Structure of functionalized nitrogen-doped graphene hydrogels derived from isomers of phenylenediamine and graphene oxide based on their high electrochemical performance

Yubo Zou[a], Wenbin Zhong[a,*], Shichao Li[a], Jinwei Luo[a], Changlun Xiong[a], Wantai Yang[b]

[a] College of Materials Science and Engineering, Hunan University, Changsha, 410082, PR China
[b] Department of Polymer Science, Beijing University of Chemical Technology, Beijing, 100029, PR China

ABSTRACT

Three functionalized N-doped graphene hydrogels were prepared from graphene oxide (GO) and isomers of phenylenediamine through hydrothermal process, which were (1) FONGH prepared with o-phenylenediamine (OPD); (2) FMNGH prepared with m-phenylenediamine (MPD) and (3) FPNGH prepared with p-phenylenediamine (PPD). As-prepared FONGH, FMNGH and FPNGH possessed different microstructures and exhibited different specific surface area: 107.8, 24.3 and 145.2 $m^2 g^{-1}$. The prepared graphene hydrogels were found with different N contents: FONGH (11.1 at.%) > FPNGH (9.8 at.%) > FMNGH (7.2 at.%). High resolution N 1s spectra of as-prepared hydrogels revealed that OPD facilitated the preparation of graphene with high doping level of nitrogen; while PPD was favorable to preparing N-doped graphene hydrogel with high moieties of amine including -NH_2 or N covalent bonded with sp^3-C of graphene. As-prepared FONGH, FMNGH and FPNGH exhibited excellent electrochemical performance with high specific capacitance (645, 365.7 and 467 $F g^{-1}$ at 1 $A g^{-1}$) and superior cycling stability (97.6%, 83.1% and 91% retention at 20 $A g^{-1}$ after 1000 cycles). The different microstructures and electrochemical performance of FONGH, FMNGH and FPNGH were caused by different positions of -NH_2 groups on the benzene rings of OPD, MPD and PPD. The present work proposes a novel idea to prepare functionalized N-doped graphene with high electrochemical performance.

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1. Introduction

Graphene has been widely applied in the fields of catalysis, adsorption, sensors and supercapacitors because of its outstanding properties including large surface area (2630 $m^2 g^{-1}$), ultra-high intrinsic electrical conductivity ($10^7 S m^{-1}$) and superior chemical stability [1–5]. When used as the electrode materials for supercapacitors, it was found in previous studies that the realistic capacitance (100~200 $F g^{-1}$) of graphene-based materials that prepared from chemical reduction of graphene oxide (GO) were much lower than the theoretical value of graphene (~550 $F g^{-1}$) [6–8]. This is mainly ascribed to the restacking of graphene sheets, which decreases the effective specific surface area and leads to unsatisfactory capacitance [7,9,10]. In recent years, much effort has been paid to resolve the restacking issue of graphene so that the prepared graphene based materials can achieve high electric double-layer capacitance, such as, through the construction of 3D network structure in these graphene based materials [11–13].

In previous researches, N-doped graphene was found able to benefit the specific capacitance of prepared graphene materials. The doped N atom can efficiently contribute additional pseudo-capacitance by redox reaction, hence improving the electrical conductivity and the interfacial wettability between the electrodes and electrolyte [14–17]. So far, N-doped graphene materials are generally prepared by chemical vapor deposition (CVD) [6], plasma treatment [15,18], solvothermal process [19,20], thermal annealing treatment [21,22], hydrothermal reaction [16,23–26] and so on. Among these methods, the hydrothermal process is an efficient and facile way to prepare N-doped graphene hydrogels by using N dopants (such as ammonia, urea, amines and so on). The prepared N-doped graphene hydrogels possess 3D network structures which can increase the specific surface area, promote the multidimensional electron transport and rapid ions diffusion, hence improving the electric double-layer capacitance when it is used as electrode.

* Corresponding author.
E-mail address: wbzhong@hnu.edu.cn (W. Zhong).

Meanwhile, N atom doped graphene can contribute extra pseudo-capacitance resulting in an excellent electrochemical performance [13,27–30].

According to the previous researches of N-doped graphene hydrogels that prepared by hydrothermal reaction, it is found that: (1) when hydrazine (N_2H_4) is used as dopant [31–33], prepared N-doped graphene usually shows a lower N doping level than most N-containing compounds, such as urea [34–36], $(NH_4)_2CO_3$ [25] and ammonia (NH_3) [16,24,37], which may be because of stronger reduction effect of N_2H_4. For example, the graphene doped by urea, NH_3 and N_2H_4 displayed the N content of 10.13%, 7.34% and 4.09%, respectively [33,35,37]. (2) As dopants contain $-NH_2$ groups, the steric hindrance of $-NH_2$ group is an important factor to affect the N-doping content in N-doped graphene hydrogels. The $-NH_2$ group in dopant with small steric hindrance is easy to react with oxygen-containing groups of GO, which can be easier to obtain graphene with high N-doping content [26,38]. The graphene hydrogel obtained by L-arginine exhibits a higher N content (8.9%) than that of L-glycine (3.0%) [26]. (3) Moreover, N-containing dopants can react with GO possessing higher N content, and as-prepared N-doped graphene hydrogel possesses higher N doping level [24,26,39]. For instance, the N-doped graphene prepared by using different N-containing dopants, such as diethylenetriamine (N content percentage, 40.7 wt %), tetraethylenepentamine (N, 37.0 wt %) and n-propylamine (N, 23.7 wt %) exhibited different N-doping level: 9.63 at.%, 9.27 at.% and 4.38 at.% [24]. Furthermore, different N species (c.a. Pyridinic-N, Pyrrolic-N and Quaternary-N) play different roles in the electrochemical performance of N-doped graphene. Pyridinic-N and Pyrrolic-N can promote the rapid diffusion and transportation of ions and increase the pseudo-capacitance for their Faradaic reaction. Quaternary-N can remarkably enhance the electronic conductivity and improve the rate capability of supercapacitors. Besides, Pyridinic-N and Quaternary-N can also effectively improve the wettability of the graphene materials [26,34,40,41]. All these results indicate the electrochemical performance of N-doped graphene hydrogels depends on both N-doping content and N species. The N-doped content and N species of N-doped graphene reported previously that prepared by hydrothermal process and using different dopants are listed in Table S1 (Supporting Information). Although the dopants containing $-NH_2$ functional group can react with GO to prepare N-doped graphene via hydrothermal process, how the structure of dopants effects on the N content and N species of as-prepared N-doped graphene, and then how to effect on the electrochemical performance of prepared N-doped graphene still need to be figured out.

Phenylenediamine isomers (o-phenylenediamine (OPD), m-phenylenediamine (MPD) and p-phenylenediamine (PPD)) have two $-NH_2$ groups on ortho-, meta- and para-position of benzene rings, respectively. Their N contents are as high as 25.9 wt %, which can be used to prepare N-doped graphene with high electrochemical performance of graphene [20,42–44]. In this work, Phenylenediamine isomers (OPD, MPD and PPD) were used to react with GO to prepare high electrochemical performance N-doped graphene hydrogels (FONGH, FMNGH and FPNGH, correspondingly) through hydrothermal process. The effect of $-NH_2$ groups position in benzene rings of OPD, MPD and PPD on the chemical structure, N content and N-doped species of as-prepared FONGH, FMNGH and FPNGH were investigated based on their optimal electrochemical performance.

2. Experimental section

2.1. Materials

Natural graphite flake (325 mesh) was obtained from Qingdao, Henglide Graphite Co., Ltd., China. Phenylenediamine isomers (OPD, MPD and PPD), Sodium nitrate ($NaNO_3$), sulfuric acid (98% H_2SO_4), hydrochloric acid (HCl), potassium permanganatepre ($KMnO_4$) and hydrogen peroxide (30% H_2O_2) were purchased from Sinopharm Chem. Reagent Co., Ltd. (Beijing, China). All reagents were used directly without any further purification.

2.2. Preparation of functionalized N-doped graphene hydrogels

GO was prepared by a modified Hummers method from natural graphite flake [13,45]. Functionalized N-doped graphene hydrogels were prepared through one-step hydrothermal process with phenylenediamine isomers. Specifically, the functionalized N-doped graphene hydrogel (FONGH) was prepared with GO and OPD: GO solution was added into the OPD (60 mg) aqueous solution with R_m (the mass ratio of GO to OPD) = 1:1, and was vigorous stirred to form a homogeneous mixture. The final concentration of GO was 2 mg mL^{-1}, and the total volume of mixture was 30 mL. After that, the solution was transferred into a Teflon vessel (50 mL). The vessel was then sealed in a stainless steel autoclave and heated at 180 °C for 7 h. After that, the whole set was naturally cooled down to room temperature. Finally, the prepared FONGH hydrogel was immersed in distilled water to remove the unreacted OPD. FMNGH and FPNGH hydrogels were prepared followed the same process, wherein FMNGH was prepared with R_m (the mass ratio of GO to MPD) = 1:10 and was heated at 150 °C for 12 h; while FPNGH was prepared with R_m (GO: PPD) = 1:5 and was heated at 120 °C for 12 h. As a reference, reduced graphene oxide hydrogel (rGH) was prepared with pure GO but without phenylenediamine under the same preparation condition of FONGH. Additionally, the functionalized N-doped graphene in FONGH, FMNGH and FPNGH was denoted as FONG, FMNG and FPNG, respectively.

2.3. Characterization

The morphologies of prepared hydrogel samples were characterized by Scanning Electron Microscope (SEM, S-4800) and Transmission Electron Microscope (TEM, JEM-2100F). The crystallographic structures of all samples were determined by XRD (Siemens D5000). The Raman spectra were recorded on a spectrophotometer (Varian LR-3) with operating wavelength of 633 nm. The isotherm of N_2 adsorption/desorption was obtained using an ASAP-2020 surface analyzer (Micromeritics Instruments, USA), and the specific surface area was measured by Brunauer-Emmett-Teller (BET) method. The specific surface area of the pores was calculated via Barrett-Joyner-Halenda (BJH) adsorption approach. The X-ray photoelectron spectrum (XPS) was performed on a Thermo 250Xi photoelectron spectrometer (Thermo Scientific).

2.4. Electrochemical measurements

Electrochemical performances of samples were tested by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) in a standard three-electrode system (on a CHI660C electrochemical workstation, Shanghai, Chenhua). Platinum and saturated calomel electrodes (SCE) were used as counter and reference electrodes. The potential range for CV and GCD tests were −0.3 to 0.7 V. EIS tests were carried out in the frequency range of 10^5–0.01 Hz with alternating current oscillation 5 mV. All electrochemical experiments were carried out in 1 M H_2SO_4 aqueous electrolyte at room temperature. The specific capacitance (C) of the electrode materials were calculated by the following equation [14]: $C=It/m\Delta V$, where I is the discharge current (A), t is the discharge time (s), m is the mass of the active material in the electrode (g), and ΔV is the potential (V) of 1 V from −0.3 to 0.7 V.