samples were activated by highly reactive steam to create micropores on the surface of RGO, achieving additional surface area and hierarchical porosity of steam-activated RGO (SRGO). Similar process was replicated for the control sample without addition of heteroatom precursors. Final N, S, and un-doped samples were named as N-SRGO, S-SRGO, and SRGO, respectively.

The distribution and existence of heteroatoms were examined by elemental mapping of the STEM as shown in Fig. 2. Overlapped image and individual elemental mapping demonstrated successful incorporation of N and S atoms into the lattice while the edge of RGO had few unreduced oxygen defects. The distribution of N and S atoms in the RGO layer was random and dense. To understand the composition and bonding configuration of the heteroatom, XPS was measured. The narrow range of the XPS spectrum in Fig. 3(a) demonstrated the

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