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Thickness sorting of two-dimensional transition metal dichalcogenides via copolymer-assisted density gradient ultracentrifugation

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Two-dimensional transition metal dichalcogenides have emerged as leading successors to graphene due to their diverse properties, which depend sensitively on sample thickness. Although solution-based exfoliation methods hold promise for scalable production of these materials, existing techniques introduce irreversible structural defects and/or lack sufficient control over the sample thickness. In contrast, previous work on carbon nanotubes and graphene has shown that isopycnic density gradient ultracentrifugation can produce structurally and electronically monodisperse nanomaterial populations. However, this approach cannot be directly applied to transition metal dichalcogenides due to their high intrinsic buoyant densities when encapsulated with ionic small molecule surfactants. Here, we overcome this limitation and thus demonstrate thickness sorting of pristine molybdenum disulfide (MoS_2) by employing a block copolymer dispersant composed of a central hydrophobic unit flanked by hydrophilic chains that effectively reduces the overall buoyant density in aqueous solution. The resulting solution-processed monolayer MoS_2 samples exhibit strong photoluminescence without further chemical treatment.

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Molybdenum disulfide (MoS_2), one of the transition metal dichalcogenides (TMDs), has been studied with great interest for a wide range of applications due to its unique electronic, optical and catalytic properties^{1–15}. The bulk MoS_2 crystal is a semiconductor with a 1.2 eV indirect bandgap and consists of covalently bonded S-Mo-S stoichiometric layers that interact with neighbouring layers via the relatively weak van der Waals interaction. When isolated as a single stoichiometric layer, MoS_2 shows strong visible photoluminescence due to the emergence of a 1.9 eV direct bandgap at the K point of the hexagonal Brillouin zone^{2,8,16}. To fully understand and exploit the unique properties of single-layered MoS_2 , many production methods have been developed including micromechanical¹, chemical^{11,17} and surfactant-assisted liquid-phase exfoliation^{18–21}, in addition to growth via chemical vapour deposition²². While the micromechanical cleavage technique produces single- or few-layered MoS_2 with high structural quality, this method lacks sufficient scalability for practical applications. On the other hand, solution-phase exfoliation of single-layered MoS_2 can be achieved by lithium intercalation, although this process drives a phase transition to the metallic 1T- MoS_2 structure, thus necessitating subsequent thermal treatments in an attempt to recover the semiconducting 2H- MoS_2 phase^{11,23}. However, complete semiconducting phase recovery has not yet been demonstrated, and the presence of the residual metallic phase can have detrimental effects, especially in electronic applications. Alternative liquid exfoliation methods can avoid the metallic 1T- MoS_2 phase transition, but typically yield a range of MoS_2 flake thicknesses. Finally, ultrathin MoS_2 growth by chemical vapour deposition requires high temperature processing and subsequent transfer from the growth substrate, which is arguably more cumbersome than solution-based approaches.

Here, we demonstrate an alternative solution-based route for preparing structurally pristine, ultrathin MoS_2 nanosheets via isopycnic density gradient ultracentrifugation (DGU). Originally used for biomolecule separations²⁴, DGU has emerged as one of the leading techniques for isolating structurally and electronically monodisperse populations of carbon nanotubes^{25–27} and graphene²⁸. The physical structure of carbon nanomaterials coupled with their surrounding hydrated amphiphilic surfactants in aqueous solution leads to subtle buoyant density differences that drive separation to their respective isopycnic points when subjected to ultracentrifugation in a density gradient medium. In previous DGU studies on carbon nanomaterials, small molecule ionic surfactants, such as sodium cholate (SC), have proven to be exceptional dispersants that also enable exquisite control over the buoyant density as a function of the carbon nanomaterial physical and electronic structure^{28,29}.

Results

Buoyant density model. To assess the applicability of DGU to MoS_2 nanosheets, the following geometrical buoyant density model was used for SC-encapsulated MoS_2 :

$$\rho(N) = \frac{\rho_s N + 2m_{\text{surf}}\sigma + 2\rho_{\text{H}_2\text{O}}t_{\text{H}}}{(N+1)t_{\text{MoS}_2} + 2t_{\text{A}} + 2t_{\text{H}}} \quad (1)$$

where $\rho_s = 3.39 \times 10^{-7} \text{ g cm}^{-2}$ is the sheet density of MoS_2 , N is the number of the MoS_2 sheets, $m_{\text{surf}} = 7.15 \times 10^{-22} \text{ g}$ is the mass of one SC molecule, $\sigma = 1.35 \text{ nm}^{-2}$ is the surface packing density of SC on MoS_2 , $\rho_{\text{H}_2\text{O}}$ is the density of water, $t_{\text{H}} = 3.3 \text{ nm}$ is the assumed hydration shell thickness, $t_{\text{MoS}_2} = 0.67 \text{ nm}$ is the MoS_2 interlayer distance, and $t_{\text{A}} = 0.355 \text{ nm}$ is the assumed anhydrous shell thickness. The values for σ , t_{H} , and t_{A} are based on previously established values for SC-encapsulated graphene²⁸. The resulting buoyant densities are presented in Fig. 1c, where

SC-encapsulated MoS_2 , even in the monolayer limit, is predicted to be more dense than iodixanol, the density gradient medium, at its solubility limit (1.32 g cm^{-3}). Evidently, the relatively large sheet density of MoS_2 compared with graphene implies that the hydration of SC is insufficient to lower the buoyant density of suspended MoS_2 nanosheets to a level compatible with isopycnic DGU.

To overcome this issue, we sought an alternative dispersant for MoS_2 that would enable greater hydration and thus lower buoyant density in aqueous solution. The nonionic, biocompatible, amphiphilic block copolymer Pluronic F68 was selected due to its relatively large molecular weight, long hydrophilic chains for effective steric hindrance, and its compatibility with the DGU process³⁰. In particular, F68 is composed of a central hydrophobic polypropylene oxide (PPO) unit surrounded by hydrophilic polyethylene oxide chains (Fig. 1a), and is known to be effective as an amphiphilic dispersant for graphene³¹ and DGU separation of carbon nanotubes³⁰. To estimate the buoyant density of F68-encapsulated MoS_2 , the parameters in the aforementioned model are modified as following: $m_{\text{surf}} = 1.40 \times 10^{-20} \text{ g}$ is the mass of one F68 molecule, $t_{\text{A}} = 1.6 \text{ nm}$, $t_{\text{H}} = 20.6 \text{ nm}$ and σ is varied between 0.058 and 0.575 nm^{-2} to account for the two likely extremes where the surface coverage of PPO chains on the MoS_2 surface ranges from 10–100%. While this model is oversimplified, it suggests that the buoyant density of F68- MoS_2 is substantially reduced compared with SC- MoS_2 and likely to fall within the achievable range of iodixanol-based density gradients, especially in the limit of ultrathin MoS_2 (Fig. 1c).

Thickness sorting via density gradient ultracentrifugation.

To assess the effectiveness of F68- MoS_2 for DGU, 1 g of MoS_2 powder was first exfoliated and dispersed in 2% weight per volume (w v^{-1}) aqueous solution of F68 via tip ultrasonication (See Supplementary Discussion for details). After ultrasonication, we found that 17.1% of the initial MoS_2 mass was dispersed, as determined by measuring the mass of the undispersed residual MoS_2 slurry. The resulting F68- MoS_2 dispersion was placed in a step density gradient and ultracentrifuged at 32 kr.p.m. for 24 h to remove thick MoS_2 flakes and enhance the population of thin MoS_2 nanosheets (Fig. 2a). After this concentration step, 0.027 mg of MoS_2 flakes with thickness $< 5 \text{ nm}$ remain, of which 24% are single-layer MoS_2 flakes as determined by AFM. This level of exfoliation is comparable to previous literature³² and may be improved with the development of emerging techniques such as shear mixing^{33,34} or ball milling³⁵. After ultracentrifugation, dense iodixanol solution containing 2% w v^{-1} F68 was injected above the sedimented aggregates at the bottom of ultracentrifuge tube to separate and allow fractionation of the concentrated MoS_2 nanosheets. The extracted F68- MoS_2 dispersion was stable for several months. We also observed that when concentrated MoS_2 nanosheets were prepared using SC as the surfactant, there was no isolation of a SC- MoS_2 band (Supplementary Fig. 2), which further illustrates the effectiveness of F68 as a dispersant for MoS_2 .

After the concentration step, the fractionated F68- MoS_2 solution was placed at the bottom of a linear density gradient and ultracentrifuged at 28 kr.p.m. for 12 h. The first iteration of DGU induces the F68- MoS_2 nanosheets to separate into multiple visible bands throughout the ultracentrifuge tube (Fig. 2b). These bands were recovered in 1 mm steps using a piston gradient fractionator and labelled with their position (that is, fractions were recovered starting from 6 mm above the first band and thus f7 indicates the fraction that encompasses the first band). For further refinement, three fractions from the most well-defined bands (f7, f17 and f27) and relatively wider bands (f9, f13 and f23) were extracted, and then placed at the top of a linear density

enriched in single-layer MoS₂, possesses a mass of 0.002 mg, which implies that DGU captures 30.8% of the exfoliated single-layer MoS₂ flakes (See Supplementary Discussion for more details on the calculation of the DGU yield). It should be noted that similar DGU results were achieved for other TMDs (for example,

DGU of WS₂, MoSe₂ and WSe₂ are shown in Supplementary Figs 3 and 4), thus demonstrating the generality of the copolymer-assisted DGU for thickness sorting of two-dimensional nanomaterials.

Structure analysis of sorted MoS₂ nanosheets. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was used to verify the 2H structural phase and characterize atomic-level defects of the MoS₂ nanosheets. Figure 3a shows a schematic illustration of the 2H structural phase with trigonal prismatic coordination. A Fast Fourier Transform from the HAADF-STEM image with two direction index is shown in Fig. 3b. Figure 3c,d show high resolution HAADF-STEM images of MoS₂ nanosheets before and after DGU. The inset in Fig. 3d shows the magnified STEM image with the position of Mo (blue) and S (brown) atoms. These STEM images reveal that the pristine 2H semiconducting structure of MoS₂ is preserved with minimal surface or edge defects following DGU processing³⁶.

Atomic force microscopy (AFM) was used to characterize the thickness and size of the sorted MoS₂ nanosheets. AFM images (Fig. 4a) indicate that the most buoyant fraction (f7) contains predominantly monolayers, while the less buoyant fraction (f17) primarily consists of MoS₂ multilayers. From the line profile, a monolayer MoS₂ flake in f7 has ~1 nm thickness. This measured thickness is slightly larger than previously reported values^{2,4}, which is reasonable due to the presence of residual F68. Figure 4b,c show the AFM-measured thickness and area histograms for MoS₂ nanosheets from the f7, f17 and f27 fractions. These histograms were obtained from >100 individual

MoS₂ flakes from each fraction. The average flake thicknesses for fractions f7, f17 and f27 are 1.02, 1.84 and 2.52 nm, respectively, thus demonstrating effective thickness sorting by DGU. In contrast, the flake area histograms show significant overlap, which is consistent with the buoyant density of two-dimensional nanomaterials being independent of lateral area (to corroborate the AFM lateral size histograms, scanning electron microscopy analysis was also performed; see Supplementary Fig. 9). Overall, it is evident that the MoS₂ DGU separation is driven by thickness instead of the lateral size with ~86% of the MoS₂ nanosheets from f7 having a thickness <1.2 nm, which corresponds to single layers of MoS₂.

On the basis of the measured thickness and buoyant density values, the MoS₂ experimental data are plotted with the geometrical buoyant density model in Fig. 5a. The experimental values (purple squares) imply a Pluronic F68 packing density σ of 0.244 nm⁻². Since the PPO chain of Pluronic F68 occupies an area of ~1.74 nm² on the MoS₂ surface, this packing density corresponds to ~42.5% surface coverage of Pluronic F68 (ref. 37). In Supplementary Table 2, the surface coverage of F68 for WS₂, MoSe₂ and WSe₂ are determined to be 61.4, 68.2 and 57.0%, respectively. These experimentally determined surface coverages correlate with the relative hydrophobicity of each TMD. In particular, the most hydrophilic MoS₂ surface shows the lowest F68 surface coverage, which is consistent with expectations since F68 interacts with the TMD surface via its hydrophobic PPO chains.

Spectroscopic characterization. Following DGU, optical absorbance spectra for fractions f7, f17 and f27 in addition to the MoS₂

Figure 3 | Atomic structure of MoS₂ before and after DGU. (a) Schematic illustration of the 2H semiconducting crystal structure of MoS₂ shown from out-of-plane and perspective view (blue: Mo, brown: S). (b) Fast Fourier Transform of the STEM images. (c,d) HAADF-STEM images of MoS₂ flakes before and after DGU, respectively. The inset image shows the magnified STEM image after DGU. The blue and brown spheres indicate the position of Mo and S atoms, respectively (scale bar, 0.5 nm).

Figure 4 | Characterization of thickness and area distribution. (a) Atomic force microscopy (AFM) images of MoS₂ nanosheets from f7 (purple) and f17 (orange) on a SiO₂ substrate and the corresponding height profiles along the dashed lines (scale bar, 100 nm). (b) Flake thickness and (c) flake area histograms for f7 (purple), f17 (orange) and f27 (red) fractions obtained from the AFM images.

Figure 5 | Buoyant density analysis and optical properties. (a) Experimental data (purple squares) are plotted with the buoyant density model using a surface coverage variation from 10–100% (black lines). The surface coverage of F68 on the MoS₂ surface determined from the experimental data, which corresponds to ~42.5%, is also shown as a purple line. (b) Optical absorbance spectra of fractions f7 (purple), f17 (orange) and f27 (red), and the MoS₂ dispersion before separation (black). (c) Raman spectra of each fraction showing the shifts in the in-plane and out-of-plane vibrational modes as a function of MoS₂ thickness. (d) Photoluminescence spectra of fraction f7 (purple) compared with a micromechanically exfoliated monolayer MoS₂ (green).

dispersion before separation were measured (Fig. 5b). The direct MoS₂ excitonic transition peaks at ~610 and ~660 nm are present in all of the samples after DGU, further confirming that the original 2H-MoS₂ crystal structure was maintained through the separation process. The two absorption peaks between 600 and 700 nm are attributed to the excitonic peaks of MoS₂. The weaker optical intensity of these peaks from f7, f17 and f27 are due to the relatively small concentration of MoS₂ in the solution following DGU. In addition, the blue shift observed in these peaks is consistent with the smaller lateral flake size following DGU (See

Supplementary Fig. 9)^{38–41}, and the strong absorption <400 nm is attributed to the density gradient medium (that is, iodixanol).

Each MoS₂ fraction was also characterized by Raman spectroscopy (Fig. 5c). In this case, MoS₂ films were prepared by vacuum filtration and transferred onto a SiO₂ substrate, at which point Raman spectra were obtained using a beam size of ~1 μm and an excitation wavelength of 514 nm. The Raman spectra from the unsorted MoS₂ sample and fraction f27 show two peaks, specifically the in-plane E_{2g}¹ mode at ~382 cm⁻¹ and the out-of-plane A_{1g} mode at ~407 cm⁻¹, which are comparable to

those of bulk MoS₂ (ref. 16). As the number of layers decreases, the E_{1g} mode is stiffened and the A_{1g} mode is softened, such that the peaks from fraction f7 are shifted to $\sim 384\text{ cm}^{-1}$ and $\sim 404\text{ cm}^{-1}$, respectively¹⁶. In addition, the width of these two peaks is reduced in the more buoyant fractions, which confirms that the flake thickness homogeneity is improved by DGU.

To further verify the isolation of MoS₂ monolayers, photoluminescence spectroscopy was performed on fraction f7 (purple line) using an excitation wavelength of 514 nm (Fig. 5d). For comparison, a photoluminescence spectrum was obtained under identical measurement conditions from a micromechanically exfoliated monolayer of MoS₂ (green line), and both spectra were normalized using their Raman spectra (optical microscopy image of the micromechanically exfoliated monolayer MoS₂ is shown in Supplementary Fig. 6). The photoluminescence spectra from each fraction show two peaks with comparable intensities at ~ 610 and $\sim 660\text{ nm}$ that are well correlated with the MoS₂ excitonic transitions. WS₂ nanosheets were similarly characterized following DGU, where photoluminescence was also observed from the most buoyant fractions (See Supplementary Fig. 7).

Discussion

In conclusion, isopycnic DGU enables solution-phase preparation of controlled thickness TMDs. Specifically, the amphiphilic block copolymer Pluronic F68 increases the hydration and thus reduces the effective buoyant density of TMDs into the range of standard density gradient media. Thickness sorting of TMDs is confirmed with AFM and Raman spectroscopy, resulting in the emergence of photoluminescence from the most buoyant single-layered nanosheets. Furthermore, atomic-resolution STEM imaging verifies that the resulting thickness-sorted TMDs possess high crystal quality with low surface and edge defect density. Since DGU has proven industrial scalability, this approach holds promise for the solution-phase production of monolayered TMDs in emerging large-volume applications including photovoltaics, catalysis, biotechnology and electronics.

Methods

Dispersion and density gradient ultracentrifugation. One gram of MoS₂ powder (American Elements) was dispersed in 70 ml of 2% wv⁻¹ Pluronic F68 (BASF) aqueous solution via ultrasonication using a 0.125-inch tip in a steel beaker at 25 W for 2 h. Then, 32 ml of dispersion was carefully added on top of a 6 ml underlayer of 60% wv⁻¹ iodixanol and ultracentrifuged at 32 kr.p.m. for 24 h at 22 °C using a SW32 Ti rotor (Beckman-Coulter). Following ultracentrifugation, 3 ml of 60% wv⁻¹ iodixanol was injected to separate $\sim 10\text{ ml}$ of concentrated MoS₂ nanosheet solution, which was then fractionated using a piston gradient fractionator (BioComp Instruments). For the first iteration, the concentrated MoS₂ solution was diluted to contain 46% wv⁻¹ iodixanol, and placed under a linear density gradient of 25–45% wv⁻¹ iodixanol. The linear density gradient was then ultracentrifuged at 28 kr.p.m. for 12 h at 22 °C. Following the first iteration, each fraction was diluted to contain 9% wv⁻¹ iodixanol and placed on top of a linear density gradient of 30–50% wv⁻¹ iodixanol for the second iteration. The linear density gradient was then ultracentrifuged in an SW41 Ti rotor (Beckman-Coulter) at 41 kr.p.m. for 12 h. All density gradient and injection solutions contained 2% wv⁻¹ F68.

Sample preparation for scanning transmission electron microscopy. MoS₂ dispersions from each step (after sonication before DGU and after DGU) were collected and placed in 20 k MWCO dialysis cassettes (Thermo Scientific) and dialysed in 750 ml of 2% wv⁻¹ F68 aqueous bath for 24 h to remove the density gradient medium. To remove the surfactant, MoS₂ dispersions were mixed with isopropyl alcohol for 24 h, filtered through mixed cellulose ester membranes (Millipore, 50 nm pore size), and rinsed with deionized water. The resulting aggregated MoS₂ nanosheets were then bath sonicated (Branson ultrasonic cleaner 3510) to redisperse in deionized water.

Sample preparation for atomic force microscopy. The separated MoS₂ fractions were dialysed in 750 ml of 2% wv⁻¹ SC bath for 48 h to enable surfactant exchange. Before deposition, a SiO₂ substrate was rinsed with acetone, methanol and deionized water and immersed in 2% polyethylenimine for 2 min to form a self-assembled monolayer. The substrate was then dried under nitrogen gas, rinsed

in deionized water and dried again. The samples were drop casted onto polyethylenimine-treated SiO₂ substrate for 5 min, dried under nitrogen gas, rinsed in deionized water, dried again and annealed at 250 °C for 1 h to remove residual surfactants and iodixanol. To increase the areal density of MoS₂ flakes, this process was repeated 5–10 times.

Sample preparation for Raman and photoluminescence spectroscopy. MoS₂ films were prepared via the vacuum filtration method. In particular, 2 ml of MoS₂ dispersion was filtered. The residual surfactant and iodixanol were then removed by rinsing with 30 ml of deionized water. The resulting film was immersed in ethanol and pressed firmly onto a SiO₂ substrate for 10 min by applying pressure with a 1.5 kg weight. To remove the membrane, the substrate was suspended above a boiling acetone bath at 85 °C at a 45° angle. After 15 min, the substrate was rinsed with ethanol, acetone, ethanol again and deionized water, and then dried with nitrogen gas.

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Author contributions

All the authors conceived and designed the experiments, J.K. and J.-W.T.S. performed the experiments, D.A., A.P. and M.J.Y. performed the STEM imaging and analysis, and all authors co-wrote the manuscript.

Additional information

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