Ionic Liquid Assisted Exfoliation of Layered Magnesium Diboride

Devina Ratnam, Saroj Kumar Das, and Kabeer Jasuja*
Discipline of Chemical Engineering, Indian Institute of Technology Gandhinagar. Gujarat 382355, India. kabeer@iitgn.ac.in

Abstract: The discovery of graphene showcased an ability to isolate atomic thin sheet from layered graphite, and presented a precedent to the scientific community for exploring a similar possibility in other layered materials. Magnesium diboride (MgB₂), which has metal atoms sandwiched in between boron honeycomb planes, represents an ionic layered material isostructural to intercalated graphite. We show that ultrasonication of MgB₂ in ionic liquid (1-butyl-3-methyl imidazolium tetrafluoroborate) results in a stable dispersion of few-layer-thick boron based nanosheets. Furthermore, these nanosheets (~3-6 µm wide, ~2 nm thick) are found to exhibit an optical band-gap of ~3.3eV along with excitation wavelength dependent photoluminescence.

Keywords: metal borides, ionic liquid, exfoliation, nanosheets, photoluminescence, 2D material

1. INTRODUCTION

Layered inorganic materials have received a renewed research attention in the past decade on account of their ability to be exfoliated into single-layer-thick or few-layer-thick nanostructures. The atomic thickness enabled quantum confinement and micron scale surface area facilitate these 2D materials to exhibit extraordinary electronic, thermal, and mechanical properties that are unprecedented and significantly different from their parent bulk crystals. Most studied of these 2D materials is graphene, which also laid the foundation for discovery of several of its inorganic analogs by extension of exfoliation to layered compounds such as MoS₂, BN, WS₂, and Ti₃AlC₂ to list a few. These inorganic analogs of graphene have enabled an access to quasi-atomic forms of the host compounds, and have led to a rapid evolution of 2D material science beyond carbon based graphene [1,2].

The element Boron, since its discovery, has always sought attention from the scientific community on account of its rich chemistry and potential for versatile applications. Several boron-based compounds find applications in medicine, catalysis, electronics, coatings, and advanced composites. The nanosheets are known to enable an enhanced access to their constituent elements due to their extremely high surface area to volume ratio. Thus, an ability to realize boron based nanosheets can present avenues to harness the true potential of boron and further widen the scope of its applications [3]. Moreover, such nanoscaled structures will also exhibit quantum confinement effects leading to a newer set of properties, which will add a further variety to the property-set of boron. Several bottom-up approaches have been reported recently in the pursuit of realizing 2D boron based nanostructures, [4]-[6]. However, exfoliative synthesis of boron based nanosheet by top-down approach has remained in incipient stages due to an apparent lack of parent layered material suitable for exfoliation. In this regard, Magnesium diboride (MgB₂), an ionic layered material with magnesium atoms sandwiched in between the layers of boron honeycomb, presents a prospective candidate for being exfoliated into 2D nanostructures comprising boron. We have recently [7] shown that layered MgB₂ crystals can be exfoliated by ultrasonication in water to yield chemically modified magnesium diboride (CMMB) nanosheets deficient in Mg and decorated with oxy-functional groups.

In this study, we demonstrate that MgB₂ crystals can also be exfoliated in an alternative solvent, ionic liquid (IL). The selection of IL as a possible exfoliation medium is driven by their well-known attribute of facilitating double displacement reactions [8]. It is expected that exposing MgB₂ crystals to IL will displace the inter-gallery Mg²⁺ ions and loosen the layered structure. This chemical
action will supplement the exfoliation that is being induced via the physical shear forces generated during ultrasonication, yielding boron based nanosheets. Furthermore, the selection of ILs is also favored by their green properties—thermal stability, non-volatility, and easy recyclability compared with organic solvents [9]. This choice is also supported by the increasing evidences of their ability to exfoliate a range of inorganic layered materials for stably dispersing the nanosheets. We show that MgB$_2$can in fact be exfoliated into a stable dispersion of few-layer-thick boron based nanosheets by ultrasonication of parent crystals in the IL 1-Butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF$_4$]).

2. EXFOLIATION OF MgB$_2$

The exfoliation process was carried out by ultrasonication of MgB$_2$ crystals in a neat IL. Briefly, 54 mg of MgB$_2$ powder (Sigma Aldrich, >99% pure, -100 mesh size) was added to 9 ml of neat IL [BMIM][BF$_4$] (Sigma Aldrich, 97% pure) contained in a 20 ml glass vial. Probe ultrasonication was conducted using a 1/8” microtip (Qsonicator, 500 watts, 20 kHz) operating at 35% amplitude and a pulse mode of 10 s on 20 s off cycle for duration of 60 minutes. An ice-bath was used to maintain the temperature of vial below 30°C during ultrasonication. A dark black suspension was obtained at the end of ultrasonication. On allowing this suspension to stand for 24 hours, we observed a partial sedimentation of dark black residues indicating the suspension to be nonhomogeneous. In order to obtain a homogeneous dispersion, the suspension obtained post ultrasonication was centrifuged at 10,000 rpm for 30 minutes, after which the top half of supernatant was collected. This process of centrifugation and supernatant collection was repeated on this recovered sample to ensure removal of any unexfoliated structures. The supernatant collected at the end of two cycles was used for further investigation to understand the nature of dispersed phase (as shown in Fig. 1).

A green laser beam was passed through the obtained supernatant to observe a strongly discernible track (Tyndall effect) indicating the presence of dispersed phase in the supernatant (Fig. 1b). Likewise, the green laser beam was also passed through neat IL as reference as shown in Fig. 1b. The presence of weak scattering of beam in neat IL can be attributed to the impurities present in it (the purity of the neat IL is 97%) [10], [11].

3. PHYSICO-CHEMICAL CHARACTERIZATION

In order to obtain further insights about the nature of dispersed phase, we acquired UV-vis spectrum of the colloidal dispersion. The absorption spectrum, as represented in Figure 2a, appears to have multiple contributions, which were obtained by a deconvolution of the parent spectrum into 4 daughter spectra (by Gaussian fitting). These daughter spectra were observed to be centered at ~257 nm, ~286 nm, ~319 nm, and ~397 nm in the UV region. The presence of daughter peaks are also
introduced in the boron based nanosheets upon functionalization [7]. In a similar way, the cationic moiety of IL can attach to boron planes to result in newer electron states, which might have led to newer daughter peaks [12], [13]. This needs to be confirmed by a supporting chemical analysis. An approximate optical band gap of the nano-sheets was obtained by generating Tauc plot from the absorption spectrum (Fig. 2b). The linear regime in Tauc plot was fitted and extrapolated to obtain an approximate optical band gap ($E_g = \frac{h \gamma}{\alpha}$) of ~3.3 eV.

The possibility of a number of new electron states observed in synthesized nanosheets encouraged us to investigate the presence of photoluminescence (PL). We obtained the PL spectra of neat IL (Fig. 3a) and IL with nanosheets dispersed, (Fig. 3b) by irradiating with a broad range of excitation wavelengths. When the neat IL was excited with shorter wavelengths (in the range 260-320nm), emission spectra were observed in the wavelength range of 310-510nm (see Fig. 3a), with the peak located at ~400nm. Similarly, when excited with higher wavelengths (in the range 320-450 nm), the emission spectra were observed in the range of 350-500nm. The existence of native PL in IL is expected due to the presence of imidazolium moiety, in agreement with the literature [14].

Interestingly, the IL with nanosheets dispersed in it exhibited modified emission spectra. Upon exciting the IL (having dispersed nanosheets) with wavelengths in the range 260-600nm, emission spectra were observed in the range of 350-570nm (see Fig. 3b). The maxima of these spectra were found to peak at 450nm residing in the visible region. Moreover, the emission spectra were found to be featureless after 500nm for neat IL, whereas significant intensity of emissions were continued to be detected for nanosheet dispersion up to 600nm. In summary, the neat IL has two distinct emission maxima (Fig. 3a) due to its inherent PL property, whereas the IL having nanosheets dispersed in it exhibit only one emission maximum. The diminishing of two maxima in neat IL and appearance of a different maximum upon addition of nanosheet in IL is likely due to the modified electronic structures of the synthesized nanosheets. The phenomenon of PL is in agreement with the previous report by Das et al. where change in electronic state in boron based nanostructure induces photoluminescence property [7]. In this study, we believe that exfoliation in IL and functionalization has induced certain changes in electronic states of boron based nanosheets, which has led them to exhibit a modified PL.
Fig. 3. Photoluminescence comparison in neat IL and IL with nanosheets dispersed in it: (a) PL intensity map for neat IL. (b) PL intensity map for IL with nanosheets dispersed in it. Emission intensity as a function of emission and excitation wavelength is represented by color scheme shown on right. The emission spectra were obtained for excitation wavelength ranges from 250-600 nm. Two distinct emission maxima with peak value located at 400 nm and 420 nm were obtained for neat IL, whereas one broad emission maximum at 450 nm was observed for nanosheet dispersion.

4. MICROSCOPY RESULTS
The exfoliation of MgB$_2$ crystals was further verified by TEM (Transmission Electron microscopy), the samples for which were prepared by drop casting the nanosheet dispersion onto a holey carbon TEM grid. Fig 4(a) shows a TEM image of an exfoliated nanosheet which is highly transparent to electron beam. This property of electron transparency suggests that the synthesized nanosheets are ultrathin in nature. Some nanosheets exhibit a moderate degree of wrinkles and have folds on their edges (Fig. 4(b) shows that). The presence of wrinkles and folds are also prevalent in graphene and its analogs due to several factors. These range from capillary effects during sample deposition to gaining thermo dynamic stability after exfoliation [7], [15]. In order to understand the morphology of the nanosheets, scanning electron microscopy (SEM) was carried out on two types of sample: (i) Nanosheets dispersed in ethanol, bath sonication of the dispersion for 20 min, followed by immediate spin coating on mica substrate; The spin coated sample was observed under FESEM for imaging and are shown in Fig. 4(c) and (d) indicating the few micrometer long nanosheets with etched edges. These etched edges are likely due to removal of magnesium atom from the MgB$_2$ crystals after the reaction with IL during ultrasonication; (ii) Powdered form of the nanosheet mounted on the carbon tape followed by platinum coating for
60s prior to analysis: Fig. 4(e-f) shows the FESEM images of the nanosheets, which are appeared to be fragmented and highly crumpled in nature. This is likely due to the shear force exerted by the probe sonication causing the nanosheets to fragment and hence generating the fragmented flakes. In order to measure the thickness of the synthesized nanosheet, AFM analysis was carried out on the ethanol dispersed sample as shown in Fig. 4g. The corresponding height profile is presented in Fig. 4h, which indicates that the lateral dimensions of nanosheets range from ~3-6µm (from SEM images) with a thickness of ~2nm.

**CONCLUSION**

Here, we have shown an ionic liquid assisted exfoliation of layered MgB$_2$ to yield nanosheets having lateral dimension of 3-6µm with an average thickness in the range of ~2-3nm. The stability of the synthesized nanosheet dispersion was investigated for a month, which showed no sign of agglomeration unlike the aqueous dispersion of nanosheet. This higher degree of stability can be attributed to the high viscosity of IL which prevents the restacking of nanosheets [16].

Furthermore, we observed that the nanostructures display an excitation wavelength dependent photoluminescence property. The UV-vis absorption studies establish that these nanosheets absorb in the UV regime, and hence, present excellent candidacy for fabricating coatings that can block UV wavelengths. Additionally, it is observed that the nanosheets form stable and homogeneous dispersion in IL. The nanosheets were found to exhibit an approximate optical band gap of ~3.3eV. This value is significantly lesser compared with the optical band gap reported by Das et al. for CMMBs ($E_g \approx 4.49$eV). Hence, it suggests that the optical band gap of the synthesized nanosheets depends on the solvent during exfoliation. It will be promising to carry out exfoliation in other solvents to study the possibility of tuning the band gap. We believe that this work reported here will provide a significant step forward to bring boron-based nanosheets closer to real-world applications, and will open up several promising avenues for fundamental research in coming future.

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REFERENCES

[1] Wang Q H, Kalantar-Zadeh K, Kis A, Coleman J N and Strano M S 2012 Electronics and optoelectronics of two-dimensional transition metal dichalcogenides Nat Nano7 699-712
[2] Nicolosi V, Chhowalla M, Kanatzidis M G, Strano M S and Coleman J N 2013 Liquid Exfoliation of Layered Materials Science340
[3] Li X-B, Xie S-Y, Zheng H, Tian W Q and Sun H-B 2015 Boron based two-dimensional crystals: theoretical design, realization proposal and applications Nanoscale7 18863-71
[4] Xu J, Chang Y, Gan L, Ma Y and Zhai T 2015 Ultrathin Single-Crystalline Boron Nanosheets for Enhanced Electro-Optical Performances Advanced Science2 1500023
[5] Tai G, Hu T, Zhou Y, Wang X, Kong J, Zeng T, You Y and Wang Q 2015 Synthesis of Atomically Thin Boron Films on Copper Foils Angewandte Chemie International Edition54 15473-7
[6] Mannix A J, Zhou X-F, Kiraly B, Wood J D, Alducin D, Myers B D, Liu X, Fisher B L, Santiago U, Guest J R, Yacaman M J, Ponce A, Oganov A R, Hersam M C and Guisinger N P 2015 Synthesis of borophenes: Anisotropic, two-dimensional boron polymorphs Science350 1513-6
[7] Das S K, Bedar A, Kannan A and Jasuja K 2015 Aqueous dispersions of few-layer-thick chemically modified magnesium diboride nanosheets by ultrasonication assisted exfoliation Scientific Reports5 10522
[8] Rogers R D and Seddon K R 2003 Ionic Liquids--Solvents of the Future? Science302 792-3
[9] Liu W, Zhao T, Zhang Y, Wang H and Yu M 2006 The Physical Properties of Aqueous Solutions of the Ionic Liquid [BMIM][BF4]. Journal of Solution Chemistry35 1337-46
[10] Nockenmann P, Binnemans K and Driesen K 2005 Purification of imidazolium ionic liquids for spectroscopic applications Chemical Physics Letters415 131-6
[11] Koel M 2005 Ionic liquids in chemical analysis Critical Reviews in Analytical Chemistry35 177-92
[12] Samanta A 2006 Dynamic stokes shift and excitation wavelength dependent fluorescence of dipolar molecules in room temperature ionic liquids The Journal of Physical Chemistry B110 13704-16
[13] Paul A and Samanta A 2006 Optical absorption and fluorescence studies on imidazolium ionic liquids comprising thebis(trifluoromethanesulphonylimide)imide anion Journal of Chemical Sciences118 335-40
[14] Paul A, Mandal P K and Samanta A 2005 On the optical properties of the imidazolium ionic liquids The Journal of Physical Chemistry B109 9148-53
[15] Cheng C and Li D 2013 Solvated Graphenes: An Emerging Class of Functional Soft Materials Advanced Materials25 13-30
[16] Zhao W, Xue Z, Wang J, Jiang J, Zhao X and Mu T 2015 Large-Scale, Highly Efficient, and Green Liquid-Exfoliation of Black Phosphorus in Ionic Liquids ACS applied materials & interfaces7 27608-12