Fabrication of Graphene by Electrochemical Exfoliation in Alkaline Electrolytes

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Introduction

Graphene (GN) has received considerable attention recently due to its unique two-dimensional carbon structure and physical properties such as superior thermal and electrical conductivity, excellent mechanical strength and elasticity, and high specific surface area [1]. The GN is often prepared in nano-sheets consisting of carbons in mono-layered or multi-layered arrangements. Electrochemical exfoliation, one of the top-down approaches to fabricate GN, is known for its efficiency and capability in producing high qualify graphene sheets [2]. Instead of adopting an acidic electrolyte in electrochemical exfoliation, in this work, we demonstrate a facile and highly efficient route by employing a weak alkaline solution.

Experimental

Graphite rods (Homytech, 99.2 wt%) were used as the working electrode serving as the graphene source. A Pt foil was placed closely to the graphite rod as a counter electrode. Ammonium hydroxide (Showa, 28~30 wt%) was adopted as the electrolyte. Prior to the exfoliation, the graphite electrode undergoes anodization treatment in ammonium electrolyte at 10 V for 30 min. Subsequently, a second anodization step was imposed for 10 and 5 V for 90 min, respectively. The exfoliated graphenes were heated at 80 degree Celsius for 2 h to remove ammonium hydroxide and ammonia, resulting in a well-dispersed suspension shown in Fig. 1.

Raman spectroscopy (LabRAM HR800) was used with 514 nm Ar laser source to characterize the graphene structure. X-ray photoemission spectroscopy (XPS; Thermo Microlab 350) was adopted to quantitatively analyze the presence of functional groups on the graphene surface.

Fig. 1. As-prepared graphene in a well-dispersed aqueous suspension.

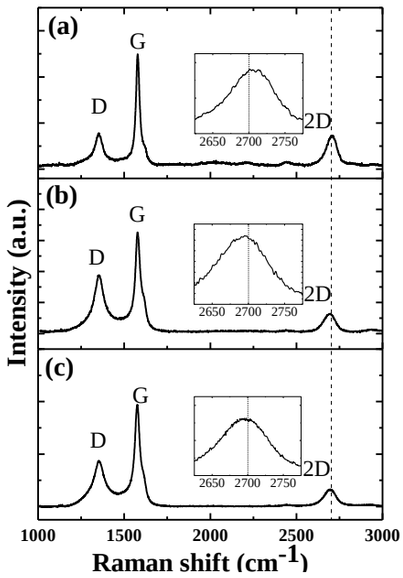

Fig. 2. Comparison of Raman spectra for (a) graphite rod, as well as graphenes from (b) 10 and (c) 5 V anodization process, respectively.

Results and discussion

Fig. 2 demonstrates the Raman spectra for graphite rod, electrochemically-exfoliated graphenes with 10 and 5 V anodization, respectively. The spectra revealed typical D-band (~1350 cm^{-1}), G-band (~1580 cm^{-1}), and 2D-band (~2700cm^{-1}) [3]. The inlet shows a significant change of peak position for the 2D-band, suggesting a different physical structure between the as-prepared graphenes and graphite rod. The degree of defective graphite can be determined by the intensity ratio of D-band (I_D) and G-band (I_G) [4]. The I_D/I_G values for the graphite rod, electrochemically-exfoliated graphenes with 10 and 5 V anodizations were 0.31, 0.58, and 0.45, respectively. The I_D/I_G ratio of 5 V sample was lower than that of 10 V one, suggesting a reduced degree of defects. Compared with that of graphite rod, the graphene samples showed larger I_D/I_G ratios because of notable reduction in the lateral dimension [5].

Fig. 3 exhibits the C 1s XPS profiles for the electrochemically-exfoliated graphenes. Notably, a broad peak was recorded for the 10 V sample and a sharp peak was observed for the 5 V sample. Curve fitting with known functional groups was performed [6] and the atomic ratios for selective individual functional groups are provided in Table 1. As listed, the 10 V sample revealed graphene oxide and the 5 V sample showed a relatively reduced graphene structure.

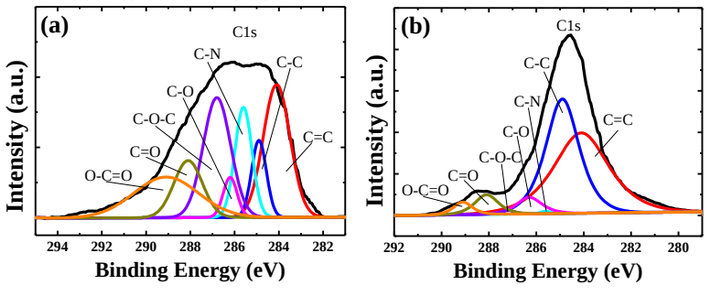

Fig. 3. C 1s XPS profiles for electrochemically-exfoliated graphenes with anodization of (a) 10 and (b) 5 V, respectively.

Table 1. The atomic ratios for C=C, C-C, C-N, C-O, C-O-C, C=O, and O-C=O from C 1s XPS curve fitting for electrochemically-exfoliated graphenes with anodization of 10 and 5 V, respectively.

	C=C	C-C	C-N	C-O	C-O-C	C=O	O-C=O
10V	24.3%	7.8%	12.9%	3.8%	22.4%	11.1%	17.9%
5V	46.6%	40.7%	0.3%	4.5%	0.5%	4.9%	2.5%

Conclusions

We demonstrated the fabrication of graphenes by carrying out electrochemical exfoliation in a weak alkaline electrolyte. Raman spectra indicated distinct physical structures far from that of bulk graphite. The XPS profiles indicated the amount of oxygenated functional groups on the graphene surface was altered contingent on the anodization voltage.

References

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