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Dielectric nanosheets made by liquid-phase exfoliation in water and their use in graphene-based electronics

Huafeng Yang\textsuperscript{1}, Freddie Withers\textsuperscript{2}, Elias Gebremedhin\textsuperscript{3}, Edward Lewis\textsuperscript{4}, Liam Britnell\textsuperscript{1}, Alexandre Felten\textsuperscript{5}, Vincenzo Palermo\textsuperscript{6}, Sarah Haigh\textsuperscript{4}, David Beljonne\textsuperscript{3} and Cinzia Casiraghi\textsuperscript{1}

\textsuperscript{1} School of Chemistry, University of Manchester, Manchester M13 9PL, UK
\textsuperscript{2} School of Physics and Astronomy, University of Manchester, Manchester M13 9PL, UK
\textsuperscript{3} University of Mons, Place du Parc 20, B-7000 Mons, Belgium
\textsuperscript{4} School of Materials, University of Manchester, Manchester M13 9PL, UK
\textsuperscript{5} Research Centre in Physics of Matter and Radiation (PMR), Université de Namur, B-5000 Namur, Belgique
\textsuperscript{6} ISOF—National Research Council, Via P Gobetti 101, I-40129 Bologna, Italy
E-mail: cinzia.casiraghi@manchester.ac.uk

Received 24 January 2014, revised 13 April 2014
Accepted for publication 12 May 2014
Published 17 June 2014

Abstract

One of the challenges associated with the development of next-generation electronics is to find alternatives to silicon oxide caused by the size-reduction constraints of the devices. The dielectric properties of two-dimensional (2D) crystals, added to their excellent chemical stability, mechanical and thermal properties, make them promising dielectrics. Here we show that liquid-phase exfoliation (LPE) in water by using low-cost commercial organic dyes as dispersant agents can efficiently produce defect-free 2D nanosheets, including mono-layers, in suspensions. We further show that these suspensions can be easily incorporated into current practical graphene-based devices. In particular, it is found that boron nitride thin films made by LPE are excellent dielectrics that are highly compatible with graphene-based electronics.

Online supplementary data available from stacks.iop.org/2DM/1/011012/mmedia
Two-dimensional (2D) crystals are a new class of stable, highly processable materials featuring distinctive properties compared to their 3D counterparts. The most famous 2D crystal is graphene [1]. Other single-layer crystals, such as h-BN, WS\textsubscript{2}, MoS\textsubscript{2}, MoSe\textsubscript{2} and MoTe\textsubscript{2}, are currently attracting much interest because of their wide range of electronic and dielectric properties, from metallic to semiconducting and insulating, depending on their exact composition. Transistors made of single and few-layer WS\textsubscript{2} and MoS\textsubscript{2} show high on/off ratio, and strong photoluminescence and light absorption, suggesting their applications in electronics and photonics [2]. Single layer h-BN is structurally similar to graphene, but unlike its carbon analogue, it is an insulator with a large band gap (∼6 eV). This, added to unique features such as excellent chemical, mechanical properties, and thermal stability, allows the use of h-BN nanosheets (BNNS) in a wide variety of applications, including as component in nanodevices, solid lubricant, UV-light emitters and as insulating thermo-conductive filler in composite material [3].

In order to find practical applications, 2D crystals must be compatible with simple and low-cost manufacturing processes. Liquid-phase exfoliation (LPE) is a scalable approach for production of 2D crystals, based on exfoliation of their bulk counterparts via chemical wet dispersion followed by ultra-sonication [4]. This technique offers many advantages for cost reduction, scalability and compatibility with any substrate, including cheap and flexible substrates [4]. The efficiency of the exfoliation is usually measured in terms of the amount of material dispersed in solution. In this work in particular we will use the concentration measured by absorption spectroscopy to quantify and compare the exfoliation efficiency. Currently LPE is mostly based on the use of organic solvents such as N-Methylpyrrolidone (NMP) and N,N-dimethylformamide (DMF) [4, 5], which are toxic, expensive and characterized by high boiling points. While those solvents can produce high concentrations of single-layer graphene in suspension [6], they are less efficient in exfoliating other layered materials [3, 4]. For example, in the case of h-BN, the bonding between neighbouring BN layers is formed by a so-called ‘lip–lip’ interaction [7], which is expected to be stronger than the weak van der Waals force between graphene layers. This makes the exfoliation of h-BN more difficult. Therefore, an alternative liquid phase process, which results in effective exfoliation of 2D nanosheets, is required. This method should also be compatible with safe, user-friendly, low boiling point solvents, such as water.

Aqueous dispersion of 2D materials can be obtained using surfactants [8]. This method is attractive because for example the percentage of single-layer graphene can be strongly increased by density gradient centrifugation [9]. However, this process can be time-consuming and difficult to precisely control because the density of the environment has to match with the density of the flake, which depends on both its thickness and lateral size. Exfoliation via surfactants is not always efficient, for example in the case of graphene and BN [8], and typically the residual concentration of surfactant is high and difficult to remove.

Surfactants can be replaced by other stabilizers. In our previous works [10] we reported the successful exfoliation of graphene in water by using low-cost commercial organic dyes, such as pyrene derivatives. This approach is based on the idea that pyrene should strongly interact with the graphene layers through π–π interaction, while the functional groups can stabilize the exfoliated graphene flakes in water. In particular, the use of pyrene derivatives allows preparing...
dispersions with exceptionally high graphene/stabilizer yields, in contrast to traditional surfactants [11]. Furthermore, the use of colored, emitting dyes allows using optical spectroscopy to estimate the amount of molecules present together with graphene in solution and also eventual changes in their chemical nature (protonation, quenching, etc), as demonstrated in [10, 12]. This is not possible with normal, aliphatic surfactants.

In this letter, we show that exfoliation in water with pyrene derivatives can be successfully applied to other 2D materials, such as h-BN, WS\textsubscript{2}, MoS\textsubscript{2}, MoSe\textsubscript{2}, and MoTe\textsubscript{2}. The nanosheets produced are defects-free, very thin (typically less than six layers, several mono-layers have been observed in the case of h-BN) and are compatible with graphene-based devices. In particular, here we use BNNS as the gating dielectric in a planar graphene-based photodetector. We also make use of different molecules and pH in order to investigate if and how the exfoliation mechanism differs from the one already reported for graphite [10]. Considering that the type of interactions between pyrene and graphene are different from the interactions between pyrene and other 2D crystals this result needs further investigation. By looking at the kinetics and thermo-dynamics for the adsorption process of the pyrene molecules on the 2D crystals, we found the exfoliation mechanism to be qualitatively the same for all the layered materials investigated because the exfoliation efficiency strongly depends on the interaction between the molecule and the solvent [10]. Therefore, our method can be applied to exfoliate any layered material in water.

Results and discussion

Aqueous dispersions of h-BN, MoS\textsubscript{2}, WS\textsubscript{2}, MoTe\textsubscript{2} and MoSe\textsubscript{2} were typically prepared by exfoliating starting powders in aqueous pyrene solutions with the aid of an ultra-sonic bath. We selected three pyrene derivatives, which are functionalized with side-groups featuring different steric structure, water-solubility, electronegativity and pH response as shown in figure 1(A). The organic dyes used are: 1-pyrenesulfonic acid sodium salt (Py-1SO\textsubscript{3}), 6, 8-dihydroxy-1, 3-pyrenedisulfonic acid disodium salt (Py-2SO\textsubscript{3}), and 1, 3, 6, 8-pyrenetetrasulfonic acid tetrasodium salt (Py-4SO\textsubscript{3}). Compared to Py-1SO\textsubscript{3} and Py-4SO\textsubscript{3}, Py-2SO\textsubscript{3} has two hydroxyl groups, −OH, so its charge can be modified by tuning the pH. After sonication, all dispersions were centrifuged to remove unexfoliated starting powder and the supernatants were collected as shown in figure 1. The concentration was calculated by measuring the UV–Vis absorption of the as-prepared 2D crystal dispersions (supporting information). The absorption coefficient has been calculated at wavelengths far from the absorption peaks of pyrene (300–500 nm, see supporting information, section S3). The concentrations are reported in table S1. In all cases Py-4SO\textsubscript{3} gives the lowest exfoliation efficiency, while Py-2SO\textsubscript{3} the highest, similar to the results previously reported for graphene [10]. This suggests a similar exfoliation mechanism when using pyrene molecules to exfoliate van der Waals bonded crystals. This is confirmed by our simulations on the kinetics and thermo-dynamics of the adsorption process of each molecule on the h-BN surface (details in S5). In particular, the calculated adsorption free energies of the dyes on h-BN (table 1) indicate a ∼22% increase in going from Py-4SO\textsubscript{3} to Py-2SO\textsubscript{3}, in line with observed trends. Figure 2 shows the potential of mean force (PMF) of the adsorption process of Py-2SO\textsubscript{3} and Py-4SO\textsubscript{3} on graphene and h-BN, including snapshots from simulations of the landing of a Py-4SO\textsubscript{3} molecule as it adsorbs on the h-BN surface. This mechanism of going from edge-on to face-on interaction, during adsorption, is observed for all pyrene derivatives on both h-BN and graphene.
On both surfaces, there are local minima (transition states) for Py-4SO₃, which act as kinetic traps (i.e. there is an energy barrier that needs to be overcome in order to go from edge-on to face-on orientation, at tilted orientations). These arise from the displacement and rearrangement of the solvent molecules between the plane of the molecule and the surface, and around the solvation shell of the −SO₃ groups. In contrast, the PMF profile of Py-2SO₃ adsorption on graphene and h-BN show a single global minimum in free energy (and very small energy barriers). These results further confirm that the hydrophobic interaction of the pyrene core with water is the key factor that facilitates the adsorption of the pyrene molecules onto the surfaces. In particular, the presence of the −SO₃ groups polarizes the pyrene core, facilitating the electrostatic interaction of the core with the surrounding water molecules, while it reduces the hydrophobic interactions by shielding the core from the solvent environment. In table 2 it can be observed that the Lennard-Jones interaction energy of the pyrene core with the surrounding water molecules slightly decreases going from Py-1SO₃ to Py-4SO₃, while the Coulomb interaction significantly varies. In particular, the increase in the number of sulfonate groups in Py-4SO₃ results, as expected, in a much larger interaction energy with the surrounding water molecules. The overall effect is an increased solubility in water and a smaller affinity for the surfaces.

Although the exfoliation mechanism is qualitatively the same for all 2D crystals, figure 2 shows that there are also some differences: the absolute values of the global minima energy are

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**Table 1.** The adsorption free energy of pyrene molecules on graphene and h-BN (Kcal mol⁻¹).

| Molecule   | ΔG graphene-pyrene | ΔG hBN-pyrene  |
|------------|---------------------|----------------|
| Py-1SO₃    | −12.84              | −23.29         |
| Py-2SO₃    | −14.56              | −27.21         |
| Py-4SO₃    | −8.42               | −22.34         |

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**Figure 1.** (A) Pyrene derivatives used in this study. ((B)–(F)) Optical images of the as-prepared 2D crystals-based dispersions using pyrene derivatives (the numbers 1, 2 and 4 refer to the number of sulphonic groups of the organic dyes shown in (A).
larger for h-BN than graphene, indicating that Py-2SO₃ has a higher affinity towards h-BN than graphene. Though this could potentially arise from larger electrostatic interactions with the polar B–N bonds, our calculations suggest that the difference mostly stems from van der Waals interactions of the molecules with the h-BN surface, as compared to graphene, with a smaller contribution from the electrostatic interaction of the charged molecules with the partially charged N and B atoms of the surface (table S1).

Note that recently Lin et al [13] reported that water alone is a good solvent to exfoliate BN bulk to produce few layers nanosheets because of sonication-assisted hydrolysis. Therefore, it is important to verify whether pyrene really plays a role in the exfoliation mechanism and can

Table 2. The Lennard-Jones (LJ) and coulomb contributions to the interaction energy of the pyrene core of the adsorbed (at global minima) pyrene molecules with the surrounding aqueous medium (Kcal mol⁻¹).

|           | LJ          | Coulomb    |
|-----------|-------------|------------|
| Py-1SO₃   | −13.73 ± 0.01| −7.27 ± 0.01|
| Py-2SO₃   | −12.64 ± 0.07| −5.45 ± 0.1 |
| Py-4SO₃   | −11.77 ± 0.13| −15.46 ± 0.13|

Figure 2. Potential of mean force (PMF) curves illustrating the adsorption kinetics of Py-2SO₃ (top panel) and Py-4SO₃ (bottom panel) on graphene and h-BN. The PMF curves of Py-4SO₃ show kinetic traps for both graphene and h-BN, which make the interaction with the surface less efficient. Simulations (see snapshots of the equilibrium structures of Py-4SO₃ at the points (A)–(E)) show that the molecular asymmetry plays a central role in favouring the approach of the pyrene towards both graphene and h-BN [10].
effectively increase the concentration. To test this, we also performed a control experiment by exfoliating the material in water without any stabilizer (supporting information, section S3). Table S1 shows that the exfoliation efficiency of h-BN in water is comparable to that of Py-4SO₃ (as expected because this specific pyrene derivative does not contribute to the exfoliation process), but is less efficient than Py-1SO₃ and Py-2SO₃, which indicates that these pyrene derivatives can effectively act as dispersants, allowing exfoliation and stabilization of the 2D crystals dispersions. Therefore, one has to carefully choose the most appropriate organic dye to maximize the concentration of the dispersion: in our case, Py-2SO₃ gives the best exfoliation efficiency for a large variety of 2D-crystals.

The exfoliation efficiency can be further increased by tuning the pH. Table S1 in the supporting information reports the changes in concentration obtained when the pH of the pyrene solution is changed by adding HCl or KOH (with a corresponding change of colour for the dispersion). The exfoliation efficiency of Py-2SO₃ is highest at pH 2 and decreases strongly with increasing pH. In contrast, the concentration of BNNS/Py-1SO₃ did not change noticeably upon a change in pH, as expected because this organic dye is not pH sensitive. The strong dependence of the concentration on the pH can be attributed to the protonation effect, which was already observed in [14]. In order to confirm this idea, another control experiment was carried out by exfoliating h-BN in two different aqueous solutions without stabilizers at pH = 2 and pH = 12 under the same conditions (supplementary data, section S3). The pure water-based BNNS dispersions showed that the highest concentration is obtained in neutral pH conditions. A strong pH dependence is observed when adding Py-2SO₃, in particular the highest concentration is obtained at pH 2 (table S1 in supplementary data). The strong pH dependence of BNNS/pyrene suspensions is very different from the case of the graphene/pyrene system, where all the organic dyes showed the same pH dependence [10]. In the case of graphene, the highest concentration was obtained in neutral condition and the concentration decreased heavily for both acidic and basic conditions (supplementary data, section S3), indicating that in the case of graphene the protonation effect is not fundamental in stabilizing the flakes in dispersion. It should be noted that B–N bonds in BN are more polarized than C–C bonds in graphene, and thus it will interact differently with the charged proton groups of Py-2SO₃.

The electrostatic stability of BNNS/Py-2SO₃ dispersion was also investigated by measuring the zeta potentials. This increases with decreasing pH (from −32.9 mV (pH 2), to −56.8 mV (pH7), to −75.7 mV (pH 12)), in agreement with previous results obtained with other type of molecules [15]. The BNNS dispersions at pH 2 with zeta potential of ~ −32 mV shows the highest concentration, which is consistent with the formation of stable colloidal dispersions [16].

After removing the pyrene molecules with a water rinse and with the aid of centrifugation, the exfoliated 2D nanosheets were characterized by transmission electron microscope (TEM) imaging, figure 3. Low magnification TEM images for all the 2D crystals (figure 3 and supplementary information S14) show electron transparent flakes with typical lateral sizes of less than 500 nm, although some larger sheets were also observed. Note however that the size can be strongly reduced by increasing the sonication time (reaching 10–50 nm for 5 days sonication). Their weak contrast relative to the vacuum suggests that they are mostly thin layers. High resolution TEM images reveal that the sheets are fairly clean and highly crystalline with the expected hexagonal crystal symmetry, figure 3. In the case of BNNS, we used the relative intensities of atomic columns in the high-resolution TEM to identify single layer BN nanosheets
in our dispersions [4]. For WS₂ and MoS₂ nanosheets, some of the flakes were oriented perpendicular to the beam, so the number of layers in each flake can be easily observed from the number of bright lines in the high angle annular dark field (HAADF) scanning transmission electron microscope (STEM) images (figure S15): the majority of flakes consisted of four to six layers, with a lower concentration of mono- and bi-layers. Note that based on our previous studies [10], atomic force microscopy (AFM) does not give reliable thickness measurements because of the residual molecules adsorbed on the nanosheet.

The structure and surface chemistry of the 2D nanosheets were further investigated by Raman spectroscopy and x-ray photo-electron spectroscopy (XPS). The Raman spectra show the typical Raman features expected for the 2D nanosheets and in some case a weak photoluminescence background, related to the residual pyrene molecules on the surface (figure S9). XPS was performed on laminates produced from the 2D nanosheets suspensions by using vacuum filtration (supplementary data, section 3.2). The XPS spectra (supplementary data, section 3.3.3) show that our exfoliation method does not oxidize the crystals and that a very small percentage of molecules are trapped in the laminate (∼1–3% in the case of BNNS laminates).

Finally, it is important to demonstrate that these dispersions can be incorporated into current practical graphene-based devices. As an example of this, we show the use of BNNS thin films in an in-plane graphene photo-detector. Figures 4(A) and (B) shows the schematic structure of the device, where a BN laminate is used as gating dielectric, i.e. to isolate a local

Figure 3. TEM images of exfoliated flakes: row (A) shows exfoliated MoS₂ nanosheets, row (B) shows exfoliated BN nanosheets, and row (C) shows exfoliated WS₂ nanosheets. Column 1 shows low magnification TEM images of flakes that, in size, shape and thickness, are typical of the sample. Column 2 shows unprocessed HRTEM images with the Fourier transform for each inset, and column 3 shows the images in column 2 after filtering. Column 4 shows regions of the images from column 3 magnified to clearly show details of the lattice fringes.
Figure 4. (A) The basic schematic of the device. (B) an optical image of the device after fabrication. (C) Electrical measurement of as-prepared graphene device (conductance $G$ as a function of the gate voltage $V_g$). (D) photocurrent maps generated in the graphene device at different gate voltages: $V_g = +25$ V, $V_g = 0$ V, and $V_g = -25$ V. (E) Average photocurrent (right panel) calculated in the dotted squares (left panel, photocurrent map) as a function of the gate voltage.
gate electrode (in our case a thin graphite flake) from the top graphene flake in order to create a p–n junction in graphene, which is required to generate photocurrent upon illumination. Details of the fabrication process are provided in the supplementary data, section S4. Figure 4(C) shows that the graphene is well isolated from the thin graphite flake and there is no detectable gate leakage in the range of +/-25 V (the thickness of the BNNS laminate used in this device is ~500 nm). The charge neutrality point is shifted to around 7.5 V indicating p-type doping, which is typical for graphene transistors measured in air [17]. Photocurrent measurements were performed using a 488 nm laser at a power of 90 μW with the laser focused to a spot size of 0.5 μm in diameter. The sample is then rastered under the laser illumination by means of a piezoelectric stage. Figure 4(D) shows photo-current maps obtained at different gate voltage (V_g): at 0 V_g (central panel) the only photo-active region is at the interface between the gold contacts and the slightly p-doped graphene, due to difference in work-function between these two materials [18]. At V_g = +25 V, the top graphene becomes strongly n-doped, so a strong p–n junction forms in the regions of the graphene flake at the edges of the gated region. This generates an intense photocurrent signal similar to the photo response seen previously in double gated bilayer graphene and at monolayer-bilayer graphene interfaces [19]. At V_g = −25 V, the top graphene gets strongly p-doped (p+), therefore revering the sign of the photocurrent at the p–n junctions either side of the thin graphite back gate, figure 4(E). The average photocurrent signal as a function of V_g is shown in figure 4(E). Finally, in order to test the use of h-BN as dielectric material, we measured the breakdown voltage of two films of different thickness: 500 nm (the device discussed above) and 600 nm BN thickness, for which we measured four points. We found the average breakdown electric field of the LPE h-BN laminates to be ~0.3 V nm⁻¹ (in vacuum), which is similar to that found for thermally oxidized SiO₂ (<0.4 V nm⁻¹) [20].

Conclusions

To conclude we have developed a facile and low-cost exfoliation method to prepare BN, WS₂, MoS₂, MoSe₂ and MoTe₂ thin flakes in water using commercial organic dyes. We have demonstrated that BNNS films produced by this method have a breakdown field similar to that of SiO₂, which allows them to be used as a gating dielectric in a graphene-based photo-detector. The versatility of the solvent-exfoliation method makes it easy to create various hybrid dispersions and films, which can be used to make low cost and mass scalable hetero-structures devices.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding sources

This work was supported by EPSRC (Science and Innovation Award), The Royal Society, US Army and European Science Foundation (ESF) under the EUROCORES Programme EuroGRAPHENE (GOSPEL). SH acknowledges the US Defence Threat Reduction Agency.
The work in Mons was also supported by the European project MMM@HPC (FP7-RI-261594), the Interuniversity Attraction Pole program of the Belgian Federal Science Policy Office (PAI 6/27), Programme d’Excellence de la Région Wallonne (OPTI2MAT project), ITN Marie-Curie project GENIUS and FNRS/FRFC. DB is a FNRS Research Fellow. AF is a FRS-FNRS Research Fellow.

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