One-pot synthesis of lightweight nitrogen-doped graphene hydrogels with supercapacitive properties

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ABSTRACT

A facile and efficient method was developed to prepare nitrogen-doped graphene hydrogels (NGHs) via a one-pot hydrothermal route with graphene oxide (GO) and urea. In the procedure, urea was used as a reducing-doping agent to continuously release NH_3, and N element of which was doped into graphene lattice by three styles (pyridinic N, pyrrolic N, and graphitic/quaternary N). The NGHs have high nitrogen content (ca. 6.04–6.84%), lightweight nature (the density of hydrogel is ca. $0.81–0.94\,g\,cm^{-3}$), and numerous interconnected three dimensional porous networks. Electrochemical characterizations demonstrated the good capacitive behavior ($230.6\,F\,g^{-1}$, at $0.5\,A\,g^{-1}$) and superior cycling stability (capacitance retention ∼90% after 1200 cycles) of NGHs. The possible mechanism of assembly process of NGHs and the N insertion pathway in the hydrothermal route were also proposed.

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1. Introduction

In recent years, graphene-based hydrogels have attracted widespread attention due to its excellent mechanical strength, electrical conductivity, thermal stability and adsorption capability [1–4]. It is also benefited from its prospective applications in energy storage, catalyst supports, sensors and biological fields [5–8]. Therefore, many efforts have been devoted to prepare graphene-based macroscopic framework, including one-dimensional (1D) carbon nano-structure [9], two-dimensional (2D) graphene film [10,11], and three dimensional (3D) graphene-based hydrogel/aerogel [4,5]. Interestingly, the 3D structures with numerous porous framework and excellent intrinsic properties provide graphene-based hydrogel with high specific surface areas and fast electron transport. Generally, self-assembly has been recognized as a simple and efficient technique for integrating nanostructured building units into macroscopic devices with 3D structures [12]. Based on the self-assembly technique, researchers reported kinds of strategies to produce 3D graphene architectures [13], including hydrothermal methods [1,4,14], chemical reduction [15,16], polymerization [17,18], and cross-linking reactions [19,20].

As an important kind of energy storage devices, supercapacitors have drawn much attention because they can provide a higher energy density along with long cycle life than traditional batteries and dielectric capacitors [21,22]. Traditional electrode materials of supercapacitors, such as metal oxides and polymeric materials, have lower rate of charge/discharge, poor durability and high cost that limit their further applications [23–25]. However, 3D graphene hydrogels were proved as a promising candidate for supercapacitor electrode materials because of their relatively low cost, high chemical stability and environmental friendliness, especially for nitrogen-doped graphene hydrogels (NGHs) [26,27]. Up to now, many synthesis methods including hydrothermal methods have been explored to obtain NGHs [26–30]. However, these methods resulted from some weaknesses involving complex process, low nitrogen content, and toxic reagents. Furthermore, most of the resulted NGHs showed high weight although they processed ultrafast super-capacitor properties.

As far as we know, a lightweight nitrogen-doped graphene hydrogel with super-capacitor properties has rarely been reported. Here, we propose an easy self-assembly approach to prepare NGHs via a one-pot hydrothermal route using graphene oxide and urea as the starting materials. The obtained NGHs have not only the lightweight nature (the density of hydrogel is ca. $0.81–0.94\,g\,cm^{-3}$, and the density of aerogel is ca. $0.021–0.028\,g\,cm^{-3}$), but also have high nitrogen content (ca. 6.0% and 6.9%). The interior microstructures of NGHs were observed by field-emission scanning electron microscopy (FE-SEM). Nitrogen adsorption/desorption experiment was used to prove that NGHs had a

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Brunauer–Emmett–Teller (BET) specific surface area of $309.7\,m^2\,g^{-1}$. Fourier transform infrared (FTIR) spectra, Raman spectroscopy, thermogravimetric analysis (TGA), power X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were conducted to demonstrate that a large number of oxygen-containing groups were removed from graphene nanosheets during hydrothermal reaction and nitrogen element was doped in NGHs. Additionally, the results of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge (GCD) measurements showed good capacitive behavior ($230.6\,F\,g^{-1}$, at $0.5\,A\,g^{-1}$) and superior cycling stability (capacitance retention ~90% after 1200 cycles). Finally, the possible mechanism of assembly process of NGHs and the possible N insertion pathway in the hydrothermal route were also proposed.

2. Experimental

2.1. Preparation of GO and NGHs

GO was prepared from natural graphite by a modified Staudenmaier's method according to our previous report [31] (see Supporting information). In a typical procedure, a $2\,mg\,mL^{-1}$ suspension of GO was prepared by the sonication of GO (40 mg) in water (20 mL) for approximately 2 h. Then, a given amount of urea (urea and GO with a mass ratio of 4:1–100:1) was added into the GO dispersion. The mixture was stirred continuously for 15 min. After that, the resulting homogeneous suspension was sealed in a 100 ml Teflon-lined stainless-steel autoclave and maintained at 180 °C for 12 h. Then the autoclave was naturally cooled to room temperature and the column product was obtained (Fig. 1a). Finally, the cylinders were immersed in deionized water at room

temperature for at last 48 h, and the water was changed every several hours to wash out any impurities. For comparison, reduced graphene oxide (RGO) was prepared by the same recipe and procedure except for the use of urea. In this study, the NGHs with different weight ratio of urea to GO are denoted as NGH-n, where the n represents the mass ratio of urea to GO. For example, NGH-30 means the mass of urea was 30 mg, and the mass of GO was 1 mg.

2.2. General characterization

The purified NGHs were directly subjected to dehydrate via freeze-drying process to maintain 3D monolithic architecture for related characterization. The microstructure and morphology of the samples were observed from FE-SEM (ZEISS, Germany). XRD analyses were carried out on a D8A25 Advance (Bruker) X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418\,\text{Å}$) in the 2θ range of 10°–70°. TGA was performed on thermogravimetric analyzer (PerkinElmer TGA-7, USA). FTIR analysis was recorded on a PerkinElmer Spectrum using KBr as a background. Raman spectroscopic analysis was carried out on a Lab RAM HR 800UV (HORIBA Jobin Yvon, France) with excitation wave length of 532 nm. The nitrogen adsorption/desorption isotherms were measured at 77 K using a specific surface area and pore size analyzer (V-Sorb 2800 TP). XPS analysis was collected from a SPeCS system (PHOIBOS 150, Germany) with Al Kα radiation ($h\nu = 1486.6\,eV$). A two-electrode system was used to measure electrochemistry performances of NGHs with a CHI 760E (CH Instruments, Inc.) electrochemical workstation. For measurement the superior cycling stability, we carried out the GCD measurement for 1200 cycles on battery tester Sunway (BTS-5V3A).
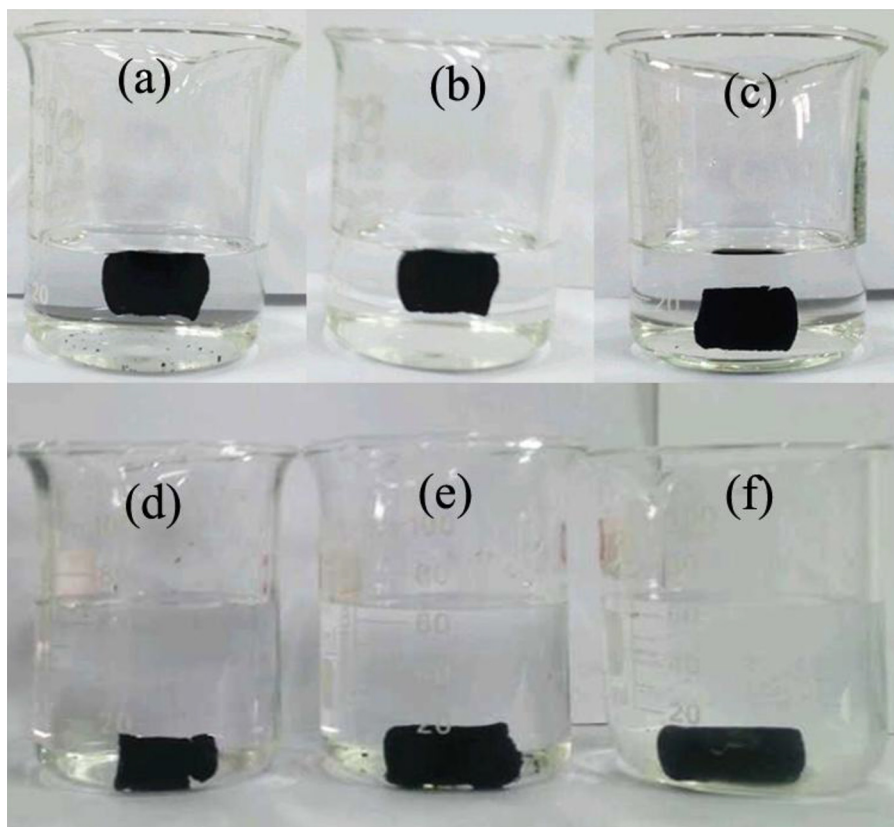
Fig. 1. Photographs of NGH-30 and other graphene hydrogels obtained by chemical reduced methods: (a) NGH-30 in a reaction solution after hydrothermal process, (b) NGH-30 in deionized water, (c) NGH-30 in ethyl alcohol, (d) V_C used as a reduced reagent [15], (e) Fe^{2+} used as reduced reagent [4], and (f) Na_2S used as a reduced reagent [15].