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# High-yield production of high-quality graphene by novel electrochemical exfoliation at air-electrolyte interface

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ABSTRACT

An end-face electrochemical exfoliation (EFEE) strategy for scalable graphene preparation is established, which has the confined area and thus guarantees uniform current density at the air-electrolyte interface, different from the traditional electrode set-up. The production of graphene is presented that has excellent yield (~100%) and outstanding conductivity ($3.8 \times 10^4$ S m$^{-1}$ with a graphene loading of 0.7 mg cm$^{-2}$). The exfoliation mechanism is also discussed.



## 1. Introduction

In recent years, the electrochemical preparation of graphene has become a potentially scalable method because it has the advantages of single-step, easy operation and eco-friendliness [1,2]. One of the most important parameter for scale-up by electrochemical exfoliation approach is the yield of exfoliated graphene. Up to now, electrochemical exfoliation of graphite anode in $(NH_4)_2SO_4$ electrolyte applying a constant voltage of 10 V can efficiently produce graphene with a yield of 75% [3]. However, the quality of graphene and the continuity of process were difficult to be effectively controlled due to the destruction of graphite electrode from the uneven current during the electrolysis [4]. Thereby Wang et al. used graphite foil coated with paraffin as working electrode to keep the electrochemical exfoliation in confined space in concentrated NaOH electrolyte, yielding ~100% low-defect graphene [5]. This method effectively solves the problem of current distribution on electrode surface during the electrolysis. However, the paraffin-sealing process of graphite and the post-treatment of alkali are tedious, making it incapable of mass preparation of graphene. Thus, the development of a simple, continuous, and controllable exfoliation method aiming at yield improvement is needed for mass production of graphene.

Herein, we demonstrate a novel EFEE method at the air-electrolyte interface to obtain the high-quality graphene with excellent yield (~100%) from the graphite foil in $(NH_4)_2SO_4$ electrolyte. By keeping the bottom end face of graphite foil in contact with the electrolyte surface continuously, a controllable and scalable production of graphene with high yield and high quality becomes promising and hopeful.

## 2. Experimental

The graphite foil ($120 \times 40 \times 0.05$ mm$^3$, density: 1.6 g cm$^{-3}$, purity: 99%) was used as anode, and a $10 \times 10$ cm$^2$ titanium mesh was used as cathode in the electrochemical system. The graphite foil was placed vertically over the electrolyte surface, and its bottom end face was always in contact with the electrolyte surface (depth: ~1.0 mm), as shown in Fig. 1a. When a constant voltage of 30 V was applied for 10 min in a 0.5 mol L$^{-1}$ $(NH_4)_2SO_4$ electrolyte, the electrolysis current was always maintained at 5.5–5.7 A (current density: ~7.0 A cm$^{-2}$) by adjusting the height of the lifting platform. The average lifting rate of the platform was 0.16 mm s$^{-1}$, and a total length of 9.5 cm graphite foil (0.2925 g) was exfoliated in the electrolyte (Fig. 1b). The dispersion was washed 5 times with deionized water, and then probe-tip sonication (400 W, 20 kHz) for 10 min. Subsequently, the dispersion was centrifuged at 2000 rpm (relative centrifugal force: 358 g) for 10 min, and no sediment was found (Fig. S1a). The yield of the obtained graphene can be considered as ~100%, which is much

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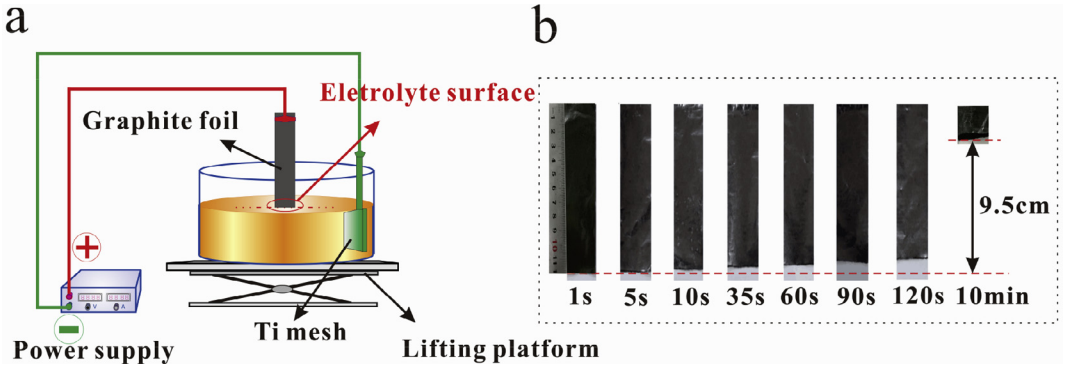


**Fig. 1.** (a) The experimental set-up diagram of the EFEE method. (b) Photographs of graphite anode with different time.

higher than those obtained from prior reported electrochemical methods, as summarized in Table S1. The dispersions (1 g $L^{-1}$) were dripped on the polyethylene terephthalate (PET), and dried overnight under 60 °C. Subsequently, the PET-graphene was rolled at 5 MPa and 80 °C to obtain a graphene paper.

At the same time, the electrochemical exfoliation of a partially immersed electrode (EEPI) was studied. The same size of graphite foil anode fixed on glass supporting plate by adhesive was immersed into a 0.5 mol $L^{-1}$ $(NH_4)_2SO_4$ electrolyte with a depth of 9.5 cm (Fig. S2a). The traditional electrochemical exfoliation process was performed, and the changes of anode edge or waterline part (blue circles), together with that of center part (red circle) with time were shown in Fig. S2b. As the structural strength of the electrode was damaged, large numbers of graphite without fully exfoliation fell off prematurely. From 100 s to 180 s, the current of EEPI decreased rapidly in the final period of electrolysis, shown in Fig. S3. Using the same post-treatment procedures as the EFEE method, large numbers of graphite particles were separated by centrifugation (Photographs in Fig. S1b, FE-SEM in Fig. S4). The obtained graphene was only 0.1372 g, a yield of 46%.

## 3. Results and discussion

Field emission scanning electron microscopy (FE-SEM) image (Fig. 2a) clearly shows crumpled silk veil and transparent morphology of as-prepared flakes, a typical morphology of few-layer graphene. Randomly observing the folded edge of the flakes (Fig. 2b) by high resolution transmission electron microscopy (HR-TEM), the image shows a 6-layer graphene, and the interlayer spacing of graphene (0.351 nm) is larger than that of graphite (0.335 nm), demonstrating that the EFEE process increases the interlayer spacing of graphite. The selected area electron diffraction (SAED) pattern in the inset of Fig. 2b exhibits a typical 6-fold symmetric diffraction with strong diffraction rings, indicating the conserved crystallinity of graphene. Fig. 2c shows the typical atomic force microscopic (AFM) image of graphene with 1.036 nm height, indicative of few-layer (<3 layers) graphene. The lateral size and thickness distribution were analyzed by selecting 62 graphene sheets from Fig. S5. The distribution of lateral size is shown in Fig. 2d, exhibiting a ranging of 0.3–5.0 μm. The thickness distribution is 0.34–4.0 nm in Fig. 2e, implying the 8 layers or less. Fig. 2f is

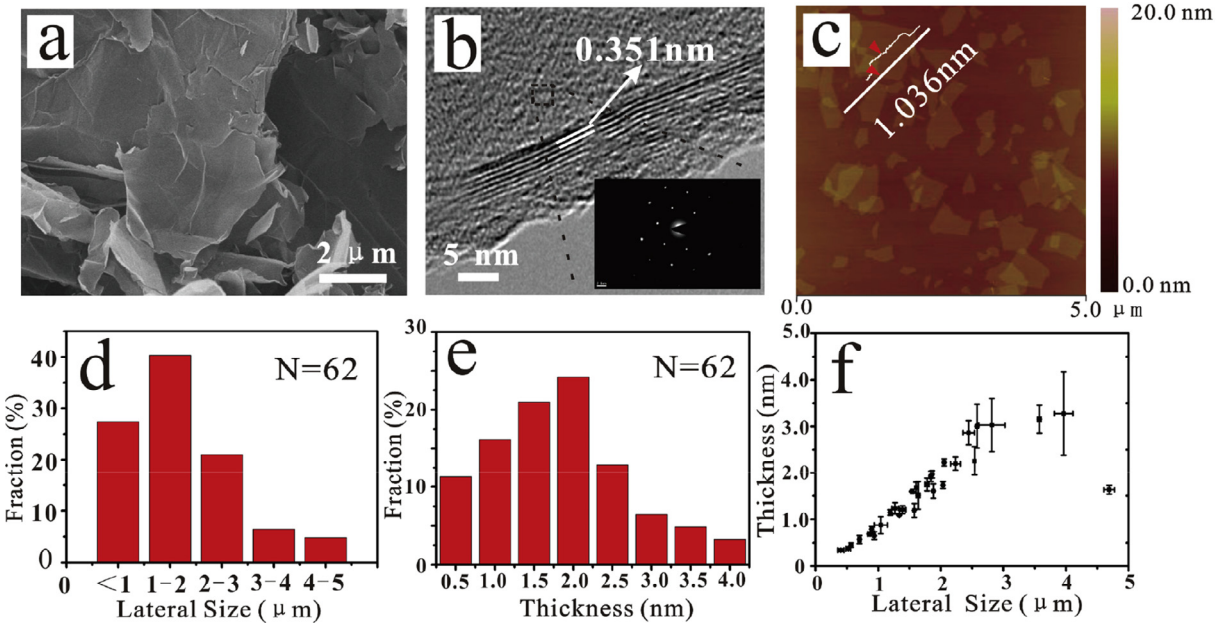


**Fig. 2.** Graphene characterization. (a) FE-SEM; (b) HR-TEM; (c) AFM; (d) Statistical lateral size analysis and (e) Statistical thickness analysis from AFM; (f) Flake thickness vs lateral size from AFM.