Two-dimensional nano-sheets produced by liquid exfoliation of layered materials

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One sentence summary:

We describe a general liquid-phase method to exfoliate layered compounds to give mono- and few-layer flakes in large quantities.
Abstract

If they could be easily exfoliated, layered materials would become a diverse source of 2-dimensional crystals whose properties would be useful in applications from electronics to energy storage. We show that layered compounds such as MoS$_2$, WS$_2$, MoSe$_2$, MoTe$_2$, TaSe$_2$, NbSe$_2$, NiTe$_2$, BN and Bi$_2$Te$_3$, can be efficiently dispersed in common solvents and can be deposited as individual flakes or formed into films. Electron microscopy confirms the material to be exfoliated into individual layers. By blending with suspensions of other nano-materials or polymer solutions, we can prepare hybrid dispersions or composites which can be cast into films. We show that WS$_2$ and MoS$_2$ effectively reinforce polymers, while WS$_2$/carbon nanotube hybrid films have high conductivity leading to promising thermoelectric properties.
Layered materials represent a diverse and largely untapped source of 2-dimensional (2D) systems with exotic electronic properties and high specific surface areas that are important for sensing, catalysis and energy storage applications. While graphene is the most well-known layered material, transition metal dichalcogenides (TMDs), transition metal oxides (TMOs) and other 2D compounds such as BN, Bi$_2$Te$_3$ and Bi$_2$Se$_3$ are also important. The latter materials are of particular interest as topological insulators and thermoelectric materials(1). However, development of these materials has been hampered by the lack of a simple method to exfoliate them to give mono- or few-layer flakes in large quantities.

TMDs consist of hexagonal layers of metal atoms, M, sandwiched between two layers of chalcogen atoms, X, with stoichiometry MX$_2$. While the bonding within these tri-layer sheets is covalent, adjacent sheets stack via van der Waals interactions to form a 3D crystal. TMDs occur in more than 40 different types (2, 3) depending on the combination of chalcogen (S, Se or Te) and transition metal(3). Depending on the co-ordination and oxidation state of the metal atoms, TMDs can be metallic, semi-metallic or semiconducting(2, 3), e.g. WS$_2$ is a semiconductor while NbSe$_2$ is a metal(3). In addition, superconductivity(4) and charge density wave effects(5) have been observed in some TMDs. This versatility makes them potentially useful in many areas of electronics.

However, like graphene(6), layered materials must be exfoliated to fulfil their full potential. For example, films of exfoliated Bi$_2$Te$_3$ should display enhanced thermoelectric efficiency by suppression of thermal conductivity(7). Exfoliation of 2D topological insulators such as Bi$_2$Te$_3$ and Bi$_2$Se$_3$ would reduce residual bulk conductance,
highlighting surface effects. In addition, we can expect changes in electronic properties as the number of layers is reduced e.g. the indirect bandgap of bulk MoS$_2$ becomes direct in few-layer flakes\textsuperscript{(8)}. Although exfoliation can be achieved mechanically on a small scale\textsuperscript{(9, 10)}, liquid phase exfoliation methods are required for many applications\textsuperscript{(11)}. Critically, a simple liquid exfoliation method would allow the formation of novel hybrid and composite materials. While TMDs can be chemically exfoliated in liquids\textsuperscript{(12-14)}, this method is time consuming, extremely sensitive to the environment and incompatible with most solvents. We demonstrate exfoliation of bulk TMD crystals in common solvents to give mono- and few layer nano-sheets. This method is insensitive to air and water and can potentially be scaled up to give large quantities of exfoliated material. In addition, we show that this procedure allows the formation of hybrid films with enhanced properties. We initially sonicated commercial MoS$_2$, WS$_2$ and BN \textsuperscript{(15, 16)} powders in a number of solvents with varying surface tensions. The resultant dispersions were centrifuged and the supernatant decanted (Section S3). Optical absorption spectroscopy showed that the amount of material retained (characterised by $A/l = \alpha C$, where $A/l$ is the absorbance per length, $\alpha$ is the extinction coefficient and $C$ is the concentration) was maximised for solvents with surface tension close to 40 mJ/m$^2$\textsuperscript{(17, 18)} (Fig. 1A-C). Detailed analysis, within the framework of Hansen solubility parameter theory\textsuperscript{(19)}, shows successful solvents to be those with dispersive, polar and H-bonding components of the cohesive energy density within certain well-defined ranges (Section S4, Figs. S2-S3). This can be interpreted to mean that successful solvents are those which minimise the energy of
exfoliation. Importantly, this information will facilitate the search for new solvents and the development of solvent blends. Some of the more promising solvents were N-methylpyrrolidone (NMP) and isopropanol (IPA)(see Table S1 for full solvent list). Optimization of the dispersion procedure (Section S5), gave concentrations as high as 0.3 mg/ml for MoS$_2$, 0.15 mg/ml for WS$_2$ (both in NMP) and 0.06 mg/ml for BN (IPA). Photographs of typical dispersions, which are stable over periods of 100s of hours (Section S8, Fig. S13), are shown in Fig. 1D. Optical absorption spectra (Fig. 1E) show features expected for MoS$_2$ and WS$_2$(20, 21). In addition, a band edge at ~5 eV is clearly observed for dispersed BN. However, the spectra appear to be superimposed on a background, possibly due to scattering (Section S6, Fig. S4). A/I scaled linearly with concentration for all samples, allowing calculation of $\alpha$ values (Fig. 1F).

We performed TEM analysis on our dispersions, typically observing 2D flakes consisting of thin nanosheets. Examples of very thin sheets observed for all three materials are shown in Fig. 2A-C. The lateral size of these objects was typically 50-1000 nm for MoS$_2$ and WS$_2$ and 100-5000 nm for BN. (Section S7, Figs. S5-S12). We can examine these objects in more detail using aberration corrected TEM (Figs. 2D-F). These images and associated Fourier transforms illustrate the hexagonal symmetry of these materials. This is in contrast to reports on MoS$_2$ and WS$_2$ exfoliated by lithium intercalation which results in significant deviation from hexagonal structure (22-24). Fig. 2G-I show sections of the images in Fig. 2D-F after performing low-pass Butterworth filtering. These images reveal B-N bond lengths of 1.45Å and MoS$_2$ and WS$_2$ hexagon widths of 3.8 Å and 4 Å, confirming that no distortions have been introduced by exfoliation. Analysis of TEM
intensity profiles, coupled with flake edge analysis, electron diffraction and EELS data suggest the presence of mono-sheets in the sample(25).

Our dispersion/exfoliation method allowed us to prepare films of BN, MoS$_2$ and WS$_2$ by vacuum filtration(17) or spraying, with thickness ranging from a few nm to hundreds of microns. Photographs of free-standing films are shown in Fig. 3A. Scanning electron and helium ion microscopy of the surface and edges of these films shows them to consist of partially aligned 2D platelets (Figs. 3B,C and S17). The versatility of the solvent-exfoliation method makes it simple to create hybrid dispersions and films simply by adding another material to the dispersion. We illustrated this by preparing hybrid films of MoS$_2$ or WS$_2$ mixed with graphene or single-walled nanotubes (SWNT) (Fig. 3D, E and Section S10). With the exception of pure BN, all films were mechanically robust (Section S10, Figs. S18, S20). Addition of graphene or SWNTs increased the DC conductivity, $\sigma_{DC}$, from $\sim 10^6$ S/m for the TMD-only films to $\sim 2 \times 10^4$ S/m for the SWNT based hybrids (Fig. 3F). We performed thermoelectric measurements on free-standing WS$_2$/SWNT hybrid films, measuring $\sigma_{DC}$ and the Seebeck coefficient, $S$. Obtaining significant increases in $\sigma_{DC}$ without degrading $S$ to give high power factor ($S^2\sigma_{DC}$) is critically important in thermoelectric research(26). Here $S^2\sigma_{DC}$ increases from 0.2 $\mu$W/K$^2$m for disordered WS$_2$ films (27) to $\sim 100$ $\mu$W/K$^2$m for WS$_2$/SWNT films (Fig. 3G, Section S10).

Solvent processing greatly simplifies composite preparation (28-31), allowing us to prepare composites of polyurethane filled with BN, MoS$_2$ and WS$_2$. We observed
significant levels of reinforcement, comparable to the best results achieved using graphene(32) or nanoclays(33) as fillers (Figs. 3H, S19 and S20).

Exfoliated flakes can be deposited on substrates by spraying. Shown in Fig. 4A and B are an SEM and an AFM image of a silicon wafer spraycoated with MoS$_2$. The objects observed are hundreds of nm wide in agreement with the TEM data (25). We can confirm the flakes consist of MoS$_2$ by Raman mapping (Fig. 4C), based on the individual flake spectrum shown in Fig. 4D. We note that the peak positions(25, 34) in Fig. 4D are consistent with trigonal prismatic (2H) mono- or bi-layer MoS$_2$ (Section S9). SEM analysis (Fig. 4 E-H) shows that while some deposited flakes are very thin, many are multilayers or clusters which have aggregated during deposition. AFM and STM imaging of individual flakes shows them to display typical thicknesses of ~3-12 nm (Figs. 4 H-J, S15, S16, Section S9). Some of these images, particularly the STM image in Fig. 4L, show steps. These are consistently ~1nm high and probably originate in layer edges. Electrical characterisation of individual flakes shows n-type field-effect behaviour characterised by mobilities of ~0.01 cm$^2$/Vs (9, 10), rather lower than observed for mechanically exfoliated MoS$_2$ flakes (Section S11).

This exfoliation process is not limited to BN, MoS$_2$ and WS$_2$. We have exfoliated MoSe$_2$, MoTe$_2$, TaSe$_2$, NbSe$_2$, NiTe$_2$ and Bi$_2$Te$_3$ in a number of the solvents in table S1 (Section S12, Figs. S23, S24), and believe similar solvents may exfoliate all MX$_2$ compounds. We propose that this exfoliation technique is general as it can be applied to TMDs, graphene, BN and Bi$_2$Te$_3$. As such, we expect to extend it to TMOs(35) and other layered compounds.
Fig. 1: Optical characterisation of nano-sheet dispersions. A), B) and C) Concentration remaining after centrifugation (plotted as A/l) for MoS$_2$, WS$_2$ and BN dispersed in a range of solvents, plotted versus solvent surface tension. D) Photographs of dispersions of MoS$_2$ (in NMP), WS$_2$ (in NMP) and BN (in IPA). E) Absorbance spectra of dispersions of MoS$_2$ (NMP, 0.16 mg/ml), WS$_2$ (NMP, 0.15 mg/ml) and BN (IPA, 0.002
mg/ml) F) Lambert–Beer plots for MoS\(_2\) (NMP), WS\(_2\) (NMP) and BN (IPA). The dispersions in D), E) and F) were prepared using optimised dispersion conditions (25).

Fig. 2: TEM of nano-sheets. A), B) and C) Low resolution TEM images of flakes of BN, MoS\(_2\) and WS\(_2\) respectively. D), E) and F) High resolution TEM images of BN, MoS\(_2\) and WS\(_2\) monolayers. Inset: Fast Fourier transforms of the images. G), H) and I) Butterworth filtered images of sections of the images in D), E) and F).
Fig. 3: Nano-sheet films, hybrids and composites. A) Photograph of free standing films of BN, MoS$_2$ and WS$_2$ (thickness ~50 µm). B) An SEM image of the surface of an MoS$_2$ film. C) He ion microscope image of the edge of a WS$_2$ film. D and E) SEM images of the surface of a graphene/MoS$_2$ hybrid film and a SWNT/ WS$_2$ hybrid film respectively. F) DC conductivity of thin (~200 nm) hybrid films prepared from mixtures of WS$_2$ or MoS$_2$ (open or closed symbols) and SWNTs or graphene (circles or squares). G) Product
of Seebeck coefficient squared and DC conductivity (the power factor) for thick (~50 µm) WS₂/SWNT hybrid films. While the WS₂ film proved too brittle to measure, Ellmer et al. measured $S^2\sigma=0.22 \mu W/K^2m$ for a disordered WS₂ film. In F) and G), the x-axis is the mass fraction of SWNTs or graphene. H) Representative stress-strain curves for composites of polyurethane filled with each layered compound at loading levels of 5wt% and 20wt%.
Fig. 4: Deposition of nano-sheets onto surfaces. A) and B) An SEM and an AFM image of MoS$_2$ flakes deposited on SiO$_2$ by spraying. C) A Raman map of the same region. D) Typical Raman spectrum of an individual flake. The Raman map plots the integral of the spectrum between 390 and 410 cm$^{-1}$. E), F) and G) A very thin flake, a multilayer and a
cluster of aggregated multilayers. The dashed line in E has been inserted to illustrate the straightness of the flake edge. H) and I) SEM and AFM images of an individual flake. J) An STM image of an individual flake. The flakes in I) and J) have heights of 5 and 10 nm respectively. (25) K) An SEM image of an MoS$_2$ flake on Si/SiO$_2$ with electrodes deposited on top. L) Source-drain conductance as a function of gate voltage for the flake shown in K).
References

25. *See supporting material on Science Online.*
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