



A modified molten-salt method to prepare graphene electrode with high capacitance and low self-discharge rate



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ABSTRACT

Graphene is known to suffer from severe aggregation and incomplete recovery of a π - π conjugated system during the reduction process from graphene oxide. Here we report that these issues can be addressed by using a modified molten salt system. The advantages of the molten salt for reducing graphene show in three aspects: (i) prevent restacking; (ii) restore the conjugated network; (iii) serve as reaction medium for KNO_3 activation and nitrogen doping. The molten-salt method-derived graphene (MNG) displays a highly sp^2 -hybrid constitution, nitrogen doping and hierarchically porous structure. With this design, the MNG-based supercapacitor manifests outstanding specific capacitance (234 F g^{-1} and 130 F g^{-1} in 6 M KOH and EMIMBF₄ electrolyte, respectively), high power density, combined with excellent cycling stability and low self-discharge rate. The facile and scalable features of this strategy will be helpful for the rational design of functionalized graphene-based materials for diverse applications.

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1. Introduction

Electric double layer capacitors (EDLCs) is a kind of energy storage device which stores charge with ions at a charged electrode surface [1,2]. It has been developed and commercially used for many decades because of their unique advantages, such as simple principle of operation, high power density, and long cycle life [3,4]. Currently, the greatest challenge of EDLC lies in the relatively poor energy density, which is at least one of magnitude lower than that of rechargeable batteries [5,6]. Considerable efforts have been devoted to developing novel carbon materials in order to achieve a high energy density but without sacrificing the power capability [7–10]. In general, a high-performance EDLC requires carbon materials with high electrical conductivity and large ion-accessible surface area. Beyond that, high ionic transport rate requires short ion diffusion length throughout the carbon electrodes [11].

Graphene, a fascinating two-dimensional (2D) material, has been counted as a promising electrode material for EDLCs because of its high electrical conductivity, large theoretical specific surface area (SSA) and easy modification [12–14]. Among various preparation strategies, reduction of graphene oxide (GO) is considered

the most cost-effective way to produce bulk quantities of graphene [15,16]. Most reduction methods, however, would lead to irreversible restacking or aggregation of graphene sheets due to the π - π interaction [17,18]. Additionally, it is difficult to deoxygenate the functional groups and heal the lattice defects completely [15,19]. These problems will result in following disadvantages: 1) inferior electrical conductivity of graphene materials; 2) insufficient inter-graphene space for ionic flow and small ion-accessible surface area for formation of EDL charge; 3) fast self-discharge (SDC) rate [12,13,18,20] and [21]. To mitigate these challenges, modified reduction strategies have been successively proposed, including chemical and/or physical activation, template-assisted method, and heteroatoms doping [22–27]. For example, Ruoff et al. prepared graphene materials with ultrahigh SSA through activation with potassium hydroxide [28]. It is notable that the porous graphene is highly restored, composing of 98% sp^2 -hybrid bonding compared with graphite. More recently, Abdelkader et al. proposed a molten-halide method to reduce GO and boost the gravimetric capacitance to 200 F g^{-1} [29]. But the operation related to the alkali metal can only be conducted under inert atmosphere, which can hardly be realized in large-scale production. Taken together, a processing- and economical-friendly way for yielding graphene materials with porous structure and optimized surface property is urgently needed.

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In this work, we report a novel strategy to prepare nitrogen (N)-doped porous graphene (MNG) through a modified molten-salt reduction process. The MNG materials display a hierarchically porous structure, highly sp^2 -hybrid constitution and N doping. Significantly, when used as electrode material for EDLC, MNG showed a maximum capacitance of 234 F g^{-1} at a current density of 1 A g^{-1} in a three-electrode system, which is almost threefold of thermally reduced graphene (TRG). A symmetric supercapacitor device composed of the MNG electrodes yielded a remarkable power density of 100 kW kg^{-1} and energy density of 41 Wh kg^{-1} ; and a much slower self-discharge rate than TRG.

2. Experimental

2.1. Materials synthesis

2.1.1. Preparation of GO

GO was synthesized from natural graphite by a modified Hummers' method as described in previous work [30].

2.1.2. Preparation of MNG materials

For a typical process, powders of GO, KNO_3 , and metal chlorides salts ($\text{LiCl/KCl} = 45/55$ by weight), in the weight ratio of 1:1:20, were mixed and homogenized with a ball mill. The homogeneous mixture was then transferred to a tube furnace, heated from room temperature to $600 \text{ }^\circ\text{C}$ under a nitrogen atmosphere at a rate of $5 \text{ }^\circ\text{C min}^{-1}$ and hold for 2 h. After natural cooling to ambient temperature, the as-obtained products were dispersed in large amounts of water to dissolve the soluble salts. The MNG sample was collected from the dispersion through filtration and finally dried overnight at $65 \text{ }^\circ\text{C}$.

2.1.3. Preparation of TRG

TRG was prepared by annealing GO powder at $600 \text{ }^\circ\text{C}$ for 2 h at a rate of $5 \text{ }^\circ\text{C min}^{-1}$ under a nitrogen atmosphere.

2.2. Materials characterization

Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were carried out with a JEOL JSM-6380LV FESEM and JEOL JEM-2010, respectively. Atomic force microscopy (AFM) images were taken in tapping mode with the SPM Dimension 3100 from Veeco under ambient conditions. Powder X-ray diffractions (XRD) was studied by Bruker D8 Advance X-ray diffractometer using $\text{Cu K}\alpha$ radiation. Raman spectra were conducted on the HORIBA Scientific Lab RAM HR Raman spectrometer system with a 532.4 nm laser. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Perkin-Elmer PHI 550 spectrometer with $\text{Al K}\alpha$ (1486.6 eV) as the X-ray source. X-ray absorption near edge spectroscopy (XANES) at the C K-edge and N K-edge were collected on the beamline 08U at the Shanghai Synchrotron Radiation Facility (SSRF). The samples were loaded in an ultrahigh-vacuum chamber at a vacuum of $5 \times 10^{-7} \text{ Torr}$. All spectra were acquired in the total electron yield (TEY) mode with an experimental resolution of 0.1 eV at room temperature. Electrical conductivity was measured by the conventional four-probe DC method (SDY-5 Four-Point probe meter). Thermal gravimetric analysis (TGA) was conducted on a TG-DSC instrument (NETZSCH STA 409 PC) in nitrogen at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from 20 to $800 \text{ }^\circ\text{C}$. The nitrogen adsorption-desorption isotherms of the samples were conducted by using a Micromeritics BK122T-B analyzer. The SSA was determined according to the BET theory in the relative pressure range (0.04–0.2). Pore size distributions were determined from the adsorption branches of the isotherms based on the non-local density functional theory (NLDFT).

2.3. Electrochemical measurements

All the electrochemical measurements were carried out on a CHI 660D electrochemical workstation system. The electrochemical impedance spectroscopy (EIS) measurements were performed at open circuit potential with the 10^{-2} to 10^6 Hz frequency range at an AC amplitude of 5 mV . The cycle life tests were conducted by galvanostatic charge/discharge measurements. The working electrodes was fabricated by mixing active material, acetylene black and polytetrafluorene-ethylene (PTFE) binder with a weight ratio of 80:15:5. The mixture was blended completely and rolled into a thin film. For the three-electrode system, a piece of film containing 5 mg active material was coated on foamed Ni grids ($1 \text{ cm} \times 1 \text{ cm}$) and pressed under a pressure of 16 MPa . The as-prepared samples served as the working electrode, a platinum plate electrode and a saturated calomel electrode served as counter and reference electrodes, respectively. For the two-electrode system, the thin film was punched into circular sheets. Then, the circular sheets were coated onto stainless steel mesh under pressure. Two-electrode system tests were conducted in a 2016-type cell with two nearly identical (by weight and size) film electrodes, using glass fiber (GF/D, Whatman) as separator and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF_4 , >98%) as electrolyte. The assembly process was carried out in an argon-filled glove box.

The gravimetric capacitance (C) was derived from galvanostatic discharge curves as:

$$C = (I\Delta t)/(m\Delta V) \quad (1)$$

where I is the constant discharge current, t is the time for a full discharge, m is the mass of electrode materials and V represents voltage drop on discharging (excluding the IR drop).

The gravimetric (E) energy density against two electrodes in device was calculated as:

$$E = CV^2/2 \quad (2)$$

where V is the operating voltage.

In the potential driving self-discharges, the single potential driving model was:

$$V \propto V_f e^{-t/\tau} \quad (3)$$

and the divided potential driving model was:

$$V \propto V_f e^{-t/\tau_f} + V_s e^{-t/\tau_s} \quad (\tau_f \geq \tau_s) \quad (4)$$

where V is the voltage of the capacitor, V_f is the voltage from which SDC starts, τ is the time constant, t is the self-discharge time.

3. Results and discussions

In our experiment, GO was first blended with a eutectic mixture of LiCl/KCl/KNO_3 and then calcinated under nitrogen atmosphere (Fig. 1a). During the heating process, GO was gradually dispersed in the mixture of molten salts which melt at $375 \text{ }^\circ\text{C}$ and subsequently underwent thermal reduction as well as reaction with KNO_3 . As shown in Fig. 1b, the edges and some parts of the basal plane of GO are terminated by hydrogen, hydroxyl, ether, and carboxylic groups. With the increasing temperature, these groups are released from carbon plane through a dehydration reaction between hydroxyl groups and oxygen groups, followed by recovery of π -bonding [15,31]. In parallel with this composition evolution, N in its highest oxidation state of +5 is reduced to the state of -3 by carbon and

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