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Melamine assisted solid exfoliation approach for the synthesis of few-layered fluorinated graphene nanosheets

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ABSTRACT

Fluorinated graphene (fluorographene) has attracted increasing attention due to the combination of unique properties of graphite fluoride and graphene. Development of fluorographene-based technology relies on the availability of fluorographene nanosheets in large quantities. Here, a melamine assisted solid exfoliation method is developed for the synthesis of fluorographene nanosheets. Under optimized solid ball milling condition, micrometer-sized ultrathin (less than 2 nm in thickness) fluorographene nanosheets can be exfoliated from graphite fluoride in the presence of melamine. The melamine assisted solid ball milling method is facile and highly efficient, and holds great promise for the large-scale preparation of few-layered fluorographene nanosheets.

1. Introduction

Fluorinated graphene, combining the unique properties of graphite fluoride and graphene [1,2], has attracted considerable attention in recent years. Fluorographene has been found to exhibits high mechanical strength, high Young's modulus, high thermal stability [3], and excellent dielectric properties [4]. Theoretical and experimental studies also show that the band-gap of fluorographene can be varied from 0 eV to 3 eV with changing degrees of fluorination [3,5–8]. Owning to the novel properties, fluorographene nanosheets have attracted great attention for the application in a wide range of fields such as batteries [9], gate dielectric [10], energy storage [11], and hydrogen storage [12].

Up to now, a number of methods have been developed to synthesize fluorographene nanosheets. High quality fluorographene has been produced by direct fluorination of graphene with F_2 [3], XeF_2 [5,7] and plasma (CF_4, SF_6 and ClF_3) [13–16]. However, the fluorination reaction usually requires toxic fluorinating agents, which may hamper the practical applications of the fluorination methods. Previous studies also demonstrated that few- or single-layered fluorographene sheets could be synthesized by ultrasonicating graphite fluoride particles in polar solvents such as sulfolane [17], isopropanol [18], cetyl-trimethylammonium bromide [19], N-methyl-2-pyrrolidone [20], ionic liquid [21] and Na_2O_2/HSO_3Cl [22]. However, the yields of fluorographene obtained from liquid exfoliation methods are usually lower than 5%. Therefore, facile and efficient method for the preparation of fluorographene nanosheets is still highly demanded.

Ball milling, a common technique in powder production industry, has been widely used for the production of inorganic nanosheets from layered materials [23–25]. Here a facile and efficient melamine assisted solid exfoliation method was developed to synthesize fluorographene nanosheets from graphite fluoride. Our results show that few-layered fluorographene nanosheets can be efficiently prepared by ball milling graphite fluoride with melamine under optimized condition. This facile solid exfoliation method is highly efficient and holds the great promise for large-scale preparation of ultrathin fluorographene nanosheets.

2. Experimental

2.1. Preparation of fluorographene nanosheets

Graphite fluoride powder with a formula of $(CF_{0.25})_n$ was purchased from Alfa Aesar. In a typical experiment, 0.40 g of mixture of $(CF_{0.25})_n$ powder and melamine (Kermel chemicals of Tianjin) with a $(CF_{0.25})_n$/melamine weight ratio of 1/3 was mechanically milled under argon atmosphere at a rate of 80 rpm for 6 h using a Retsch PM400 planetary ball mill. All the manipulations were conducted inside a glove box filled with purified argon. After ball milling, the product was washed with hot deionized water to

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remove melamine from the product. The obtained sample was centrifuged, washed with ethanol, and dried in vacuum at room temperature.

2.2. Characterization

Scanning electron microscopy (SEM) images were performed on a Quanta 200 FEG (FEI Co.) scanning electron microscope. Transmission electron microscopy (TEM) images were obtained with JEOL 2000EX. High resolution transmission electron microscopy (HRTEM) images were obtained with JEOL 2100 Transmission Electron Microscope. Atomic force microscopy (AFM) analysis was conducted in veeco multimode 3D. Powder X-ray diffraction (XRD) patterns were recorded on an X'Pert Pro (PANAnalytical) diffractometer with Cu K_{α} radiation. Raman spectra were taken with a He/Ne laser (514 nm) as the excitation source by using a Renishaw Raman spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 infrared spectrometer. The X-ray photoelectron spectroscopy (XPS) measurements were performed using an Escalab 250 Xi X-ray photoelectron spectrometer (Thermo Scientific) with nonmonochromatic AlKa radiation.

3. Results and discussion

SEM image shows that the pristine $(CF_{0.25})_n$ particles have grain size in the range of 2–15 μm (Fig. 1a). The post milled $(CF_{0.25})_n$ sample shows a decreased grain size in the range of 0.5–5 μm (Fig. 1b). TEM image reveals that milled $(CF_{0.25})_n$ sample exhibits typical nanosheet structure, and the nanosheets are almost transparent under the electron beam (Fig. 1c). HRTEM and AFM were further applied to explore the thickness of the $(CF_{0.25})_n$ fluorographene nanosheets. HRTEM image shows that the majority of the exfoliated $(CF_{0.25})_n$ fluorographene nanosheets are less than 2 nm in thickness, and the number of constituting layers mostly ranges from 2 to 8 (Fig. 1d). AFM result also confirms that the ultrathin $(CF_{0.25})_n$ fluorographene nanosheet has an average thickness of approximately 2 nm (Fig. S1), which is in agreement with the HRTEM observation.

The XRD pattern of $(CF_{0.25})_n$ fluorographene nanosheets is almost identical to that of pristine $(CF_{0.25})_n$, revealing that no structural change occurred during the solid ball milling process (Fig. 2a). The intensity of (002) peak of $(CF_{0.25})_n$ fluorographene decreases obviously compared with that of pristine $(CF_{0.25})_n$ due to the ultrathin thickness of $(CF_{0.25})_n$ fluorographene nanosheets. A weak D band (1338 cm^{-1}) which is associated with the graphitic lattice vibration mode with A_{1g} symmetry can be observed in the Raman spectrum of pristine $(CF_{0.25})_n$ (Fig. 2b). The intensity of D band of $(CF_{0.25})_n$ fluorographene increases apparently, indicating a significant amount of edge defects have been introduced into the $(CF_{0.25})_n$ fluorographene nanosheets. Additionally, the D′ band at 1601 cm^{-1}, associated with the structural defects, appears as a shoulder peak of G band in the Raman spectrum of $(CF_{0.25})_n$ fluorographene. The pristine $(CF_{0.25})_n$ gives an asymmetric and split 2D band at around 2701 cm^{-1}. Remarkably, a relatively sharp and symmetric 2D peak can be observed for the $(CF_{0.25})_n$ fluorographene nanosheets. XPS was also used to identify the chemical composition and bonding states of the exfoliated $(CF_{0.25})_n$ fluorographene nanosheets. Three C1s peaks centered at 284.8, 286.8 and 289.8 eV, corresponding to the C-C, C-F_2 and C-F bonds, respectively, can be observed for $(CF_{0.25})_n$ and $(CF_{0.25})_n$ fluorographene (Fig. 2c). The intensity of C1s peak at 286.8 eV decreases significantly after exfoliation, indicating that some F_2 absorbed on

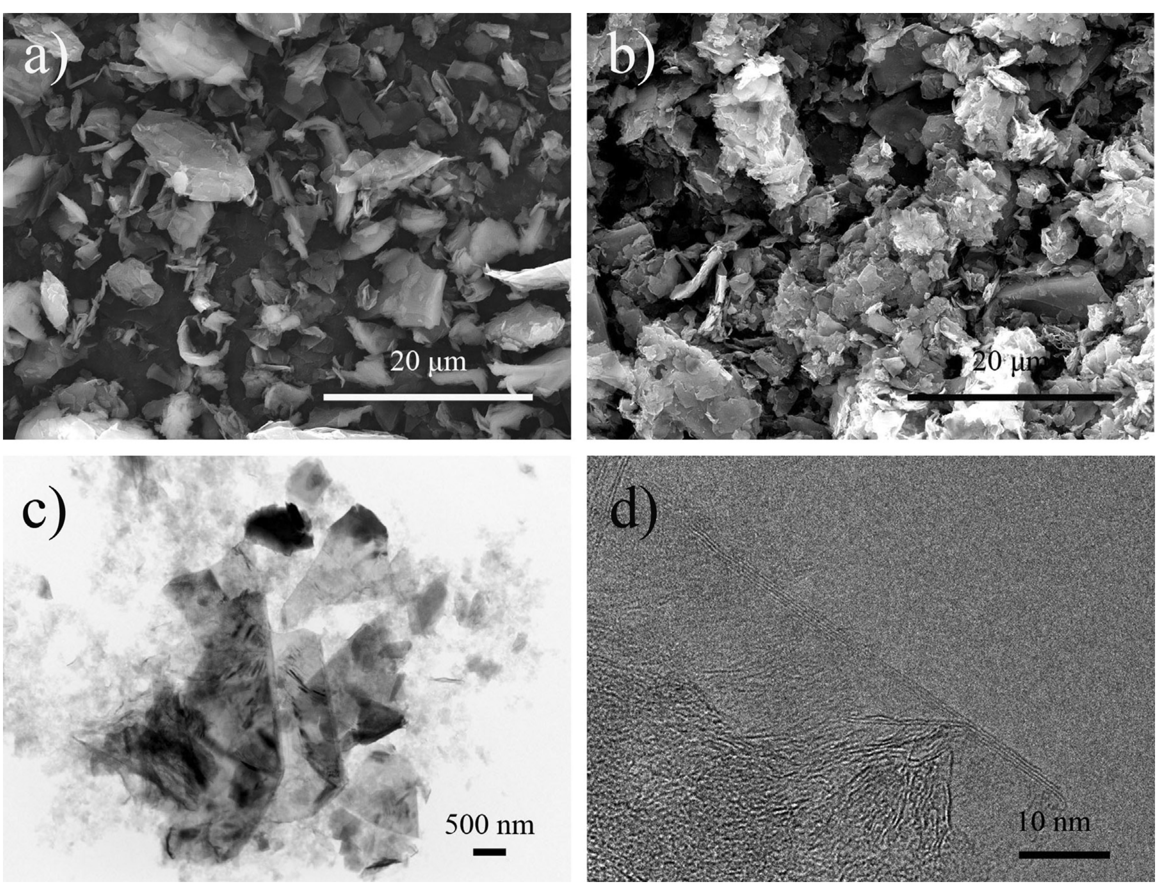

Fig. 1. SEM images of (a) pristine $(CF_{0.25})_n$, (b) $(CF_{0.25})_n$ fluorographene nanosheets, (c) TEM, and (d) HRTEM images of $(CF_{0.25})_n$ fluorographene nanosheets.