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Preparation of graphene nanosheets through detonation

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Abstract: Graphene nanosheets were synthesized using graphite oxide as a precursor by detonation. The composition, and structure of graphene nanosheets were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, scanning and transmission electron microscopy, selected area electron diffraction, and Raman spectroscopy. Results indicated that the as-prepared material was transparent and wrinkled, and comprised 2-5 graphenes with a highly crystalline structure. The exfoliation and reduction of graphite oxide to graphene nanosheets was induced by the self-generated thermal energy and shockwave of detonation.

Keywords: Graphene nanosheets; Graphite oxide; Detonation; Exfoliation

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1 Introduction

Graphene is a sheet of carbon atoms bound together with double electron bonds (called as sp^2 bond) in a thin film only one atom thick and is a basic building block for zero-dimensional fullerenes, one-dimensional carbon nanotubes, and three-dimensional graphite[1]. Since its discovery by Novoselov and Geim in 2004, it has attracted numerous investigations into its novel fundamental properties and practical applications[2]. Owing to its high values of mobility of charge carriers, specific surface area and Young's modulus, graphene and chemically modified graphene are promising candidates as components in applications such as nanoelectronic devices, energy storage materials, and polymer composites[3-5].

Many approaches have been developed to prepare graphene materials, mainly including micromechanical or chemical cleavage of graphite, epitaxial growth on silicon carbide or on metal substrates, and bottom-up approaches by chemical synthesis[6-11]. However, reproducible production of graphene sheets in bulk quantity is still a challenge. Recently, Schniepp and coworkers reported a method to produce functionalized single graphene sheets in bulk quantities through thermal expansion of graphite oxide (GO). The mechanism of exfoliation is mainly the expansion of CO_2 evolved into the interstices between the graphene sheets during rapid heating[12-13]. It is well known that a fast decomposition of explosives can produce high temperature and powerful shock wave. Making use of detonation technology to prepare graphite nanopowders has been explored[14].

Herein, we prepared graphene nanosheets (GNS) by detonation, involving complete oxidation of natural graphite (NG), rapid decomposition of explosives, and exfoliation of GO. The as-prepared GNS were systematically characterized, and the exfoliation mechanism of GO was proposed.

2 Experimental

GO was prepared from flake NG (~30 μm, Huayi Co., Ltd, Shanghai) by a modification of Staudenmaier method[15]. NG (5 g) was reacted with concentrated nitric (45 mL) and sulfuric acid (90 mL) with potassium chlorate (55 g). The reaction flask was placed in an ice bath, and the potassium chlorate was added slowly to avoid sudden increase in temperature. The reaction was allowed to hold for 120 h to fully oxidize NG into GO. The GO was thoroughly washed with deionized water until the pH of the filtrate was neutral. The GO slurry was dried and stored in a vacuum oven at 60 ℃ until use.

Exfoliation of GO prepared above was performed by placing premixed GO (2 g) and picric acid (2 g)

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in a sealed stainless steel pressure vessel (10 mL). The detonation was induced by a rapid heating (50 ℃/min) to 200 ℃. When the detonation occurs, about 20 MPa pressure (shock wave) and 900 ℃ temperature were generated inside the vessel. After the detonation, the vessel was cooled in air, gaseous products generated were released, and the solid products were collected.

X-ray diffraction (XRD) measurements were performed using a Rigaku D/max 2500X X-ray diffractometer operated with a step size of 0.02° with Cu $K\alpha$ radiation. Scanning electron microscopy (SEM) was carried out on a FET Quanta 200 FEG. Transmission electron microscopy (TEM) and Selected area electron diffraction (SAED) was carried out on a FEI TECNAI G^2 S-TWIN operated at 200 kV. Raman spectroscopy was performed by using a Renishaw Micro-Raman 2000 with 514 nm argon ion laser. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Ultra using Mg anode.

3 Results and discussion

3.1 XRD patterns

For a successful exfoliation, it is essential to completely eliminate the intergraphene spacing associated with NG during the oxidation stage. The XRD patterns of NG, GO, and GNS are shown in Fig. 1. NG showed a sharp and intensive peak at $2\theta = 26.6^{\circ}$, indicating a highly ordered crystal structure with an interlayer spacing of 0.336 nm. After oxidation for 120 h, the 002 diffraction peak of NG disappeared, revealing a full oxidation of NG. The interlayer spacing of GO was 0.81 nm, which is close to the reported value of 0.83 nm depending on the ratio between GO and water. The increase in the interlayer spacing should be attributed to the oxygen-containing functional groups bonded to the graphene sheet. In contrast, no apparent peaks were detected in the pattern for the as-prepared GNS, indicating a complete elimination of stacked layers to high degree of exfoliation. This feature is similar to that of chemically reduced graphene[16].

3.2 SEM and XPS spectra

Figs. 2a and 2b show the SEM images of NG and GO, respectively. During the oxidation process, the sizes of NG flakes decreased from 30 to 10 μm of GO. Although the interlayer spacing of GO is roughly twice of NG, the surface morphology was not changed seriously. The appearance of bright edges and smooth stages across the area arises from the presence of oxygenated functional groups. Fig. 2c shows the SEM image of GNS derived from the detonation of GO, with an expanded, loose and porous structure. The top view (Fig. 2d) of GN particle reveals the agglomeration of rippled silk-like GNS. The side view (Fig. 2e) of GN particle further confirms the appearance of transparent GNS with wrinkles and folds. Comparing with the worm-like structure of exfoliated graphite reported above, such GNS gave much thinner thickness and higher degree of GO exfoliation[17].

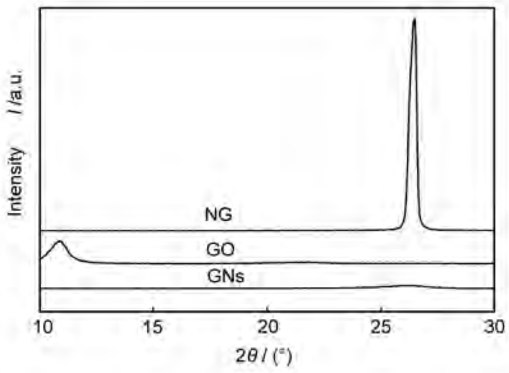

Fig. 1　XRD patterns of NG, GO and GNS

XPS analysis was carried out to investigate the element composition of GO and GNS, as shown in Fig. 2f. Two peaks centered at 284.5 eV and 532.6 eV can be assigned to C1s and O1s signals. Quantitative analysis of GO showed a C/O molar ratio of 2/1, attributed to the oxygen-containing functional groups attached to the graphene sheets, which is consistent with the literature report[7]. For GNS obtained from detonation, XPS gave a C/O molar ratio of 10/1, which resulted from the decomposition of oxygen groups. Such an oxygen content is similar to that of hydrazine-reduced graphene oxide, indicating the reduction of GO in the detonation process.

3.3 TEM and SAED pattern

Figs. 3a and 3b show the TEM images of as-prepared GNS. The transparent GNS were corrugated with size of a few square micrometers. The low contrast feature indicates the small thickness. The corrugation is intrinsic to GNS, which results from the fact that the 2D membrane structure becomes thermodynamically stable via bending. Fig 3c shows a high-resolution TEM image of a single graphene. The visible graphitic lattices revealed that the GNS only consist of 2-5 graphitic layers. The SAED pattern of the featureless region shows the typical hexagonally ordered lattice of carbon in graphene (Fig. 3d). The sharp diffraction dots confirm the high crystalline structure of the as-prepared GNS. The intensity ratio of I{1100}/I{2110} < 1 is a unique feature for

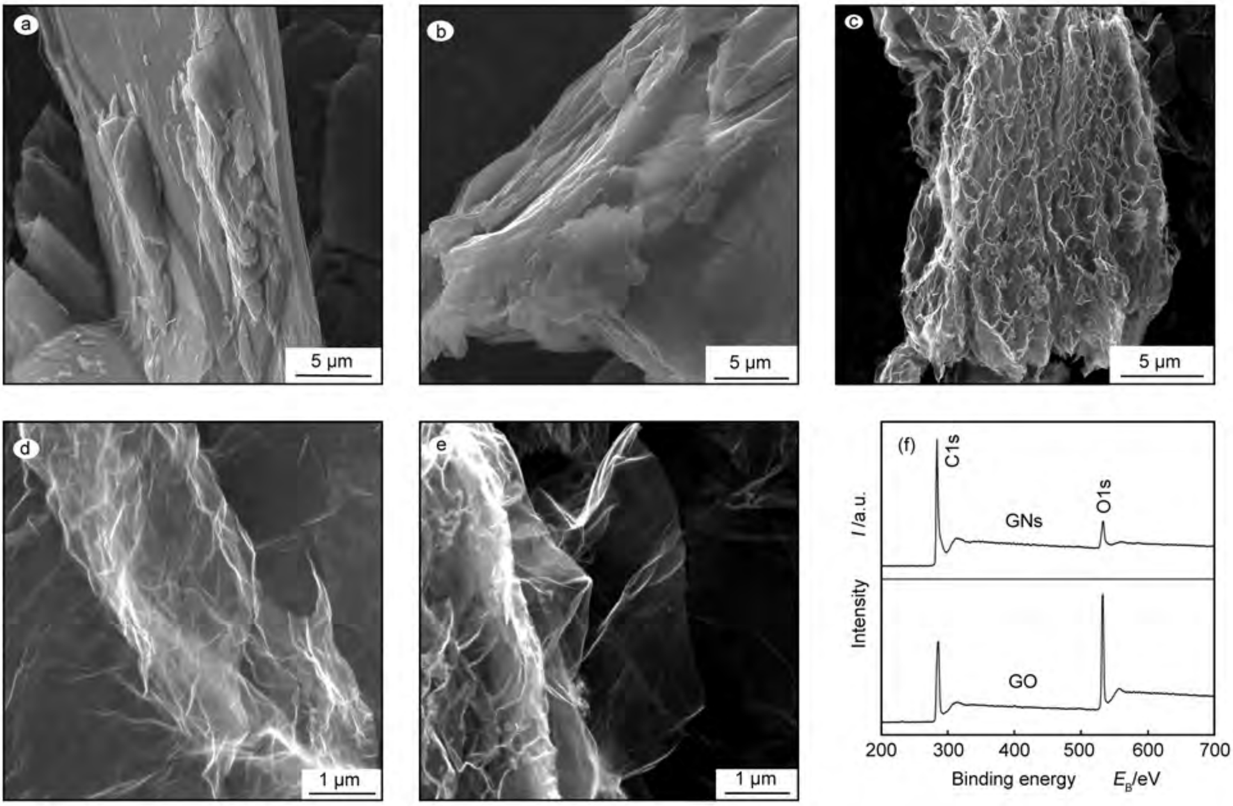

Fig. 2　SEM images of (a) NG, (b) GO and (c) GNS particle. (d) Top view and (e) Side view of GN particle shown in (c). (f) XPS spectra of GO and GNS

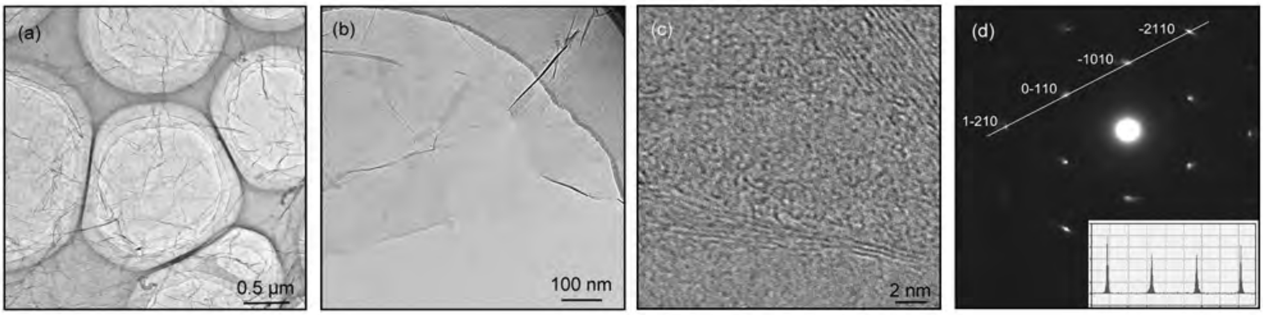

Fig. 3　(a, b) TEM and (c) high resolution TEM images of GNS. (d) SAED pattern of transparent region

multilayer graphene[18]. Therefore, the TEM and SAED results demonstrated that the obtained GNS were graphene with a few layers.

3.4　Raman spectroscopy

Raman spectroscopy is a powerful nondestructive tool to characterize carbonaceous materials. The G band corresponds to the E_{2g} phonons of C sp^2 atoms, whereas the D band is a breathing mode or k-point photons of A_{1g} symmetry. The intensity ratio of D and G bands, I_D/I_G, is a measure of disorder degree and average size of the sp^2 domains. Fig. 4 shows Raman spectra of NG, GO, and GNS. NG exhibited a strong G band at 1582 cm^{-1} and a relatively weak D band at 1350 cm^{-1}. For GO, the G band broadened significantly and shifted upward to higher frequency of 1595 cm^{-1}, and I_D/I_G increased to 1.5, indicating the reduction in size of the in-plane sp^2 domains due to the extensive oxidation. For GNS, the G band sharpened and shifted back to 1585 cm^{-1}, and I_D/I_G decreased to 0.75, indicating the restore of the in-plane sp^2 domains, due to a graphitic "self-healing" in heat treatment. The 2D band is the most prominent feature in the Raman spectrum of graphene, and its position and shape are sensitive to the number of layers of graphene[19]. The GNS exhibited a single, symmetrical 2D band at 2700 cm^{-1}, corresponding to the graphene with a few layers. The Raman results provide further

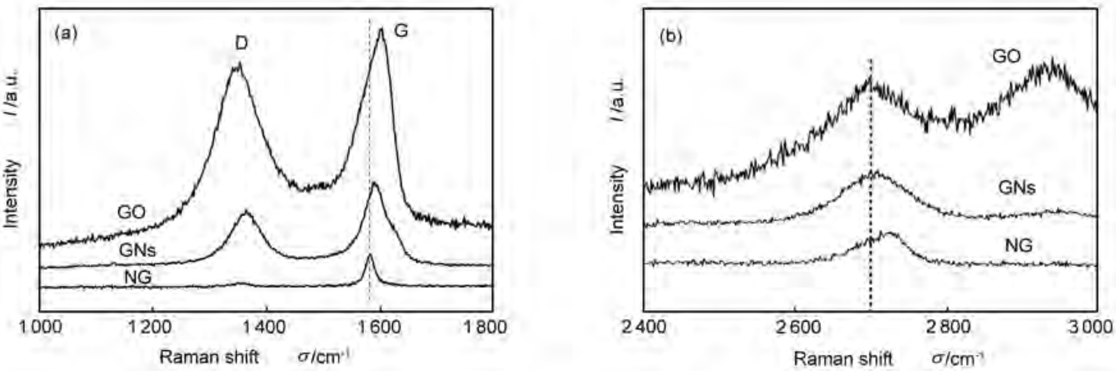

Fig. 4 Raman spectra of NG, GO and GNS, in the region of the (a) D and G bands and (b) 2D bands

evidence to the synthesis of graphene with a few layers by detonation.

3.5 Mechanism of exfoliation

Based on the above analysis, the exfoliation mechanism of GO is proposed in Fig. 5. First, NG was completely oxidized into GO, resulting in abundant oxygen-containing functional groups bonded to the basal planes of the graphite structure. Second, the detonation of GO was induced by a rapid heating and the self-generated enormous thermal energy and a powerful shockwave at a microsecond scale. Last, GO was rapidly heated to high temperature and its oxygen-containing functional groups decomposed into CO_2 and H_2O. The expansion of the gases evolved into the interstices between the adjacent graphite sheets resulted in the exfoliation of GO. The reduction of GO was simultaneously completed accompanied with the decomposition of functional groups. The shockwave formed during the detonation sheared GO into small fragments.

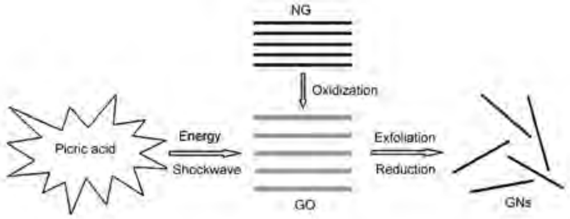

Fig. 5 Schematic illustration of the exfoliation and reduction of GO

4 Conclusions

Detonation was demonstrated to be an effective method for simultaneous exfoliation and reduction of GO to GNS. The synthesized GNS exhibited transparent wrinkled structure and comprised few graphitic layers. This method offers a fast, convenient, and energy-saving option to prepare GNS of high quality in large scale.

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爆炸法合成石墨烯

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摘　要： 以石墨氧化物为前躯体,采用爆炸法合成石墨烯。利用 XRD,SEM,XPS,TEM,SAED 和 Raman 等测试手段对石墨烯的形貌,成份和结构进行表征。结果表明,石墨氧化物在爆炸产生的热量和冲击波的作用下发生完全剥离并被还原成石墨烯。新合成的石墨烯呈透明褶皱状,含有 2 层 ~5 层石墨层,并具有较好的晶体结构。

关键词： 石墨烯;石墨氧化物;爆炸;剥离

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