

Restacking-inhibited nitrogen-incorporated mesoporous reduced graphene oxides for high energy supercapacitors

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ABSTRACT

Graphene is considered a promising active electrode material due to a large surface area, high electronic conductivity, and chemical and mechanical stabilities for supercapacitor (SC) applications. However, the current bottleneck is the fabrication of restacking-inhibited graphene on an electrode level which otherwise loses the capability to achieve the aforementioned properties. Herein, we demonstrate the synthesis of restacking-inhibited nitrogen (N)-incorporated mesoporous graphene for high energy SCs. The melamine-formaldehyde acts as a restacking inhibitor by forming a bonding with reduced graphene oxide (RGO) through a condensation reaction and as an N precursor to be decomposed to create open pores and N sources upon heat treatment. The d-spacing increases up to 0.352 nm and the surface area is as high as 698 m² g⁻¹ with high mesoporosity, confirming restacking inhibition by N incorporation decomposed by melamine-formaldehyde. The restacking-inhibited RGO-based SC cells in organic electrolyte show the specific capacitance of 25.8 F g⁻¹, the energy density of 21.8 kW kg⁻¹ and 85% of capacitance retention for 5000 cycles, which are better than those of pristine RGO-based cells. These improved SC performances are attributed to the fast ion transport through a mesoporous channel in crumpled structure and the doping effect of N incorporation. This work provides a simple yet effective chemical approach to fabricate restacking-inhibited RGO electrodes for improved SC performances.

1. Introduction

The demand for efficient energy storage devices is ever increasing for the replacement of fossil fuel by renewable energy sources and an emerging market such as electrical vehicles [1,2]. Amongst various energy storage devices, supercapacitors (SCs) have gained significant attention because of their high power, fast rate capabilities, and long cycle life [3,4]. The charge storage mechanisms of SCs are based on electric double layer capacitance (EDLC), where charges are stored at an electrochemical double layer by directing ions towards the oppositely charged electrode surface. Consequently, the capacitance is proportional to the amount of charges accumulated on the accessible surface area of the electrode [5,6]. Among various active materials with a high surface area, carbon-based materials such as activated carbon, carbon nanotubes, carbon nanofibers and graphene are in the forefront of SC research [7–9].

Graphene is considered as a promising electrode material owing to its large surface area, high electrical conductivity, and chemical, mechanical and thermal stabilities for SC applications [10]. Theoretically, a single-layer graphene sheet achieves ~ 2600 m² g⁻¹ of specific surface area and can provide specific capacitance up to 550 F g⁻¹ derived

from the intrinsic EDLC of 21 μF cm⁻² [11]. Considering that a large-scale production of graphene is essential for a practical application of SC, solution-based synthesis is suitable for achieving this goal [12]. As a representative solution chemistry, Hummers' method has been revisited to synthesize graphene oxides (GOs) by exfoliating and oxidizing graphite flakes. Although the oxygen functional groups of GOs offer a good dispersion capability due to an electrostatic repulsion and steric hindrance [13], they cannot be applied to SC electrode because the oxygen functional groups reduce the electronic conductivity drastically. The restacking of reduced graphene oxides (RGOs) arising from the reduction of GOs and the fabrication of thick electrode remains a critical challenge for SC applications [10].

Recently, several strategies to inhibit restacking of graphene such as physical and chemical bondings of intercalated compounds or nanoparticles onto the graphene layers have been demonstrated [14,15]. Other chemical methods such as partial oxidation and functionalization acting as pillars have been developed [16,17]. This present work aims to inhibit the restacking of RGO for achieving a high capacitance. To achieve this purpose, we used melamine-formaldehyde as an N precursor present between interlayers of GOs, which was decomposed into a pillar after a heat treatment, prohibiting restacking as demonstrated

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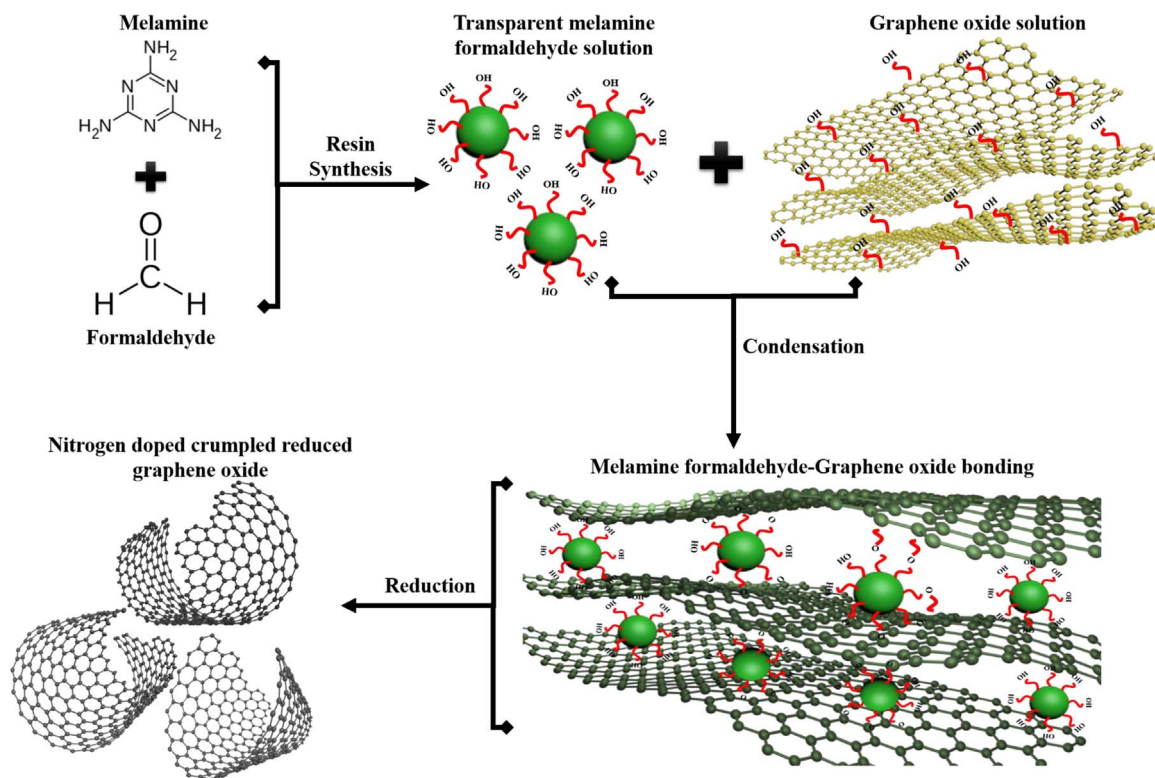


Fig. 1. Synthetic procedure for the synthesis of restacking-inhibited nitrogen-incorporated reduced graphene oxide.

by an enlarged interlayer spacing. The original mesoporosity arising from interlayer voids was preserved after a thermal decomposition of melamine-formaldehyde, while the crumpled structure became more significant by the existence of N species.

2. Experimental section

2.1. Synthesis of N-incorporated RGO

A melamine-formaldehyde solution was prepared by adding melamine and formaldehyde at a weight ratio of 1:2 in 25 ml of DI water with 10 wt% of NaOH solution. A homogeneous solution was observed after it was heated up to 80 °C during a vigorous stirring. A GO dispersion of 10 mg ml⁻¹ was added directly and stirred for about 12 h. The melamine-formaldehyde molecules were adsorbed on the surface of GO, where sample was precipitated in the solution. This precipitate was further purified three times using a centrifuge at 5000 rpm for 15 min to remove residual impurities and dried at 80 °C in a vacuum oven overnight. The partially cured melamine-formaldehyde coated on GO was heat treated at multiple steps of 150, 350, 600 and 800 °C at a heating rate of 2 °C min⁻¹ and the soaking time of 1 h at every step. The samples with a weight ratio of GO to melamine precursor of 1:2 and 1:5 were termed as 2M-NRGO and 5M-NRGO. Finally, RGO was synthesized in similar procedure except for the addition of melamine-formaldehyde and used as comparison samples.

2.2. Characterization

Field-emission scanning electron microscopy (FE-SEM) images were recorded using a JEOL 7100F instrument with Pt metal coating. Transmission electron microscopy (TEM) images were collected on a JEM-3010 high-resolution transmission electron microscope (HR-TEM, 300 kV). The crystallography information perceived through Rigaku D/max IIC (3 kW) with a θ/θ goniometer equipped with a Cu-K α radiation generator. X-ray photoelectron spectroscopy (XPS) data were

obtained using a Thermo MultiLab 2000 system with an Al Mg α X-ray source at 200 W. X-ray diffraction (XRD) data were obtained using a Rigaku D/max IIC (3 kW) with a θ/θ goniometer equipped with a Cu K α radiation generator. Raman spectroscopy was conducted using a SENTERRA Raman microscope (Bruker) with a 532-nm laser. The porous structure was analyzed using a gas analyser (Belsorp-Mini II, BEL Japan Inc.). This test was performed by degassing the sample at 200 °C for 3 h, and Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were carried out to determine the average surface area and pore size distribution.

2.3. Assembly of full cell SCs

A coin cell type of full cell SC was assembled in a symmetric manner. The device performances were characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) through an electrochemical workstation (Bio-Logic Science instrument-VSP). The full cell SCs were fabricated by coating the slurry of sample and PVDF with a weight ratio of 8:2 with NMP as a solvent. The slurry was pasted on the aluminum foil and dried in vacuum for 12 h at 60 °C. The dry sample coated on the aluminum foil was punched into circular discs (SCD) with punching machine. Furthermore, the full cell was assembled placing the SCD, separator, oaring, SCD, wavering, metal disc as depicted in Fig. S1 and sealed with another end disc of the coin cell. An electrolyte of 1M TEABF₄ in acetonitrile (ACN) solvent dropped before and after placing the separator so during the coin cell fabrication. Typically, the mass loading of active materials for all the electrochemical tests was 1 mg cm⁻¹.

3. Results and discussion

Melamine and formaldehyde were reacted to form a methylo-melamine compound. The high ratio of formaldehyde was added in order to bring down the molecular weight of the resin and increase the nucleation sites. The GO solution was then added and its hydroxyl and

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