



Fabrication of nitrogen and sulfur co-doped graphene nanoribbons with porous architecture for high-performance supercapacitors



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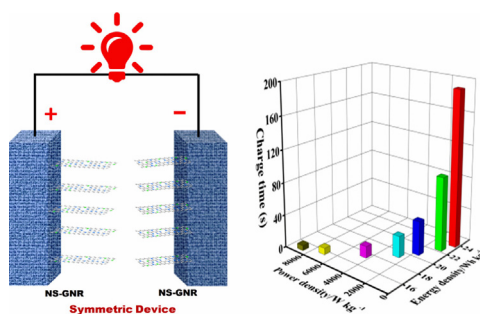
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HIGHLIGHTS

- A novel approach for the synthesis of unique porous NS-GNR by thermal annealing method has been established.
- The highly synergistic NS-GNR is proposed here for the first time as an electrode for supercapacitors.
- NS-GNR exhibited an excellent specific capacitance of 442 F g^{-1} at 0.5 A g^{-1} and extraordinary rate capability.
- The assembled NS-GNR//NS-GNR device showed high energy density of $\sim 23.85 \text{ Wh kg}^{-1}$ at a power density of $\sim 448 \text{ W kg}^{-1}$.

GRAPHICAL ABSTRACT



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ABSTRACT

Heteroatom co-doped carbon-based materials have been demonstrated to be an effective way to realize their new functions in electrode materials for energy storage devices. Herein, a novel strategy for synthesis of highly porous nitrogen-sulfur co-doped graphene nanoribbons (NS-GNRs) with enhanced active sites was developed. The highly porous NS-GNR channels provide efficient ion transport path for electrolyte ions, which enhances the overall conductivity and stability of the electrode materials by energising storage sites. The TEM and STEM-EDS analysis revealed that the NS-GNR materials exhibit uniform distribution of N and S heteroatoms into GNRs matrices. The NS-GNR electrode materials exhibited a high specific capacitance of 442 F g^{-1} at 0.5 A g^{-1} , excellent rate capability and cycling performance with $\sim 98.6\%$ retention of the initial capacitance after 10,000 cycles. Most importantly, the fabricated symmetric supercapacitor device with a wide operating voltage window of $\sim 1.8 \text{ V}$ yield an excellent energy density of $\sim 23.85 \text{ Wh kg}^{-1}$, high power density of $\sim 8753 \text{ W kg}^{-1}$ and superior cycle life (97.9% capacitance retention after 10,000 cycles). Thus, these results exhibit a novel metal-free and low-cost design of electrode materials for high-performance energy storage devices.

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1. Introduction

As energy storage devices, supercapacitors play an important role in portable electronic devices and hybrid electric vehicles

due to their high power density, fast rate capability, long cycle life, and high reliability [1–4]. However, the increasing demand for energy storage system in large scale requires high energy density as well as power density [5,6]. In general, microporous activated carbon with high surface area of $\sim 1500 \text{ m}^2 \text{ g}^{-1}$ have been used for commercial supercapacitors [7]. However, the rate capability of activated carbon is limited because of their difficult ion paths, ensuing in poor pore accessibility of the electrolyte ions at fast charge-discharge process. In order to overcome the problem, numerous research have been focused to develop the other carbon based materials such as carbon nanotubes, graphene, and cubic mesoporous carbon [8–12]. Unfortunately, poor capacitive performance due to their low density/high pore volume impedes its large scale application in supercapacitors at the commercial level [13]. Thus, the development of large scale, advanced porous carbon materials for supercapacitors with high energy and power densities remains a challenging task for the research community.

Recently, graphene nanoribbons (GNRs) extensively were used in high-performance energy storage device application due to their unique porous morphology, high active surface area, low pore volume, excellent electronic properties, and distinctive semi-conducting to semi-metal electrical properties [14–17]. Such chemically oxidized GNRs possess rich edges that would be helpful for enhancing the electrochemical properties, but still basal planes are electrochemically inert to some extent that cannot be entirely utilized. Recent investigations have shown that substitutional doping of GNRs with heteroatoms could significantly enhance the surface activity, electrical conductivity, chemical reactivity, and mechanical properties [18–20]. Nevertheless, further surface modification of GNRs is still needed to provide more active sites.

Atomic-level modifications of carbon nanostructures have provoked significant interest in achieving tuned properties of doped carbon materials [21–23]. More importantly, novel functional materials could be accomplished by atomic doping into carbon as a promising substitute for existing metal oxide-carbon composite materials [24]. Based on the difference in electronegativity between heteroatoms (nitrogen, boron, sulfur and phosphorous) and carbon atoms, heteroatoms doped carbon network with modified electronic structure deliver highly electrocatalytically active sites with a minimized change of conjugation length due to extraordinary charge polarization [25–27]. This unique characteristics of heteroatoms provide carbon materials with superior electrical properties that can be used in various energy storage and conversion devices such as Li-ion batteries, supercapacitors, fuel cells and solar cells [26,28–31]. Although single-doped carbon materials could improve the electrochemical properties to some extent, multiple doping can further enhance the electron transfer progressively because of their different structure and bonding when compared to single atom doped materials. Recently, multiple hetero-atom doping has been shown to offer synergistic effects associated with carbon and doped species [24,32–34]. The introduction of co-doped heteroatoms into carbon material enhance the electrical properties, chemical activity and easy electron transfer, all of which are essential for energy storage applications [35–37]. In general, nitrogen (N) doping into carbon materials has been explored to enhance the structural and electronic properties of the carbon based materials. Besides this, sulfur (S) atom possesses interesting properties that have been used in electronic applications where its easily polarizable electron pairs lead to excellent chemical reactivity [38,39]. In this context, highly active N and S co-doped components provide significantly better structural and electrical properties to the carbon matrix compared to solely doped species. Consequently, to realize this objective, in the present work, it is highly anticipated to process N and S doping into GNRs to obtain exceptional electrochemical properties for

supercapacitors. To our knowledge, the application of N and S co-doped GNR (NS-GNR) in supercapacitors has not been reported.

In this present investigation, we have developed a novel strategy for synthesis highly porous architecture of NS-GNR with enriched electroactive sites for symmetric supercapacitor device application. The NS-GNR material was synthesized by simple, scalable and in-situ thermal annealing method using GONR, cyanamide as a N precursor, and benzyldisulphide as S precursor. The unique porous and highly synergistic NS-GNR material shows highest specific capacitance (442 F g^{-1} at 0.5 A g^{-1}), admirable rate capability, and longer cycle life ($\sim 98.6\%$ capacitance retention after 10,000 cycles) in $1 \text{ M Na}_2\text{SO}_4$ aqueous electrolyte compared to other carbon based materials [7,40,41]. Remarkably, the assembled symmetric supercapacitor exhibits very high energy density ($\sim 23.85 \text{ Wh kg}^{-1}$) with an exceptional rate capability and long cycle life compared to the carbon based symmetric devices. Therefore, NS-GNR would be a promising aspirant for other prospective applications such as metal-free catalysts, fuel cells, lithium-ion batteries, photo catalytic systems, solar cells and biosensors.

2. Experimental

2.1. Synthesis of graphene oxide nanoribbons (GONR)

MWCNTs were synthesized through chemical vapour deposition method reported previously [42]. GONR were synthesized from chemical oxidative unzipping of MWCNTs following the optimized procedure reported in the literature [43]. In a typical synthesis process, MWCNTs (0.15 g) was suspended in concentrated sulfuric acid (36 mL) and stirred at room temperature for 1.5 h, followed by the addition of phosphoric acid (4 mL) for 15 min. Then, potassium permanganate (0.75 g) was added, and stirred for 1 h. The above suspension was heat treated at 65°C for 2 h, then the resulting mixture was cooled to room temperature and poured into ice water (400 mL) with $30\% \text{ H}_2\text{O}_2$ (10 mL). The obtained precipitate was washed with DI water, diluted HCl, ethanol and ether for several times to remove the impurities and also maintain the pH at ~ 7 . Finally, the as-synthesized GONRs (245 mg) were obtained by filtration and drying in vacuum oven at 60°C for 12 h.

2.2. Synthesis of NS-GNR

NS-GNRs were prepared via two-step process: The first step involves the solvothermal treatment by stirring GONRs, cyanamide and benzyldisulphide (1:5:5, weight ratio) in 30 mL pure ethanol at 80°C for 12 h. In second step, the resultant mixture was annealed at 900°C for 2 h under argon atmosphere, ensuing in the NS-GNR. For comparison, N-GNRs and S-GNRs were synthesized using the same procedure without benzyldisulphide and cyanamide, respectively. The pristine GNRs were obtained by thermal treatment of GONRs without the use of precursors of N and S under similar conditions used for doped GNRs synthesis.

2.3. Materials characterization

The morphology of the as-synthesized materials were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL, Japan) installed in the Center for University-Wide Research Facilities (CURF) at Chonbuk National University, high resolution transmission electron microscopy (HR-TEM), scanning TEM (STEM) with elemental mapping (JEM-2200 FS, JEOL Ltd., Japan) at 200 kV in the Jeonju center of KBSI. The morphology of the material was further analyzed by using atomic force microscopy (AFM; XE-100, Park System Co., Korea). The Raman spectra of the materials were obtained using a Nanofinder 30 (Tokyo

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