Synthesis and characterization of graphite nanoplatelets

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Abstract. We report a facile method for the synthesis of graphite nanoplatelets (GNPs) from a carbon rod. GNPs were produced by vacuum filtration of a suspension obtained from electrochemically exfoliated carbon rods. The resulting GNPs were characterized using scanning electron microscopy, atomic force microscopy, ultraviolet-visible spectroscopy, and Raman spectroscopy. GNPs had sizes of 40–170 nm, thickness of 2.8–5.8 nm and were well dispersed in dimethyl sulfoxide. We discuss a possible mechanism for the formation of GNPs in our experiments.

1. Introduction
Graphite nanoplatelets (GNPs) have recently attracted considerable attention as a cost effective substitute for carbon nanotubes in many applications [1]. GNPs combine beneficial properties of graphite such as thermal and electrical conductivity with those derived from their unique size and shape [1]. However, in spite of the intriguing properties of these materials there are few reports about the synthesis of such materials. Therefore, it is important to explore ways of synthesing them and understanding their properties. Electrochemical exfoliation is a promising strategy for the preparation of graphene nanosheets [2,3,4] yet its potential for producing GNPs has not been explored. In addition, electrochemical exfoliation of graphite-based materials has heavily relied on ionic liquids, which are very expensive and thus not attractive for the large scale production of GNPs.

Here, we produced GNPs by electrochemical exfoliation of carbon rods in an electrolyte solution. We utilized an aqueous solution of sulphuric acid (H₂SO₄) as an electrolyte, which is low-cost but highly efficient in exfoliating GNPs from carbon rods. GNPs were successfully separated from the reaction solution by vacuum filtration. GNPs exhibited uniform shapes, a narrow size distribution, and unique optical properties. Our method enables the low cost, large scale production of GNPs.

2. Experimental

2.1. Synthesis of GNPs by electrochemical exfoliation of a carbon rod
Figure 1 is a schematic illustration of the electrochemical exfoliation of a carbon rod by our method. The carbon rod was taken from an exhausted battery and employed as the source of GNPs. A Pt wire was placed in parallel to the carbon rod at a distance of 3 cm. The two electrodes were immersed in an aqueous solution of H₂SO₄ (concentration 0.722 M). To initiate the electrochemical exfoliation, a DC bias of +15 V was applied to the carbon rod with the Pt wire grounded. The resulting suspension was
filtered and repeatedly washed in distilled water. The solid material that remained on the filter membrane was collected and ultrasonically dispersed in dimethyl sulfoxide (DMSO) for 5 min. Finally, the DMSO dispersion was vacuum-filtered through a 0.2 μm polytetrafluoroethylene (PTFE) membrane, and the filtration was collected for characterization.

**Figure 1.** Schematic illustration of the electrochemical exfoliation of a carbon rod for synthesis of graphite nanoplatelets (GNPs).

2.2. Characterization

Scanning electron microscopy (SEM) images of GNPs were observed in an Hitachi S-4800 field-emission scanning electron microscope. Atomic force microscopy (AFM) images were performed in tapping mode using a PicoScan2500 atomic force microscope (Agilent). AFM data were visualized and analysed using Gwyddion software package (http://gwyddion.net/). UV-VIS spectroscopy was performed on a V-670 spectrophotometer (JASCO). Raman spectra of GNPs were collected with a NRS-7100 Raman system (JASCO) with the 532 nm green laser line. In UV-VIS measurements, filtration was directly used with a DMSO reference solution. For other characterization, the samples were prepared by dropping the filtration solution onto a silicon substrate and drying in air.

3. Results and discussion

As observed by naked eyes, the carbon rod corroded continuously during electrochemical exfoliation. As a result, the electrolyte solution was increasingly filled with black particles and sheets, which might contain graphite-based particles of varying sizes. In addition, we expected some undesired components such as binders (from the carbon rod) to be incorporated in the solution. Therefore, appropriate processing of the resulting solution was required to produce a suspension of high purity GNPs. Thus, we have devised an efficient protocol consisting of three steps: washing, ultrasonication, and filtering. The solution was first filtered and repeatedly washed with distilled water and ethanol to eliminate impurities, and then the solid material on filter paper was ultrasonicated in DMSO to dissolve soluble particles. Finally, the DMSO suspension was filtered through a 0.2μm PTFE membrane in order to remove particles larger than the membrane pore size. Only the filtrated solution was collected for subsequent characterization. It should be noted that in most previous studies on electrochemical exfoliation of graphite-based materials, the filtration is normally treated as waste, and only the solid material on the filter membrane is collected for characterization. However, we found that the filtrated solution obtained using the 0.2μm PTFE membrane contained large quantities of GNPs, which are the focus in this study.
Figure 2(a) shows a typical SEM image of GNPs obtained in our experiments, and Fig. 2(b) shows our statistical analysis of this image, which contains about 720 GNPs. The statistical analysis shows that the size of GNPs varied from 50 nm to 170 nm, with the majority found in the range 70–140 nm.

![Figure 2. FE-SEM image (a) and size distribution (b) of GNPs](image)

The morphology of GNPs was further investigated by using AFM. Figure 3(a) shows the AFM topography of GNPs, with data levelled by mean plane subtraction for easy visualization. Figure 3(b) shows the two corresponding cross section profiles. From these profiles, the thicknesses of GNPs were estimated to be from 2.8 nm (few-layer graphene) to 5.8 nm (more than 10 layers of graphene), assuming the graphite interlayer spacing to be about 0.35 nm. We did not observe any GNPs thicker than 10 nm. Furthermore, as shown in Fig. 3(b), the sizes of GNPs was within 40–90 nm, which is in approximate agreement with SEM observations.

![Figure 3. AFM tomography (a) and cross section profiles (b) of GNPs](image)

The absorbance spectrum of GNPs is shown in Fig. 4. A single strong and sharp adsorption peak appeared at 259 nm was observed. We assign this feature to the $\pi \rightarrow \pi^*$ transition of C = C double bonds in GNPs [5]. The C = C double bonds are formed because graphite is partly oxidized in acidic solution due to the applied voltage. The formation of oxidized carbon in GNPs results in electrostatic repulsion among GNPs when they are dispersed in a polar solvent such as DMSO. In agreement with this, our GNPs are stable in DMSO for months after preparation.
If the oxidation takes place at the basal plane, then C\(-\)O\(-\)C bondings will be formed. As a result, a broad shoulder peak is expected to appear at around 300 nm due to \(n \rightarrow \pi^*\) transition [6]. However, such a peak was not observed. This suggests that GNPs are only partly oxidized at the edge of GNPs.

Figure 5 shows the Raman spectrum of GNPs. Two strongest peaks centered at 1351 cm\(^{-1}\) and 1602 cm\(^{-1}\) correspond to D band and G band vibrations of graphite, with a \(I_D/I_G\) ratio of 0.95. The D band is caused by structural imperfections such as oxidized carbon at the edge [7]. The G band corresponds to the in-phase vibration of the graphite lattice [8].

We suggest that there are two main factors involved in the formation of GNPs in our experiment. The first one is the role of water. Water molecules intercalate into interlayer space of graphite domains in the carbon rod and donate their electrons when a positive voltage bias is applied to the rod. This process leads to the formation of oxygen with increasing density, and finally gaseous oxygen is liberated, resulting in the exfoliation of graphite domains. This factor is, however, responsible for the formation of graphene sheets rather than GNPs. Therefore the second factor must be associated with the composition and structure of the carbon rod employed in this work. In high purity graphite, the size of graphene layers is on the micrometer scale. Our carbon rod was produced by graphitizing a mixture of graphite powder and binders at high temperature, therefore, graphite domains at nanoscale do exist. After size screening by vacuum filtration, GNPs could be obtained.
4. Conclusions
We demonstrated that electrochemical exfoliation is a promising route for preparing GNPs. The successful preparation of GO from waste carbon rods may offer an alternative and inexpensive way of producing high-quality GO for both fundamental research and practical applications.

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