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Short Communication

Synthesis of Nitrogen-Doped Graphene with Microwave

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This letter proposes a novel strategy for synthesis of nitrogen-doped graphene with microwave assisted. We prepared graphite oxide via Hummers method with flake graphite as raw material. Then nitrogen-doped graphene was synthesized by microwave processing of functional graphene sheets (FGS) which is obtained by treating graphite oxide with ethylenediamine (EDA). The nitrogen-doped graphene presents outstanding structure properties. The results showed that nitrogen-doped graphene sheets (NGS) can be successfully synthesized and doped with nitrogen in this method. The synthesized nitrogen-doped graphene was transparent and wrinkled.

Keywords: microwaves; graphene; nitrogen-doped; microwave

1. INTRODUCTION

Graphene is a two-dimensional monolayer of carbon atoms packed into a honeycomb lattice that possesses a wealth of new physics and many fascinating properties, such as extraordinarily high electrical and thermal conductivity, large surface area, and transcendental chemical stability [1-4]. Microwaves, an alternative energy input source, have been widely used because of their internal and volumetric heating of materials, in the field of organic synthesis [5, 6], environmental remediation [3], preparation of catalysts [7] and activated carbon [8]. 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 [9-12].

As a result, most of experiments which synthesize nitrogen-doped graphene prefer NH_3 as the reagent. However, for the reason that NH_3 possesses serious toxicity and corrosion, it sets a great demand on instruments. NH_3 is not the appropriate candidate for mass production [13, 14]. In this letter, we propose a rapid and effective solid microwave method with EDA as nitrogen source to synthesize nitrogen-doped graphene. The ring-opening reaction between EDA and epoxy groups of GO which can graft EDA molecules on the surface of GO is used to synthesize FGS. Then FGS is placed into a microwave oven to carry out deep reduction and nitrogen doping in graphene.

2. EXPERIMENTAL

2.1 Materials preparation

All the chemicals were of analytical reagent and used as received without further purification. In a typical preparation progress, Graphene oxide (GO) was synthesized from flaky graphite powder by a modified Hummers method. In brief, 5g of graphite and 130ml concentrated sulfuric acid were put into a 1000mL graduated beaker and stirred continuously in ice bath for 2h. Then 15g of potassium permanganate was slowly added and the solution was stirred in ice bath for another 2h. After that, the solution was stirred in water bath at $35^{o}C$ for 1h, further promoting the oxidation of graphite, and this is the mesothermal reaction stage. 230ml deionized water was added and the suspension was heated up to $98^{o}C$ for 30min, which is hyperthermal reaction stage. At the end of hyperthermal reaction stage, 400ml 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 1mg/ml, and then 120ml of the solution and 1.5ml EDA were mixed in a 250ml flask, and refluxed for 6h at $95^{o}C$. 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 in the argon protection environment at full power for 1min.

3. RESULTS AND DISCUSSION

3.1 SEM and EDS of FGS and NGS

As shown in Fig.1(a), the GO material was in packing state due to strong interlayer van der Waals (vdW) forces. In Fig.1(b), graphite flakes were interconnected randomly, forming a three dimension solid net framework structure, which results in the higher space utilization and larger specific surface area compared with GO. Fig.1(c) shows typical TEM images of the obtained NGS.

Continuous, transparent and crumpled graphene sheets were stacked together, forming the multilayered structure. This kind of structure is conductive to make electrode materials be thoroughly exposed to electrolyte, providing space for forming EDLC [15].

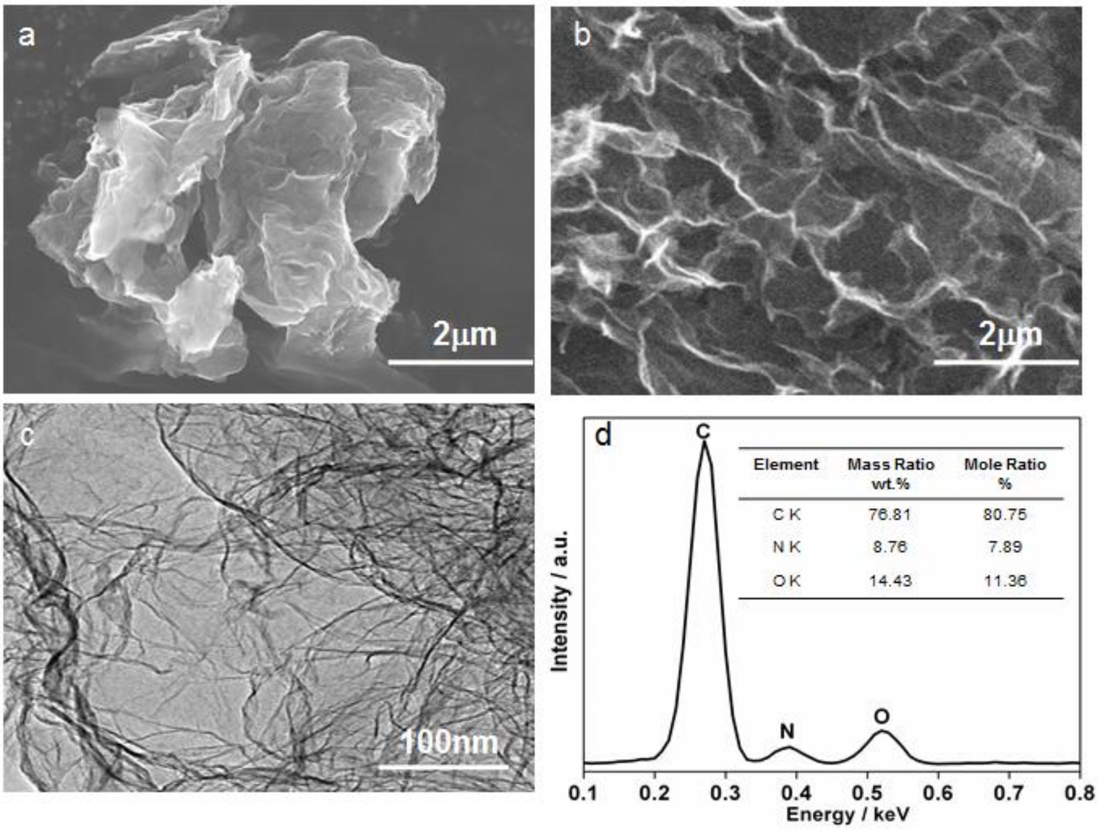

Figure 1. SEM and TEM images of GO, and NGS as well as EDS analysis of NGS

As shown in Fig.1 (d), the chemical states of elements and their mass and mol ratio in NGS were analyzed by EDS. The spectrum of NGS exhibited three peaks at 0.28, 0.37 and 0.50keV, which were the C1s, N1s and O1s peaks, respectively. After function and microwave processing, the polar oxygen-containing functional groups decomposed significantly resulting in that the oxygen mole ratio was just 11.36% which was much less than that of GO. In addition, the nitrogen mole ratio was 7.89%, which indicated the perfect doping of nitrogen in graphene. It is much better than the nitrogen mole ration in the article [14].

3.2 XRD of GO, FGS and NGS

Fig.2 shows the XRD patterns of GO and NGS. The diffraction pattern of GO showed a clear (001) peak centered at 11.48°. However, the (001) peak totally disappeared in the diffraction of NGS, indicating that the introduction of EDA and the following microwave processing sharply weakened interlayer van der Waals (vdW) forces and brought about a great deal of destructive effect to the ordered layered structure of graphite. Furthermore, NGS present a wide (002) peak between 20° and 30°, which demonstrated that its layers were out of order, and its central position shifted to the right, deviating from the (002) peak of graphite. It was due to the reason that the introduction of nitrogen atoms resulted in partial lattice parameter changes of graphene [16].

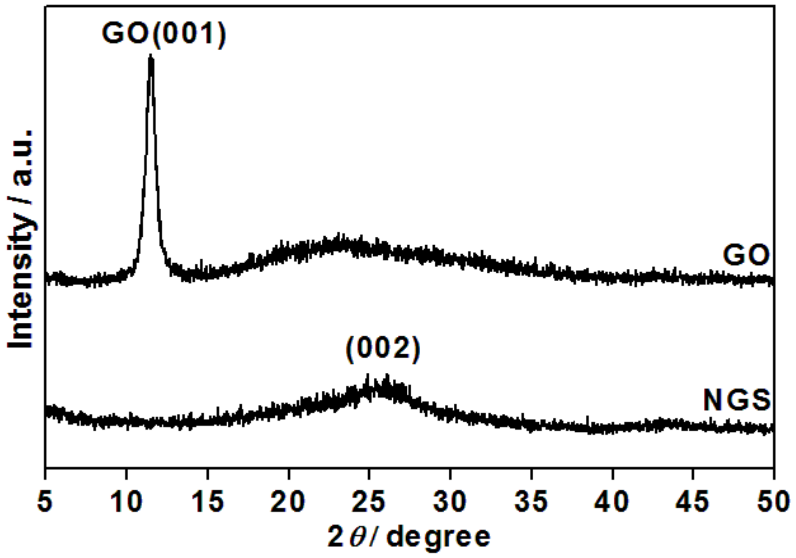

Figure 2. The XRD pattern of GO, FGS and NGS

3.3 Raman of GO, FGS and NGS

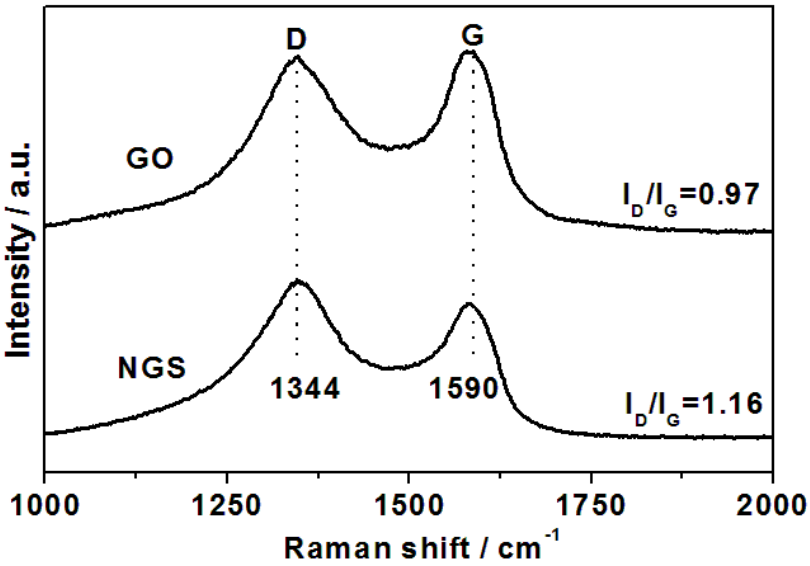

Figure 3. Raman spectra of GO, FGS and GS

Raman spectroscopy is the most direct and nondestructive technique to characterize the structure and quality of carbon materials, particularly to determine the defects, the ordered and disordered structures, and the layers of graphene. Fig.3 shows the Raman spectra of GO and NGS with different exposure time. Both of GO and NGS possessed two remarkable characteristic peaks at 1344cm^{-1} and 1590cm^{-1} corresponding to the well-defined D band and G band, respectively. After intense intercalation reaction, the I_D/I_G of GO was 0.97 which was much higher than that of flake graphite. The EDA function processing brought about more sp^3 hybridization in FGS, which can increase I_D/I_G. However, at the high temperature caused by microwave processing, the functional groups on the surface can be removed efficiently and then the lattice structure can be restored. On the basis of these two factors, the I_D/I_G of NGS was 1.16 [17]. The result is better than the references [18].

3.4 Reaction mechanism in the preparation of NGS with solid microwave method

Plenty of oxygen-containing functional groups grew on the surface of GO during the intense intercalation reaction. They can graft EDA molecules onto the surface of GO through ring-opening reaction with amidogen of EDA. There was a great deal of partially oxidized conjugated area in FGS which can absorb microwave intensely. The high temperature caused by microwave irradiation could remove oxygen-containing functional groups from FGS. At the same time, the grafted EDA molecules decomposed and then were doped into lattices accomplishing nitrogen doping [18-20].

4. CONCLUSIONS

In summary, graphene particles have been prepared by a simple and cost-effective approach. The structure of highly oxidized graphite shows a smooth surface with tightly packed sheets. The good structure and excellent performance suggest its promising application in supercapacitors. This method is quite easy to get than the article [20]. The results showed that nitrogen-doped graphene sheets (NGS) can be successfully synthesized and doped with nitrogen in this method. The synthesized nitrogen-doped graphene was transparent and wrinkled.

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