



Study on Graphene Dispersed in Ionic Liquid†

JING WANG*, JUNPING WANG, RAN CHEN, DESHENG FENG, YUNPENG LI and JIN ZHANG

School of Materials & Science Engineering, Anhui University of Science & Technology, Huainan 232001, Anhui Province, P.R. China

*Corresponding author: E-mail: jinwang@aust.edu.cn

Published online: 10 March 2014;

AJC-14862

The dispersion behaviour of graphene in different ionic liquids was investigated. As-prepared graphenes could be well dispersed in [BMIM]PF₆. The graphene dispersions were made of sheets about a few micrometers large and exhibited long-term stability. These results should facilitate the manipulation and processing of graphene-based materials for different applications.

Keywords: Graphene, Ionic liquid, [BMIM]PF₆, Dispersions.

INTRODUCTION

Graphene, a flat monolayer of sp^2 -bonded carbon atoms tightly packed into a two-dimensional honeycomb crystal lattice¹, has received significant attention due to its excellent physical, chemical and electrical properties², which ensure its potential application in solar cells³, composite materials⁴ and nano-electronics⁵. However, graphenes readily form irreversible aggregates due to the strong van der Waals interactions between them⁶, making further processing and application difficult.

Recently, numerous approaches have been successfully developed to prepare stable graphenes dispersion, but there have been few reports on using the ionic liquids as graphene dispersions⁷. In this paper graphene was dispersed in two different ionic liquids in some different concentrations with the aid of bath ultrasonication, and the dispersions were allowed to settle for several days. The graphene dispersions were characterized by spectrophotometer and polarizing microscope, then the two ionic liquids dispersions were compared in their stability.

EXPERIMENTAL

Preparation of graphene: Natural flake graphite (SP-1, 30 μm nominal particle size) was fabricated into graphite oxide by the Hummers oxidation method and then it was reduced with hydrazine hydrate. The reaction product graphene sheets was washed copiously and dried.

Preparation of graphene dispersions: The dried product was first ground with a mortar and pestle and then added to the ionic liquid (3 mL) and sonicated in an ultrasound bath cleaner for 0.5 h. Graphene dispersions were tested in the following ionic liquids: 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆) as A and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄) as B (Table-1).

TABLE-1

Solution	Quality of graphene (mg)				
	1	2	3	4	6
A	A1	A2	A3	A4	A6
B	B1	B2	B3	B4	B6

The graphene dispersions were characterized by spectrophotometer and polarizing microscope. The dispersions were allowed to settle for several days and recorded by camera once a day.

RESULTS AND DISCUSSION

Graphite oxide (GO) and graphene sheets (GNS): The crystal structure of graphite oxide and graphene sheets are characterized by XRD (Nikon E400), shown in Fig. 1 (left). Compared graphite oxide with graphene sheets, the feature diffraction peak of exfoliated graphite oxide appears at 11.8° (002) is observed with interlayer space (d-spacing) of 0.64 nm. This value is larger than the d-spacing (0.34nm) of the feature diffraction peak of graphite ($2\theta = 26.5^\circ$), indicates the

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

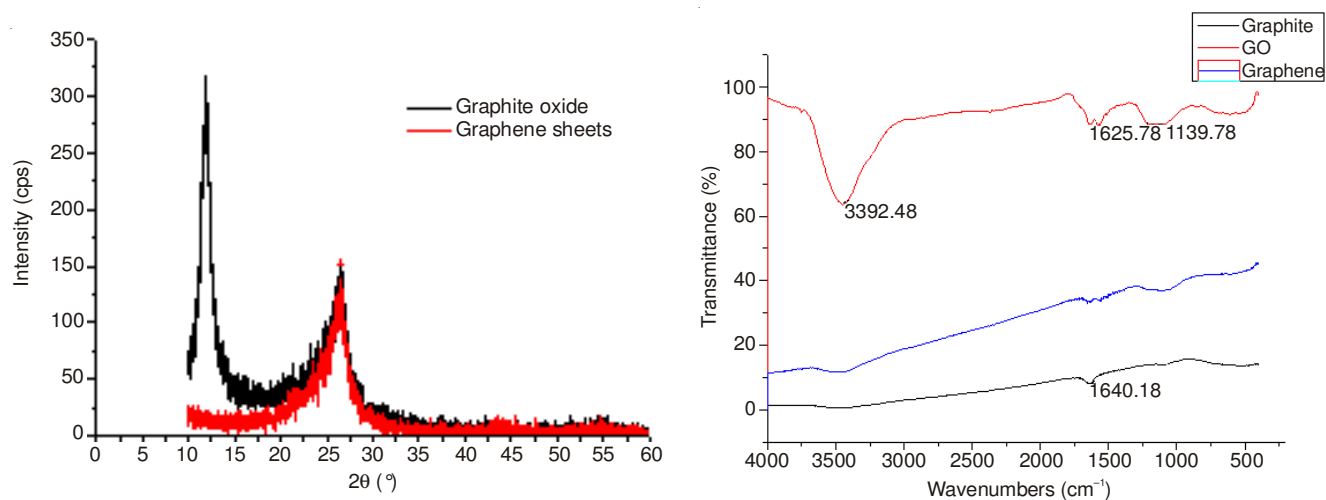


Fig. 1. XRD patterns of graphite oxide and graphene sheets the pristine graphite (left), FT-IR spectra of graphite oxide and graphene (right)

introduction of oxygenated functional groups on carbon sheets. For the resulting graphene sheets the peak located at 11.8° disappeared, confirming the great reduction of graphite oxide and the exfoliation of the layered graphene sheets^{8,9}.

The reduction of the oxygen-containing groups in graphite oxide by hydrazine hydrate was confirmed by FTIR spectroscopy (Nicolet 380) (Fig. 1 (right)). The FTIR spectra of graphite oxide shows a strong absorption band at 1625.78 cm^{-1} due to the C=O stretching, O-H ($\nu_{\text{O-H}}$ at 3392.48 cm^{-1}) and C-O-C ($\nu_{\text{C-O-C}}$ at 1113 cm^{-1}). After the graphite oxide was reduced into Graphene, the characteristic absorption bands of oxide groups ($\nu_{\text{O-H}}$, $\nu_{\text{C=O}}$ and $\nu_{\text{C-O}}$) decreased significantly, indicating that such graphite oxide has been reduced to the graphene sheets.

Graphene dispersions: Spectrophotometer was employed to gain insight into the capability of the solvents to disperse. For the just sonicated samples, it can be found that the transmission rate is 0 even for the lowest concentration of the samples-A1 and B1. That is to say graphene could be dispersed in two ionic liquids after sonication.

Fig. 2 shows pictures of all of the dispersions and graphene could be dispersed in all of the solvents. However, graphene dispersions in [BMIM]BF₄ displayed short-term stability and

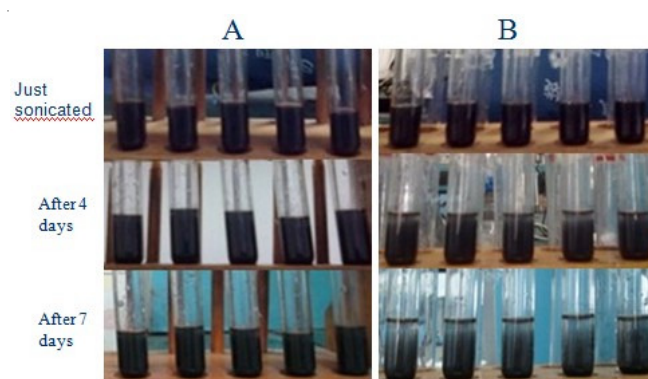


Fig. 2. Pictures of graphene dispersed in [BMIM]PF₆ and [BMIM]BF₄ through bath ultrasonication 0.5 h. Top: dispersions immediately after sonication. Middle: dispersions 4 days after sonication. Bottom: dispersions 7 days after sonication

precipitated in a few days. By contrast, graphene dispersions in [BMIM]PF₆ solvents were seen to exhibit long-term stability.

Figs. 3 and 4 show polarizing microscope images of graphene dispersions in [BMIM]PF₆ and [BMIM]BF₄ solvents. The black lump in the pictures are graphenes which are reunited in ionic liquids. The partial size of black lump is about 3-5 μm . The magnification of polarizing microscope is 100×12.5

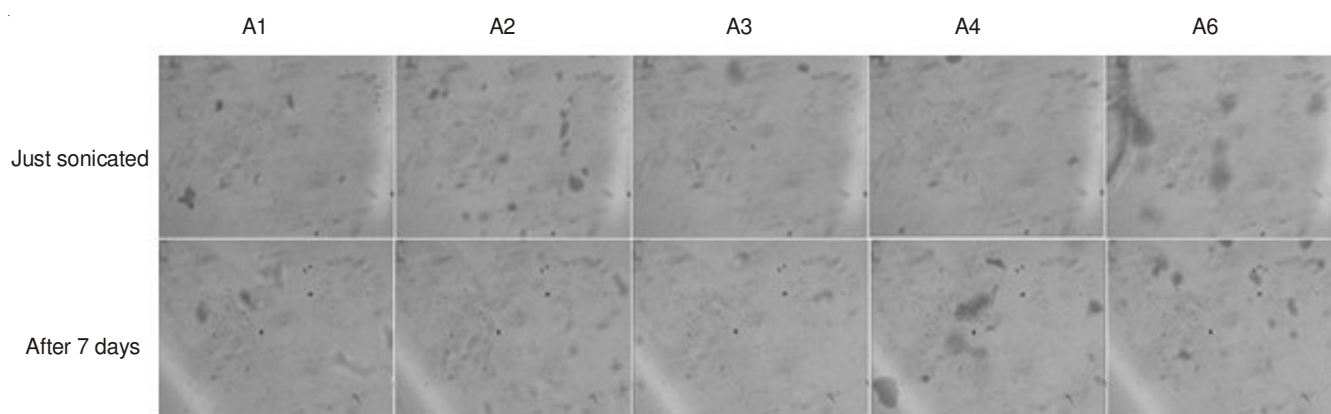


Fig. 3. Polarizing microscope images of graphene dispersions in [BMIM]PF₆ solvents. Top: dispersions immediately after sonication. Bottom: dispersions 7 days after sonication

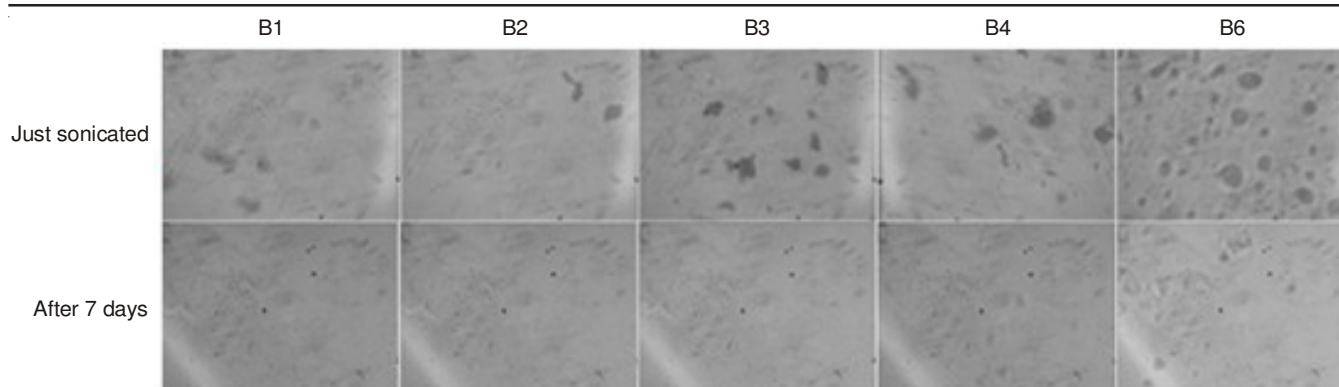


Fig. 4. Polarizing microscope images of graphene dispersions in [BMIM]BF₄ solvents. Top: dispersions immediately after sonication. Bottom: dispersions after 7 days sonication

(1250). Calculated that the partical size of lump is about 2.4–4 μm. For the just sonicated pictures, it can be noticed that the agglomerates in [BMIM]PF₆ did not changed significantly with the different concentration, but in [BMIM]BF₄ the agglomerates were larger and more obvious with the concentration increased. The partical size of black lump in [BMIM]PF₆ is also much smaller than that in [BMIM]BF₄. This result show that graphene dispersed better in [BMIM]PF₆ than [BMIM]BF₄. Comparing pictures of graphene dispersions after 7 days with which immediately after sonication, the black lump had no obvious change in [BMIM]PF₆. However, the black lump almost disappeared in [BMIM]BF₄ after 7 days, because they aggregated and sedimented, which is consistent with the conclusions from Fig. 2 above.

Conclusion

In summary, we have identified that graphene can form dispersions in ionic liquid([BMIM]PF₆) with long-term stability and the particle size of lump in dispersion is about 2.4–4 μm. Such dispersions can be used for the preparation of many graphene-based materials and therefore should facilitate the further manipulation and processing of these materials. Next, we plan to explore the surface-modified graphene and the stability of graphene dispersion in other ionic liquids.

ACKNOWLEDGEMENTS

This project was supported by National Natural Science Foundation of China (51002002).

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