



Full Length Article

An all-in-one material with excellent electrical double-layer capacitance and pseudocapacitance performances for supercapacitor



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ABSTRACT

3D porous nitrogen-doped graphene nanosheets (PNGs) are facilely prepared via a simple one-step segmented thermal annealing method, using graphene oxide (GO) as carbon source, urea as nitrogen source and pore generator. During the pyrolysis process at 300 °C, urea and oxygenous groups on GO sheets can release large amounts of gas such as NH₃, HCNO and H₂O, which act as pore generators to tear and strike GO nanosheets to form 3D porous nanostructured material. When the temperature is increased up to 800 °C, a large amount of nitrogen-containing gas can react with the functional groups on GO. Consequently, the pore forming and nitrogen doping processes of GO are successfully realized and 3D PNGs are prepared. The research results show that the PNGs with an optimal N-doping content of 6.9% display a high surface area of 490.2 m² g⁻¹ and excellent electrochemical capacitive performance. The outstanding electrical double-layer capacitance and the increasing pseudocapacitance are attributed to the large specific surface area and the high nitrogen content, respectively. In 1 M H₂SO₄ electrolyte, the PNGs exhibit a specific capacitance of 337.0 F g⁻¹ and a low capacitance loss of 2.4% after 5000 cycles. Moreover, a symmetric supercapacitor with a cell voltage of 1.3 V is assembled, which displays both high energy density and high power density of 19.9 W h kg⁻¹ and 650 W kg⁻¹, respectively. The all-in-one material with excellent electrical double-layer capacitance and pseudocapacitance is promising in supercapacitor.

1. Introduction

Due to the limited reserves of fossil fuels and the associated pollution, exploring clean and environmental friendly energy sources becomes the most concerned problem [1–3]. In decades, supercapacitors (SCs) have drawn wild attention as a new energy storage device owing to their long-term cycling life, high safety and high power density [4–6]. However, compared with other energy storage devices, such as lithium ion batteries, low energy density is one of the uppermost factors to restrict the development and application of SCs [7]. It is expected to be widely used in electric or hybrid electric vehicles (EV or HEV) and other electronic devices if the energy density can be improved dramatically but not sacrifice their high power density and excellent cycle stability.

Generally, the energy density (E) of SCs can be expressed by $E = 1/2 CV^2$, where C represents the specific capacitance (F g⁻¹), V represents the working potential window (V) [8,9]. Apparently, there are two

kinds of measures to improve E, one is to broaden the working potential V and the other is to increase the specific capacitance C through optimizing electrode materials [10,11]. The former depends mainly on the electrochemical decomposition voltage of electrolyte [12]. For example, in aqueous electrolyte, the operating potential is limited at about 1.0 V while the organic-electrolyte-based SCs can be broadened to 3.5 V, and even a 4.0 V ultrahigh potential can be achieved in ionic liquid electrolyte [13–15]. But regrettably, the poor electrical conductivity and expensive cost of organic electrolytes have seriously hindered their application [16]. And the later can be divided into two types, one is electrical double-layer capacitance (EDLC) and the other is pseudocapacitance (PsC) [17]. EDLC, based on the electrostatic charge accumulated on the electrolyte/electrode interface, depends predominantly on the specific surface area (SSA) of electrode material. The electrode materials usually use carbon-based materials (such as carbon nanotubes, active carbon, graphene and porous carbon) due to their large SSA, good electrical conductivity, physicochemical and cycling

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stabilities. [18–22]. PsC, based on quick redox reactions, usually uses redox-active materials including organic conducting polymers (PANI, PPy, etc.) and transition-metal hydroxides/oxides (RuO_2 , MnO_2 , NiO / Ni(OH)_2 , etc.) owing to their much higher theoretical specific capacitances compared to carbon materials [23–28]. Nevertheless, redox-active materials usually present much higher electrical resistivity [29]. In addition, the cycling stability is seriously restricted by the great changes of volume, morphology and structure during the charge–discharge processes [30]. Therefore, taking the characteristics of the above two kinds of materials into consideration, combining redox-active material with carbon material is the most widespread strategy to improve the specific capacitance of the composite. Besides, the cycling stability and service life of the composite were significantly optimized owing to the synergistic effect of redox-active material and carbon material [31–33]. Although the electrochemical capacitance performance of composite material has been improved compared to that of carbon material or redox-active material, the electrochemical capacitance characteristics of the two materials could not be brought into full play due to the shielding effect caused by the mutual contact of the two materials [34,35]. Therefore, preparing an all-in-one electrode material with the outstanding EDLC and PsC performances to replace the composite material is the first-rate choice to reach its full electrochemical capacitance performance.

Recently, implanting functional groups (such as oxygenous groups and nitrogenous groups) and introducing heteroatoms (such as N, P and S) into carbon framework to improve electrochemical performance of carbon materials have been studied extensively [36,37]. N is one of the most promising dopants to replace C atom in carbon materials due to its similar atomic radius to C as well as the wealthy electrons character [38]. Bonding configurations of N-doped carbon materials can be classified into pyrrolic-N, pyridinic-N and quarternary-N [39]. The large amount of pyridinic species can modify the electron donor/acceptor properties of the surface and thereby result in a fast and reversible faradaic redox reaction [40]. The pyridinic-N and pyrrolic-N can trigger redox reactions and are contributed to PsC, while the quarternary-N can enhance the conductivity of carbon materials [41]. That is to say, the doped carbon materials have enormous potential to become all-in-one materials with excellent EDLC and PsC performances.

Graphene, as an attractive carbon material, shows advantages of excellent conductivity, high theoretical SSA and relatively low cost of production [42–44]. Graphene oxide (GO), one of the most important derivatives of graphene, does not present excellent physicochemical properties like graphene due to the sp^2 hybrid orbital structure of graphene was destroyed as a result of implanting abundant oxygenous functional groups [45]. In order to restore its excellent performance and be better applied to SCs, reduced graphene oxide (rGO) was prepared by chemical or thermal annealing method [46]. However, rGO is easy to aggregate and stack owing to the removal of oxygenous groups, leading to a significant decrease in surface area and resulting in a much lower electrical double-layer capacitance. On the other hand, the abundant oxygenous functional groups make GO have more defects and reaction sites, which is beneficial to doping and modification for improving its electrochemical capacitance performance [36]. Therefore, it is very meaningful to develop an effective preparation method, which can not only restrain the aggregation of GO in the reduction process, but also be beneficial to heteroatoms doping so that an all-in-one material with excellent EDLC and PsC performances attributed to its large SSA and high heteroatoms content can be prepared.

In this work, we developed a novel one-step segmented thermal annealing method to prepare 3D porous nitrogen-doped graphene nanosheets (PNGs) with graphene oxide (GO) as carbon source, urea as nitrogen source and pore generator. During the pyrolysis process at 300 °C, urea and oxygen-containing groups on GO sheets can release large amounts of gas such as NH_3 , HCNO and H_2O , which act as pore generators to tear and strike GO nanosheets to form 3D porous nanostructured materials. When the temperature was increased up to 800 °C,

a large amount of nitrogen-containing gas can react with the functional groups on GO. Consequently, nitrogen was doped into graphene skeleton, and PNGs with 3D structure and high nitrogen content were prepared, the PNGs with an optimal N-doping content of 6.9% displayed a high surface area of $490.2 \text{ m}^2 \text{ g}^{-1}$. In 1 M H_2SO_4 electrolyte, the PNGs exhibited a specific capacitance of 337.0 F g^{-1} and a low capacity loss of 2.4% after 5000 cycles.

2. Experimental section

2.1. Materials

Graphite flake natural (~325 mesh, 99.8%, from Alfa Aesar), sulfuric acid (H_2SO_4 , 98%), phosphorus pentoxide (P_2O_5), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl, 37%), urea, poly(tetrafluoroethylene) (PTFE), N-methyl-2-pyrrolidone (NMP) acetylene black. All reagents are analytical grade from Sinopharm Chemical Reagent Co. Ltd., were used as received without further purification.

2.2. Preparation of nitrogen-doped graphene nanosheets

Modified Hummers method was applied for synthesizing GO [47,48]. The PNGs were synthesized through a pyrolysis process using urea as the dopant, and the typical route was as follows, GO suspension was prepared by adding 100 mg GO into 100 mL distilled water and ultrasonic treatment for 1 h. Subsequently, a calculated amount of urea was gradually added into the solution and the mass ratio of urea to GO was controlled at 10:1, followed by ultrasonic treatment for 0.5 h to get a homogeneous suspension. The suspension was moved to a petri dish and dried at 60 °C, and the obtained composite was grinded into fine powder. Subsequently, the powder was pyrolyzed at 300 °C for 3 h at a heating rate of $2 \text{ }^\circ\text{C min}^{-1}$ and then at 800 °C for 2 h at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under N_2 atmosphere. The resulted samples were denoted as PNGs₃₀₀₋₈₀₀. Besides, effects of the mass ratio of urea to GO on the morphology, structure and electrochemical capacitance performance of PNGs were investigated. The related results and discussions could be seen in supporting information. In order to explore the action mechanism of urea in annealing process of GO at different stages, the powder was pyrolyzed at 300 °C at a heating rate of $2 \text{ }^\circ\text{C min}^{-1}$ and 800 °C for 5 h at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under N_2 atmosphere, respectively. The resulted samples were denoted as PNGs₃₀₀ and PNGs₈₀₀. In addition, GO was thermally treated by the identical process in the absence of urea, and the product was marked as rGO for comparison.

3. Materials characterization

Thermal gravimetric analysis (TGA, NETZSCH-409PC) was conducted from room temperature to 800 °C at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ with about 10 mg sample in N_2 (99.999%) with flow rate of 50 sccm. Morphologies and structures of samples were measured by scanning electron microscopy (SEM, Hitachi S-4800). Raman spectra were measured at 632 nm excitation in a Raman spectrometer (Labram-010, France). Elemental compositions of PNGs were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha 1063) equipped with a monochromatic Al K α X-ray source (1486.6 eV). All XPS spectra were recorded by using an aperture slot of Φ 500 μm , survey spectra were recorded with a pass energy of 30 eV. Nitrogen adsorption/desorption isotherms were measured by a Brunauer-Emmett-Teller apparatus (BET, Beckman Coulter SA-3100, USA) and pore size distribution was calculated by Barrette-Joyner-Halenda (BJH) model. About 200 mg samples were used in nitrogen adsorption/desorption measurements and the degassing process took 10 h at 200 °C.

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