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Nitrogen-doped graphene for supercapacitor with long-term electrochemical stability

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ABSTRACT

Nitrogen-doped graphene is prepared by a solid microwave method with EDA (ethylenediamine) as the nitrogen source. The experimental results reveal that nitrogen atoms from the grafted EDA molecules on the surface of graphene are successfully doped into the lattices. The NGS (nitrogen-doped graphene nanosheets) sample exhibits outstanding specific capacitances of 197 and 151 F g^{-1} at the current densities of 0.5 and 5 A g^{-1} in 6.0 mol L^{-1} KOH aqueous electrolyte, respectively. Furthermore, the sample also displays more superior rate capacity, which can possess high specific capacitance retention of 77% and 70% at the high current densities of 5 and 40 A g^{-1}, respectively. In addition, a capacity fading lower than 2% after 5000 cycles of charging and discharging is obtained, indicating its long-term electrochemical stability.

1. Introduction

Following the astonishing discoveries of fullerene and CNT (carbon nanotube) in earlier decades, the emergence of graphene has recently opened up an exciting new field in the science and technology of two-dimensional nanomaterial with continuously growing academic and technological impetus [1–3]. Owing to its outstanding intrinsic physical properties, such as extraordinarily high electrical and thermal conductivity, large surface area, and transcendental chemical stability, graphene exhibits great potential for application in supercapacitors [4,5]. Furthermore, the doping in graphene with nitrogen atoms has drawn much attention because conjugation between the nitrogen long-pair electrons and the graphene π-system can change its chemical and physical properties, like modulating electrical conductivity, accelerating the growth of nanoparticles, enhancing the generated materials activity [6,7].

Nitrogen-containing functional groups can be introduced through either in situ doping method or post-synthesis method [8–10]. In situ doping method, nitrogen source is added in chemical vapor deposition process to assure nitrogen atoms are doped in situ in lattices of graphene as it grows [11–13]. By contrast, in post-synthesis method, graphene is treated with nitrogenous molecules at high temperature to conduct nitrogen doping. In this method, GO (graphite oxide) has been most widely used and confirmed to be the most successful raw material for mass production of graphene [14–16], due to the outstanding properties such as high efficient, low-cost operation and environmental friendliness compared with in situ doping method. As a result, post-synthesis method has a much more promising future [17].

NH_3 has been by far the most frequently used reagent to introduce nitrogen atoms into graphene [18]. However, because of the serious toxicity and corrosion, NH_3 sets a great demand on instruments, which is not appropriate for mass production [19,20]. In this study, we develop a rapid and effective solid microwave method with EDA (ethylenediamine) as nitrogen source to synthesize nitrogen-doped graphene. In brief, we utilize the ring-opening reaction between EDA and epoxy groups of GO to fabricate FGS (functionalized graphene nanosheets), and then treat the dried FGS with microwave irradiation to carry out deep reduction and nitrogen doping at the same time.

2. Experimental

2.1. Synthesis of GO

GO was synthesized from flaky graphite powder by a modified Hummers method. In brief, 5 g of graphite powder (180

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mesh, Sinopharm Chemical Reagent Co. Ltd.) and 130 mL concentrated sulfuric acid (98%, Sinopharm Chemical Reagent Co. Ltd.) were put into a 1000 mL graduated beaker and stirred continuously in ice bath for 2 h. Then 15 g of potassium permanganate (Analytic grade, Sinopharm Chemical Reagent Co. Ltd.) was slowly added and the solution was stirred in ice bath for another 2 h. After that, the solution was stirred in water bath at 35 °C for 1 h, further promoting the oxidation of graphite, and this is the mesothermal reaction stage. 230 mL deionized water was added and the suspension was heated up to 98 °C for 30 min, which is hyperthermal reaction stage. At the end of hyperthermal reaction stage, 400 mL deionized water was added, and the solution was centrifuged and washed until neutral to obtain GO suspension.

2.2. Preparation of nitrogen-doped graphene

The GO suspension was diluted to 1 mg mL^{-1}, and then 120 mL of the solution and 1.5 mL EDA (Sinopharm Chemical Reagent Co. Ltd.) were mixed in a 250 mL flask, and refluxed for 6 h at 95 °C. After the reaction, the obtained precipitate was freeze-dried to prepare solid FGS. Nitrogen-doped graphene was obtained by treating the solid FGS in an automated focused microwave system under argon flow at full power for 1 min.

2.3. Characterization

SEM (scanning electron microscopy) images of samples were performed on a JEOL S-4800 FESEM (field emission SEM), while the TEM (transmission electron microscope) image of NGS (nitrogen-doped graphene nanosheets) was obtained on a Philips Tecnai G20 TEM. Surface functional groups were measured using a Bruker Equinox 55 FTIR (Fourier transform infrared spectrometer). XPS (X-ray photoelectron spectra) were obtained on a VG ESCALAB MK II X-ray photoelectron spectrometer. The XRD (X-ray diffraction) patterns were recorded on a Rigaku D/Max2400 diffractometer. Raman spectra were recorded using Renishaw Raman Spectrometer, Germany.

2.4. Electrochemical measurements

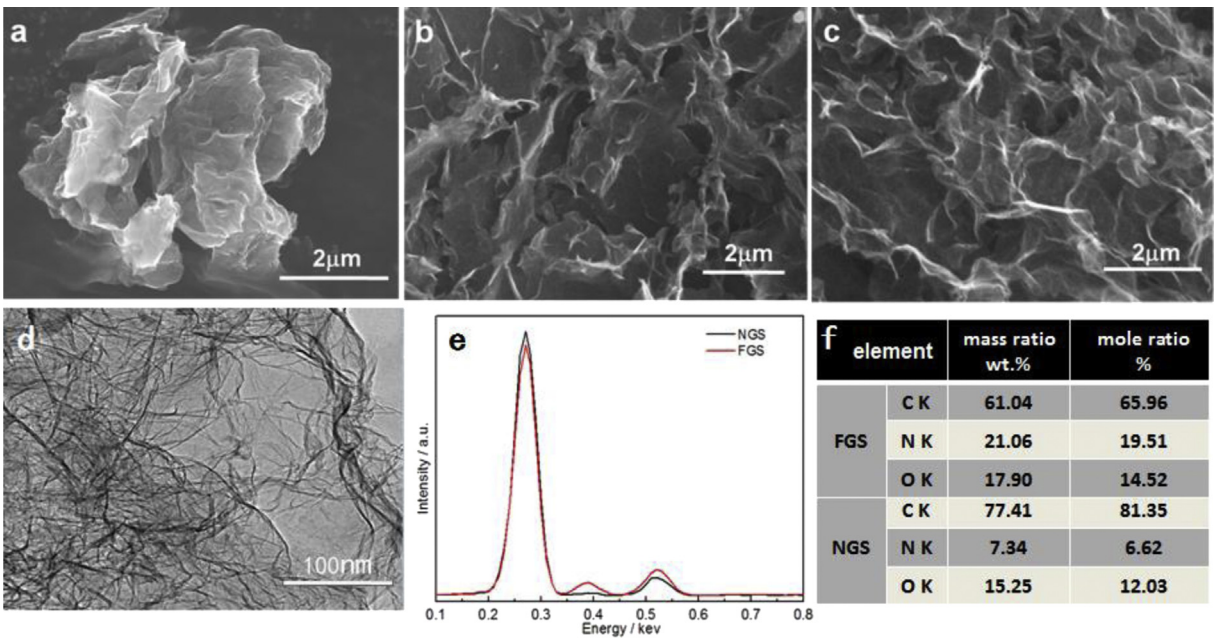
In order to evaluate the capacitive performances of the NGS sample in electrochemical capacitors, a mixture of 80 wt.% the NGS sample, 15 wt.% acetylene black and 5 wt.% PTFE (polytetrafluoroethylene) binder was fabricated using ethanol as a solvent. Slurry of the above mixture was subsequently pressed onto nickel foam under a pressure of 20 MPa, serving as the current collector. The prepared electrode was placed in a vacuum drying oven at 120 °C for 24 h. A three electrode experimental setup taking a 6.0 mol L^{-1} KOH aqueous solution as electrolyte was used in cyclic voltammetry and galvanostatic charge–discharge measurements on an electrochemical working station (CHI660D, ChenHua Instruments Co. Ltd., Shanghai). The prepared electrode, platinum foil (6 cm^2) and SCE (saturated calomel electrode) were used as the working, counter and reference electrodes, respectively. The whole electrochemical measurements were carried out at ~25 °C.

3. Results and discussion

3.1. SEM, TEM and EDS of FGS and NGS

As shown in Fig. 1(a), the GO material was in packing state due to strong interlayer vdW (van der Waals) forces. Functionalization and microwave irradiation effectively reduced the packing state degree of graphene sheets as shown in Fig. 1(c). Furthermore, the exfoliated sheets were distributed randomly and there were numerous winkles on the surface, indicating that graphene could be successfully synthesized through functionalization and microwave irradiation. Fig. 1(d) shows the typical TEM image of NGS. Continuous, transparent and crumpled graphene sheets were stacked together forming the multilayered structure, which was probably caused by the nitrogen atoms doped into the graphene lattices [21]. This kind of structure is conductive to make electrode materials be thoroughly exposed to electrolyte, providing space for forming EDLC (electronic double layer capacitor).

The chemical states of elements in FGS and NGS were analyzed by EDS (Energy Dispersive Spectrometer), as shown in Fig. 1(e), and



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element		mass ratio wt.%	mole ratio %
FGS	C K	61.04	65.96
	N K	21.06	19.51
	O K	17.90	14.52
NGS	C K	77.41	81.35
	N K	7.34	6.62
	O K	15.25	12.03

Fig. 1. SEM and TEM images of GO, FGS and NGS as well as EDS analysis of FGS and NGS.

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