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A new method for few-layer graphene preparation via plasma-assisted ball milling

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ABSTRACT

We report a new method for few-layer graphene (FLG) preparation via plasma-assisted ball milling with carbide, nitride or oxides as ball-milling media and expandable graphite raw material. Scanning electron microscopy, transmission electron microscopy and Raman spectroscopy were applied to characterize the FLG. FLGs prepared by using different ball-milling media such as boron nitride (BN), tungsten carbide (WC), zinc oxide (ZnO), iron oxide (Fe_2O_3) and germanium oxide (GeO_2) were used to determine the relationship between the FLG layer number and inductive capacity of the ball-milling media. Parameters for the synthesis of high-quality FLGs were also optimized.

1. Introduction

Since graphene was discovered by Geim and Novoselov [1], it has been a significant topic of global research interest. As a type of two-dimensional material, graphene is formed from a regular hexagonal carbon layer, which makes it the thinnest and most robust material globally [2]. Graphene shows good application in the electronics, information, energy and material science field [3–9].

Thus far, the main preparation methods for graphene include mainly mechanical exfoliation [10–15], oxidation-reduction [16–21], chemical vapor deposition [22–25], peeling carbon nanotubes [23], electric arc processing [26–29], epitaxial growth [30–32] and thermal expansion [33–37]. These methods may be imperfect. Although high-quality graphene has been prepared by mechanical exfoliation, carbon could be amorphous in this method [38,39]. For epitaxial growth, strict temperature conditions (>2740 K) and the high cost of single-crystal substrates such as SiC [31] and Ru [32] prevent the mass production of graphene. Oxidation–reduction is considered to be a feasible preparation method, however the incomplete reduction of the oxygen-containing group prevents the decrease in electric conductivity. Because traditional ball-milling techniques could destroy graphite to yield amorphous carbon, a new simple ball-milling method should be developed to solve this problem. Minimal previous research has focused on the influence of a ball-milling medium on graphene. We provide evidence to show that the ball-milling medium influences the graphene quality.

We report a new method for few-layer graphene preparation via plasma-assisted ball milling (P-milling) and control the number of graphene layers by varying the ball-milling media. P-milling offers a simple, cost-effective and pollution-free method for preparing nanomaterials. It accelerates mechanochemical reactions to pave the way for the future large-scale production of energy storage materials [40–44]. In this work, few-layer graphene (FLG) was prepared via plasma-assisted ball milling, with expandable graphite as raw material and BN, WC, ZnO, Fe_2O_3 and GeO_2 as ball-

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milling media. The structure and morphology of the FLG were characterized by Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Six-layer FLG nanosheets were prepared by P-milling for 8 h with WC as ball-milling medium. The inductivity capacity of the ball-milling media influenced the number of FLG layers. When the inductive capacity of the ball-milling media approached 8, the prepared FLG was of the highest quality and the FLG layer number was less than 7.

2. Experimental

2.1. Chemicals

WC, GeO_2, BN(h), Fe_2O_3 and ZnO (99% purity) was purchase from Aladdin Industrial Corporation (Shanghai, China). Expandable graphite (100 mesh, 99% purity) was obtained from Qindao Xinghua Graphite Products Co., Ltd. All of the reagents employed in this study are commercially available analytical-grade and used as received without further purification.

2.2. Few-layer graphene sample preparation

Expandable graphite was calcined at 1000 °C for 15 min at 5 °C/min under Ar atmosphere to obtain worm-like expanded graphite (EG). A mass ratio (4:1) of WC to EG was mixed and placed in a stainless steel vial. Stainless steel balls were sealed with the mixture under argon and the weight ratio of the ball to powder was 50:1. The detail and mechanism of the P-milling is explained and described in our previous paper [45,46]. The ball mill and the milling cylinder were vibrated with a double amplitude of 7 mm and a frequency of 16 Hz. During P-milling, the voltage was 15 kV, the current was 1.5A and the discharge frequency was 60 kHz. The WC and EG mixtures were treated by P-milling for 2 h, 5 h, 8 h and 10 h and WC/FLG-2h, WC/FLG-5h, WC/FLG-8h and WC/FLG-10h samples were achieved, respectively. For comparison, different ball-milling media GeO_2, BN, Fe_2O_3 and ZnO were used to prepare samples GeO_2/FLG, BN/FLG, Fe_2O_3/FLG and ZnO/FLG for 10 h, respectively, in the same way. After preparation, the FLGs prepared by Fe_2O_3 or ZnO were washed by 1 M H_2SO_4 aqueous solution to achieve high carbon content samples. For the other samples such as the FLGs prepared by WC, which could not be eliminated by chemical method, we dispersed it into ethanol and got the supernatant after centrifugation in 100 rpm for 1 min. After drying ethanol solution, the FLGs could be obtained. The purified samples were dispersed in ethanol and then they were dropped in aluminum foil before the EDX measurement.

2.3. Instrumentation and measurements

The sample structure and phases were identified by X-ray diffraction (XRD, Mini Flex 600) with Cu–Kα radiation. The morphology was analyzed by SEM (Carl Zeiss Supra 40). Structural details were characterized further by TEM (JEOL JEM-2100) at 200 kV. For the TEM observant ions, samples were prepared by dispersing the as-prepared powders on Cu grids. Raman spectra were obtained on a Jobin-Yvon Labor Raman HR-800 Raman system with an Ar-ion laser of 514.5 nm at 10 mW.

3. Result and discussion

In P-milling process, it mainly offers mechanical energy, electron impact and heating impact to prepare FLG sample. Mechanical energy is generating by the friction and collision from the milling media and the stainless steel balls providing shearing force to exfoliate graphite [47]. Meanwhile, a breakdown of argon gas generates plentiful plasmas and electrons providing shocks to create a large pressure on the powder and keep it in high stress state [48]. Then, partial metal overheats occur in the stress points of powder and it leads to the thermal explosion to form ultramicro particles. During traditional ball-milling, graphite forms amorphous carbon more easily. EG could form FLG more easily by using plasma discharge as the ball milling media can insert into the graphite layer and exfoliate it more efficiently. The mechanism of preparation process of few-layer graphene is illustrated in Fig. 1.

3.1. FLG prepared by WC as ball-milling medium

Fig. 2 shows the SEM image of FLG prepared with WC as ball-milling medium for different ball milling times. After P-milling, white and elliptical WC particles were coated with some translucent few-layered graphene. As the P-milling period increases from 2 to 5, 8 and 10 h as shown in Fig. 2 (a) to (d), respectively, the coating graphene becomes more blurred and translucent, which shows that the graphene becomes thinner and thinner.

Fig. 2 also shows the TEM image of the WC/FLG samples. After 2 h of plasma-assisted ball milling, the FLG appears as a folding lamellar structure. The number of layers is only 12 in the thin area but it reaches more than 20 in the thick area as shown in Fig. 2(e). When the P-milling period increases to 5 h, the number of graphene layer decreases to 16 as shown in Fig. 2(f). This indicates that the graphite layers were exfoliated more completely as the P-milling period increased. When the P-milling time reached 8 h, the number of layers was 6 as shown in Fig. 2(g). The selected-area diffraction pattern (SADP) as inserted in Fig. 2(g) shows the diffraction pattern of WC with the crystal plane (1 0 0), so WC still retained a crystal shape after 8 h of P-milling. The diffraction rings from the (0 0 2), (1 0 1) and (0 0 4) crystal planes of the carbon material appear in the SADP. The graphite crystal structure was broken and shows a typical nanocrystalline character after 8 h of P-milling. When the ball milling time increases to 10 h, the WC remains the same, whereas the graphene has a non-layered structure as shown in Fig. 2(h). These results indicate that both graphite crystals had been damaged and formed an amorphous structure as confirmed by the inserted SADP in Fig. 2(h). Fig. 3(a) shows the error bar diagram for the layer number of WC/FLGs samples, the short lengths of error bars in different P-milling periods proves that the layer number has been well controlled through DBDP method. The data were selected from the typical few-layer graphene structure of the TEM images. After the purification process which is described in the experimental section, the samples with high carbon content were achieved. Fig. 3 (b) and (c) show the energy dispersive spectrometer (EDS) analysis of the purified FLGs prepared by WC and Fe_2O_3 respectively, only carbon element peak, which was contributed by FLGs, and aluminum element peak, which was offered by Al foil are found, and it proves that the contamination had been eliminated. The TEM results show that 8 h is the most ideal P-milling time for FLG preparation, when WC was chosen as the ball-milling medium. Dielectric barrier discharge P-milling is different from conventional mechanical milling in that it exhibits a synergistic effect of rapid heating of the discharge plasma, high-energy electron acceleration by the high voltage that is applied between the positive and negative electrodes and the impact stress of mechanical milling. This method has been used to prepare Sn/graphite composite anodes for Lithium-Ion Batteries (LIBs) [49], where Sn particles could be refined rapidly and be well-dispersed in the graphite matrix.

Raman spectroscopy is a useful tool to investigate the electronic properties of carbon-based materials. The Raman spectra of the WC/FLG that were prepared by using EG and unexpanded graphite with different ball-milling times are given in Fig. 4. All WC/FLGs