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Short communication

One-step chemical exfoliation of graphite to ~100% few-layer graphene with high quality and large size at ambient temperature

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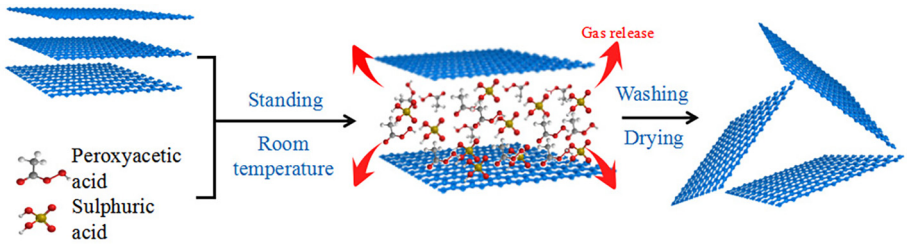
HIGHLIGHTS

- A novel system for the one-step chemical exfoliation of graphene is proposed.
- Peroxyacetic acid is used to exfoliate graphite into graphene for the first time.
- The exfoliation yield is ~100% with ~64% of the graphene sheets being < 5 layers.
- The average areal size for the graphene sheet is up to 190.8 μm^2.
- The prepared graphene possesses a high electrical conductivity of 1.46×10^5 S m^{-1}.

GRAPHICAL ABSTRACT

The Peroxyacetic acid (CH_3COOOH, PAA) and H_2SO_4 binary-component system is first used to exfoliate graphite into few-layer graphene by one-step at room temperature. In the novel system, PAA acts as the oxidant to open the graphite edge. At the same time, the excess PAA may be partly dragged into the gallery by H_2SO_4 during its intercalation. Due to its chemical instability, the dragged PAA may decompose and release O_2 gas to cause the instantaneous pressure rise within the graphite interlayer gallery. Once the pressure rise is big enough to overcome Van Der Waals force between the graphite layers, graphite will be exfoliated into the graphene sheets.



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ABSTRACT

The development of cost-effective preparation routes for high-quality graphene is important for its large scale application. Here, we propose an one-step scalable preparation method of few-layer graphene (FLG) by the exfoliation of flake graphite in a novel binary-component system comprised of peroxyacetic acid and sulfuric acid. This provides a ~100% yield of FLGs from the starting graphite in 4 h at room temperature. The as-prepared FLG sheets behave a few-layer feature (average layer number < 5 layers) and possess large areal sizes (the maximum areal size can be up to 420 μm^2, average sheet areal size is 190.8 μm^2). Furthermore, the resulting FLG also exhibits a high quality with few structure defects (the oxygen content is only 1.2%) and thus possesses a superior electrical conductivity of 1.46×10^5 S m^{-1}. The present method shows great promise for the mass production of high-quality graphene sheets.

1. Introduction

Graphene is a single layer material formed by the sp^2 electron orbital hybridization of carbon atoms [1]. Owing to its unprecedented properties, graphene has become the most focused nanomaterial of the past decade [2,3]. Nevertheless, The realization of the commercial application of this two-dimensional material currently suffers from the lack of scalable methods for its high-efficiency and low-cost production. Liquid-phase exfoliation usually exfoliates graphene from natural graphite at room temperature and atmospheric pressure by intercalating solvent molecules such as *N*-methylpyrrolidone (NMP) between graphite under the assistance of ultrasound [4], However, this method

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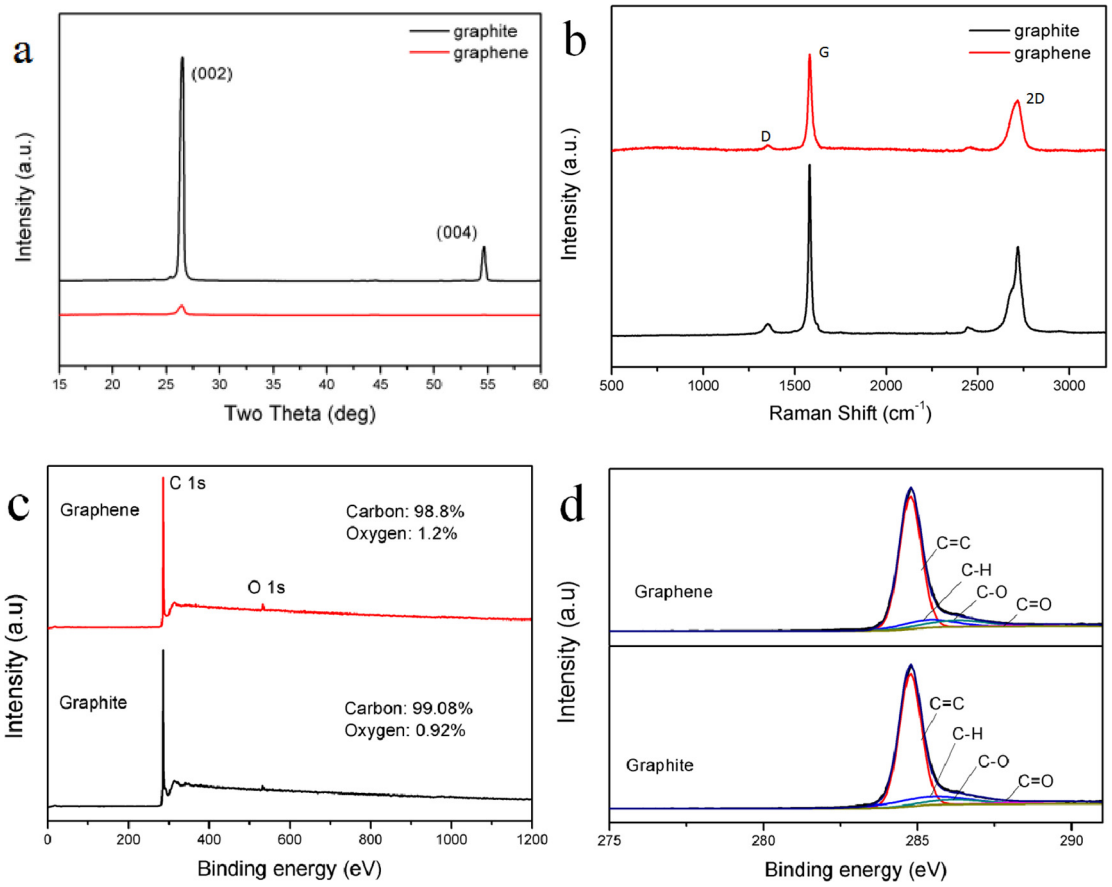

Fig. 1. Structure characterizations of NG and as-obtained graphene, (a) XRD patterns of NG and as-obtained graphene; (b) Raman spectra of NG and as-obtained graphene; (c) XPS survey spectra of NG and graphene; (d) High resolution XPS spectra of C 1s.

suffers from the problems of low yield and being time-consuming, which will hinder its practical application. Moreover, since the graphite sheets are easily broken up into little fragments under ultrasonic treatment, the size of graphene flakes obtained are very small, leading to the difficulty in the collection of the flakes [5]. Oxidation-reduction of graphite is the commonly used method for the industrial production of graphene at present [6]. Nevertheless, this traditional approach often requires the use of hazardous oxidizing agent (e.g., $KMnO_4$), toxic reductants and rigorous reaction conditions (e.g., high reduction temperature), thereby leading to the structural damage and the inferior quality of graphene as well as the environmentally detrimental impact caused by the effluent of the waste acid. Thus, the facile and scalable methods for the low-cost and high-efficiency production of high-quality graphene are still urgently desired.

Recently, Tour et al. [7]. developed a cost-effective chemical exfoliation method of graphite to graphene nanosheets. The exfoliation of flake graphite is performed in the tricomponent system made by a combination of ammonium persulfate ($(NH_4)_2S_2O_8$), concentrated sulfuric acid, and fuming sulfuric acid, acquiring a ~100% yield of graphene nanosheets in 4 h at room temperature. However, the exfoliated graphene nanosheets are relatively thick, most of them being 10–35 nm in thickness. Thereafter, Ding et al. [8], successfully prepared few-layer graphene sheets (≤10 layers) by exfoliation of graphite in a binary-component system of sodium persulfate ($Na_2S_2O_8$) and concentrated H_2SO_4. However, the removal of Na^+ metallic ion existing in the sewage will bring an extra cost, which is unfavorable to the large scale application of this method.

Herein, we proposed a facile and cost-effective method to produce few-layer graphene sheets by exfoliation of graphite in a novel binary-component system. This chemical exfoliation system is comprised of peroxyacetic acid (PAA) and sulfuric acid, and PAA is used to exfoliate the graphite for the first time. The preparation procedure is simple and feasible. By mixing the graphite in the binary-component system and then standing for 4 h at room temperature, the starting graphite completely loses its interlayer registry and transforms into the few-layer graphene sheet with a ~100% yield, not involving the use of mechanical action such as stirring or sonication.

2. Experimental

2.1. Sample preparation

To prepare the graphene, firstly, 10 mL of concentrated sulphuric acid was mixed with 3 mL of PAA. Then, 0.1 g of natural graphite (NG, purity of 99%, +50 mesh, produced in Man Country, China) was added into the resultant mixture and stirred simply under ambient conditions, acquiring a turbid liquid comprised of PAA, H_2SO_4 and NG. The mixing was accompanied by gas evolution from the partial decomposition of the peroxyacetic acid. After simple standing for certain time at room-temperature, the complete exfoliation of the NG was achieved in 4 h. Finally, the reaction mixture was quenched with deionized water, and, the as-prepared graphene turbid liquid was washed with deionized water until the filtrate was neutral. The obtained graphene was dried in air until there is no water surplus.

2.2. Characterization

X-ray diffraction (XRD) powder patterns of the samples were taken on Rigaku D/MAX-2500 powder diffractometer with Cu-Kα radiation (λ = 0.154 nm) operated at 40 kV and 200 mA. Raman spectra were