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High yield exfoliation of two-dimensional chalcogenides using sodium naphthalenide

Jian Zheng¹, Han Zhang¹, Shaohua Dong¹, Yanpeng Liu¹, Chang Tai Nai¹, Hyeon Suk Shin², Hu Young Jeong², Bo Liu¹ & Kian Ping Loh¹

Transition-metal dichalcogenides like molybdenum disulphide have attracted great interest as two-dimensional materials beyond graphene due to their unique electronic and optical properties. Solution-phase processes can be a viable method for producing printable single-layer chalcogenides. Molybdenum disulphide can be exfoliated into monolayer flakes using organolithium reduction chemistry; unfortunately, the method is hampered by low yield, submicron flake size and long lithiation time. Here we report a high-yield exfoliation process using lithium, potassium and sodium naphthalenide where an intermediate ternary Li_xMX_n crystalline phase (X = selenium, sulphur, and so on) is produced. Using a two-step expansion and intercalation method, we produce high-quality single-layer molybdenum disulphide sheets with unprecedentedly large flake size, that is up to $400\ \mu\text{m}^2$. Single-layer dichalcogenide inks prepared by this method may be directly inkjet-printed on a wide range of substrates.

¹Department of Chemistry and Graphene Research Centre, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore.

²Interdisciplinary School of Green Energy and Low Dimensional Carbon Materials Center, UNIST Central Research Facilities (UCRF), Ulsan National Institute of Science and Technology (UNIST), UNIST-gil 50, Ulsan 689-805, Korea. Correspondence and requests for materials should be addressed to K.P.L. (email: chmlhkp@nus.edu.sg).

Post graphene discovery, single-layered transition-metal dichalcogenides (LTMDs), such as MoS₂ and WS₂, have attracted great attention as next generation two-dimensional (2D) materials owing to their large intrinsic bandgap^{1–13}, which is particularly attractive in view of the gapless nature of graphene^{14–16}. Single-layer MoS₂ has attractive attributes such as a direct bandgap (1.9 eV), large in-plane mobilities (200–500 cm² V⁻¹ s⁻¹), high current on/off ratios (exceeding 10⁸), as well as remarkable mechanical and optical properties^{17,18}. Two-dimensional quantum confinement of carriers can be exploited in conjunction with chemical composition to tune the optoelectronic properties of the metal chalcogenides at the nanoscale. These properties are of great interest for applications in optoelectronic devices such as thin film solar cells, photodetectors, flexible logic circuits and sensors^{19–23}.

Transition-metal chalcogenides (TMC) possessing lamellar structures can serve as hosts for the intercalation of a wide variety of electron-donating species ranging from Lewis base to alkali metals^{24,25}. One well-known class of intercalants is the organolithium compounds. MoS₂ can be intercalated with lithium to give the reduced Li_xMX_n phase (X = Se, S, and so on) with expanded lattice, this can be exfoliated in a second step into single-layer sheets by ultrasound-assisted hydration process^{26–29}. However long lithiation time (for example, 3 days at 100 °C) is typically needed when *n*-butyl lithium is used as lithiation agent due its inclination to form dimeric, trimeric and higher aggregates, which diffuse slowly into the interlayers in large-sized TMC crystals. Subsequent exfoliation from the lithiated MoS₂ suffers a low yield of single-layer flakes, disintegration into submicron-sized flake, formation of metal nanoparticles and precipitation of Li₂S^{5,29}. This has limited the development of solution-processed LTMDs in most applications that demand clean and large-sized flakes. An electrochemical approach has been developed recently to produce single-layer MoS₂ and WS₂ flakes; however, the upward scaling of this process is limited by volumetric resistance in battery-type cells³⁰. In such electrochemical cells, 10% acetylene black nanoparticles are typically added to the host materials to reduce volumetric resistance but this creates one problem: carbon nanoparticles are mixed with LTMDs and these contaminants are hard to be dislodged from the surface. Similar to the research directions in solution-processed graphene, there is a clear need to explore new chemistry to make high-quality single-layer LTMDs in high yield.

The intercalation of lithium into layered molybdenum disulphide may be described as an ion–electron transfer topotactic reaction. In most reported papers, organolithium reagents were used as intercalating agents because of its solubility in a wide range of solvents and the formation of stoichiometric LiMoS₂ ternary products^{26–29}. Compared with Li ions, other alkali ions such as Na or K were less commonly used in exfoliation chemistry. The ionic radii of Na and K are several times larger than that of Li ions, which means that in principle these ions can expand the lattice in the *c*-axis direction to a larger extent. More importantly, Na and K intercalation compounds react more violently with water than Li compounds, implying that single-layer TMDs should be exfoliated more efficiently. Intercalation of Na and K can also produce different structural and electronic effect compared with Li due to different coordinative complexation by the host. In Li_xMX_n, Li is always octahedrally coordinated; however, K and Na can occupy octahedral or trigonal prismatic site. This has important implications electronically due to the metallic to semiconductor properties transition in these compounds. Metal electride solution consisting of Na in concentrated liquid ammonia can be a

powerful reducing agent, except that ammonia molecule has a tendency to coordinate with Mo and displace S, this can result in decomposition and segregation of Mo nanoparticles^{31,32}. In spite of numerous reports that discussed the exfoliation of LTMDs, few of these methods can meet the demand of producing high yield, high purity and large-sized flakes^{33,34}.

Our search for alkali metal adducts lead us to naphthalene, which forms intensely coloured compounds with alkali metals. In sodium naphthalenide (Na⁺C₁₀H₈⁻), for example, the metal transfers an electron to the aromatic system to produce a radical anion which has strong reducing properties. Although sodium naphthalenide was first investigated in 1936 by Scott *et al.*³⁵, the synthetic utility of this alkali metal adduct has not been fully explored. It is interesting to consider whether single-layer LTMDs can be produced by reacting MoS₂ with various alkali metal naphthalenide adduct in a radical anion solution.

Motivated thus, we prepare naphthalenide adducts of Li, K and Na and compare the exfoliation efficiency and quality of MoS₂ generated. Using a two-step expansion and intercalation method, we report the production of high-quality single-layer MoS₂ flake sheets with unprecedentedly large flake size, that is, up to 400 μm² when the Na adduct was intercalated. Single-layer MoS₂ inks prepared by this method could be directly jet-printed on a wide range of substrate.

Results

Production of LTMDs. Figure 1 shows the schematic diagram of the processing steps involved in obtaining well-dispersed samples of LTMDs. First, bulk MoS₂ crystals (or powders) are expanded by reacting with hydrazine (N₂H₄) in hydrothermal condition (Fig. 1a). The expansion mechanism can be explained by a redox-rearrangement model in which part of the N₂H₄ is oxidized to N₂H₅⁺ upon intercalation. The intercalated N₂H₅⁺ is not thermally stable and will be decomposed to N₂, NH₃ and H₂ upon heating the intercalated MoS₂ films at high temperature. Decomposition and gasification of intercalated N₂H₄ molecules expands the MoS₂ sheets by more than 100 times compared to its original volume. In a second step, the expanded MoS₂ crystal is intercalated by alkali naphthalenide solution (Fig. 1b). Finally the intercalated MoS₂ is exfoliated by dipping in ultrasonicated water operated at low power to avoid fragmentation of the sheets. A black suspension consisting predominantly of 90% single-layer MoS₂ can be obtained after centrifugation and decanting the supernatant (Supplementary Fig. S1). The generic applicability of this method has been tested successfully on a wide range of LTMDs, which includes the high yield exfoliation of monolayer TiS₂, TaS₂, and NbS₂, as well as few layer (2–4) diselenide TiSe₂, NbSe₂, and MoSe₂ (Supplementary Fig. S2).

Intercalation and exfoliation. XRD measurements were done on freshly intercalated, hermetically sealed samples after drying in argon and vacuum. The position and intensity of the (002) peak originating from the hexagonal 2H-MoS₂ can be used to judge the extent of intercalation and exfoliation. In freshly intercalated samples, the (002) peaks of the pristine MoS₂ is shifted completely toward lower angles, indicating expansion of the lattice along the *c*-axis and formation of stoichiometric ternary compounds (Fig. 2). The spacing between adjacent layers in the expanded lattice of the each intercalated phase are K *c*/2 = 7.92 Å, Na *c*/2 = 7.05 Å and Li *c*/2 = 6.18 Å, respectively. The increase in the interlayer distance as a result of the intercalation is Δ*c*/2 = (*c*/2 - *c*₀/2), K Δ*c*/2 = 1.88 Å, Na Δ*c*/2 = 1.01 Å and Li Δ*c*/2 = 0.14 Å. It is worth noting that these Δ*c*/2 values are much smaller than that of naphthalene-intercalated MoS₂ produced by an exfoliating-restacking process, which indicates that the organic

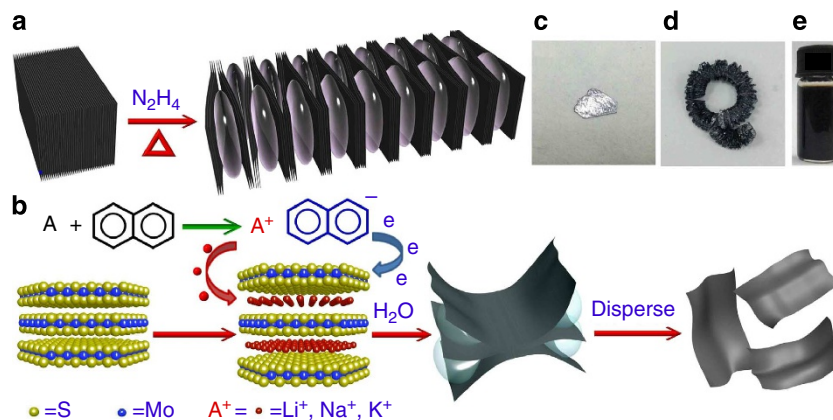


Figure 1 | Schematic of fabrication processes. (a) Bulk MoS₂ is pre-exfoliated by the decomposition products of N₂H₄. (b) Pre-exfoliated MoS₂ reacts with A⁺C₁₀H₈⁻ to form an intercalation sample, and then exfoliates to single-layer sheets in water. (c) Photograph of bulk single-crystal MoS₂, (d) photograph of pre-exfoliated MoS₂, (e) photograph of Na-exfoliated single-layer MoS₂ dispersion in water.

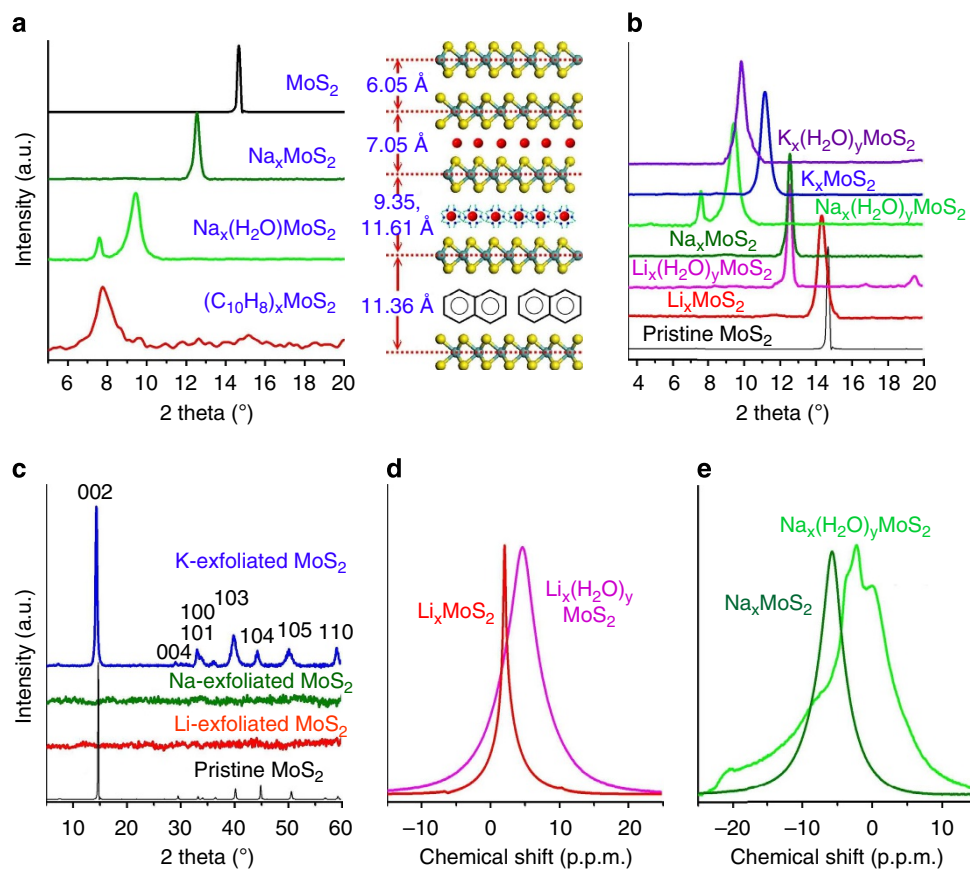


Figure 2 | Characterization of intercalated and exfoliated MoS₂. (a) XRD pattern and schematic of pristine MoS₂, Na-intercalated MoS₂, after exposure of Na-intercalated MoS₂ to the ambient for 3 days, exfoliated-and-restacked naphthalene-intercalated MoS₂. (b) Li-, Na- and K-intercalated MoS₂, after exposure of intercalated sample to the ambient for 3 days. (c) Li-, Na- and K-exfoliated MoS₂ without any annealing. (d) Solid-state ⁷Li NMR spectra of Li_xMoS₂ and Li_x(H₂O)_yMoS₂, (e) Solid-state ²³Na NMR spectra of Na_xMoS₂ and Na_x(H₂O)_yMoS₂.

anion is not intercalated in the MoS₂ crystal. Fig. 2b shows that after three days of storage in wet air (humidity around 27.5 g m⁻³), the intensity of the (002) peaks is reduced and they shift toward smaller angles (K $c/2 = 8.99$ Å, Na $c/2 = 9.35$ and 11.61 Å and Li $c/2 = 7.08$ Å). This additional shift is ascribed to the continuous hydration of the intercalated ions, leading to further lattice expansion.

The intercalated compounds are exfoliated by hydration, and the exfoliated sheets are dried into powder form and characterized by XRD (Fig. 2c). In the case of K-intercalated MoS₂, peaks due to the intercalated host compound as well as restacked (002) peak of MoS₂ show significant intensities, which reflects incomplete exfoliation. However the (002) peaks vanish completely in the exfoliated Na-intercalated and Li-intercalated

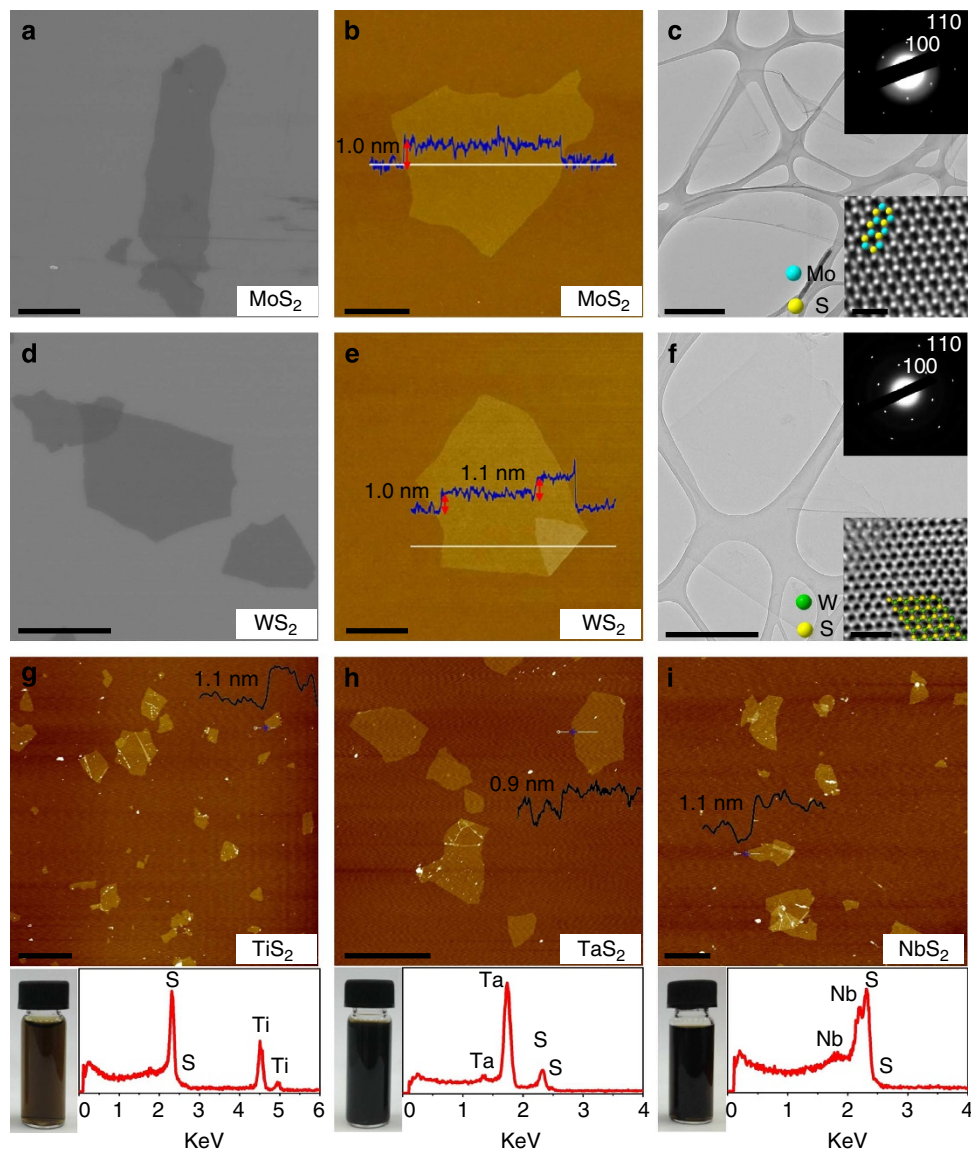


Figure 3 | Morphology characterization of LTMDs. (a) SEM images of Na-exfoliated single-layer MoS₂. (b) AFM images of Na-exfoliated single-layer MoS₂. (c) TEM images of Na-exfoliated single-layer MoS₂, insets are the corresponding SAED and aberration-corrected HRTEM images. (d) SEM images of Na-exfoliated single-layer WS₂. (e) AFM images of Na-exfoliated single-layer WS₂. (f) TEM images of Na-exfoliated single-layer WS₂, insets are the corresponding SAED and aberration-corrected HRTEM images. (g) AFM images TiS₂, and corresponding EDS and photograph of dispersion in water. (h) AFM images of TaS₂. (i) AFM images of NbS₂. (g–i) give average thickness of ~1 nm, confirming that single-layer is successfully produced by our method. Scale bars in (a) is 10 μm, in (b,d,g,h) are 5 μm, in (c,e) are 1 μm, in (f) is 500 nm, in (i) is 2 μm, in inner images of (c,f) are 1 nm.

samples, which is a signature of complete exfoliation^{29,30}. After annealing at 150 °C to remove water, weak (002) peaks recover in the Na and Li-exfoliated samples due to limited degree of restacking (Supplementary Fig. S3). Solid-state NMR is used to study the local coordination environments of the alkali metal cations before and after hydration (Fig. 2d,e). The central peaks in freshly intercalated MoS₂ are sharp and symmetrical indicating a highly uniform chemical environment for most intercalated cations. After hydration, both central peaks of Li⁷ and Na²³ solid NMR are broadened and shifted to lower frequencies, which can be attributed to dynamic processes or complex coordination environment with H₂O molecules.

Morphology characterization. The uniformity and size distribution of the single-layer LTMDs sheets are examined using scanning electron microscopy (SEM) (Fig. 3a,d). One remarkable

result is that 80% of the single-layer MoS₂ sheets has lateral widths of around 10 μm, this about 10 times larger than solution-exfoliated flakes reported using *n*-butyl lithium methods^{28,30}. As shown in Fig. 3a, a typical single-layer MoS₂ flake has a surface area of 400 μm². When the same intercalation-and-exfoliation process is performed on WS₂ crystals, 80% of the exfoliated flakes obtained are determined to be single layers with lateral dimensions between 3 and 10 μm, which essentially match the grain size of WS₂ powder before exfoliation (Fig. 3d). To assess the effectiveness of this method, the exfoliation yield in terms of micron-sized flakes is compared with the commonly used exfoliating agent *n*-butyl lithium on the same starting materials, the results show that only submicron-sized flakes can be generated using the latter (Supplementary Figs S4–S6).

The thickness of the exfoliated sheets is characterized by atomic force microscopy (AFM). Fig. 3b,e show typical tapping mode AFM images of exfoliated MoS₂ and WS₂ deposited on a

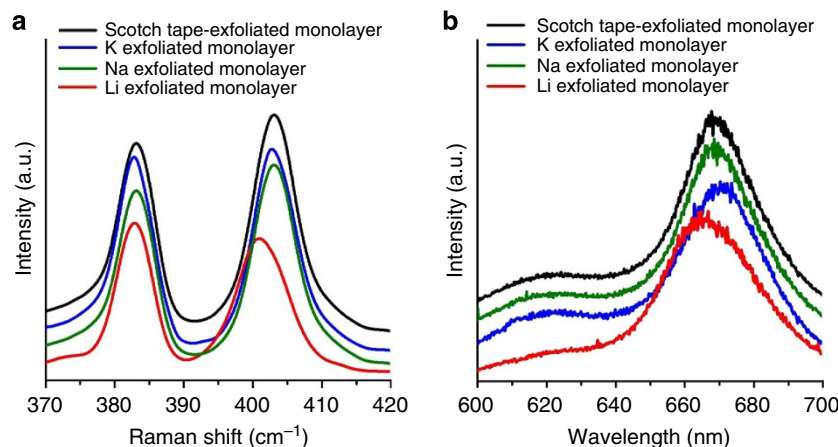


Figure 4 | Raman and photoluminescence spectrum of MoS₂. (a) Raman spectra of scotch-tape-exfoliated single-layer MoS₂ and Na-, K- and Li-exfoliated single-layer MoS₂ deposited on Si/SiO₂ substrate. (b) Photoluminescence spectrum of scotch-tape-exfoliated single-layer MoS₂, and Na-, K- as well as Li-exfoliated single-layer MoS₂ nanosheet deposited on Si/SiO₂ substrate.

SiO₂/Si substrate by spin-coating. The average topographic height is around 1 nm, which agrees with typical height of a single-layer MoS₂ (between 0.6 and 1.0 nm)³⁰. Statistical analysis of 100 flakes produced by the three different alkali metal adduct reveal 20, 90, and 80% of the flakes to be monolayer for K_xMoS₂, Na_xMoS₂, and Li_xMoS₂, respectively (Supplementary Fig. S7). Although K_xMoS₂ reacts more violently with water than Na_xMoS₂ and Li_xMoS₂, its large ionic radius precludes full intercalation. Intercalating WS₂ with sodium naphthalenide also produces single-layer WS₂ flakes with a yield of ~90%.

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on the exfoliated flake suspended on a lacey carbon TEM grid (Fig. 3c,f). The SAED patterns of exfoliated MoS₂ and WS₂ exhibit high crystallinity (the inset in Fig. 3c,f, Supplementary Fig. S8), as judged from the characteristic honeycomb lattice. From XPS analysis, the Na-exfoliated MoS₂ film shows Mo 3*d* peaks with peak position and width characteristic of the 2H phase²⁸ (Supplementary Figs S9–S11).

Optical characterization. The Raman spectra of the exfoliated MoS₂ flakes were recorded using a 532-nm excitation line (Fig. 4a and Supplementary Fig. S12). For Na-exfoliated samples, the E_{2g}¹ phonons stiffen with decreasing number of layers and a blue shift of the peak from 380 cm⁻¹ of the thick layers to 383 cm⁻¹ of monolayer MoS₂ occurs. On the other hand, A_{1g} phonons soften with decreasing number layers, giving rise to a red shift from 407 cm⁻¹ in the bulk material to 403 cm⁻¹ in the monolayer. The Raman signature obtained is consistent with that of mechanically exfoliated single-layer MoS₂ (ref. 36). The corresponding Raman peaks in Li-exfoliated MoS₂ are much broader, which can be due to slight doping and possible presence of defects.

Single-layer MoS₂ exhibits a unique signature in its optical spectrum in the form of photoluminescence (PL) due to the transition from an indirect to a direct-bandgap semiconductor (Supplementary Fig. S13). MoS₂ appears in two distinct symmetry: 2H (trigonal prismatic D3h) and 1T (octahedral Oh) phases. The 2H phase is semiconducting while 1T is metallic (Supplementary Note 1). In this work, PL can be observed on the exfoliated flakes after a brief bake at 200 °C to transform it to the 2H phase. As shown in Fig. 4b, the PL spectrum of a Na-exfoliated single-layer MoS₂ exhibits a peak centred at 668 nm

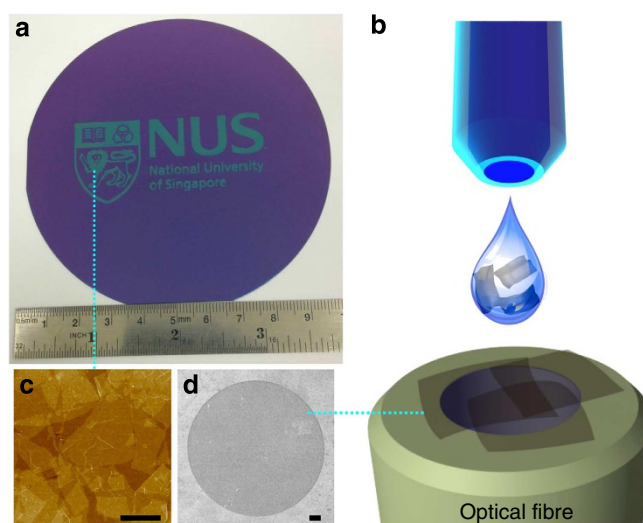


Figure 5 | Inkjet printing of MoS₂. (a) Wafer-scale MoS₂ pattern jet-printing. Large area, continuous and highly uniform MoS₂ thin film pattern were directly printed on a 4-inch Si/SiO₂ wafer by inkjet printing. (b) Schematic showing the printing of MoS₂ thin film on the optical fibre pigtail. (c) AFM image of MoS₂ thin film, showing a thickness of 1-4 layers. (d) SEM image of MoS₂ thin film-coated optical fibre pigtail. Scale bar is 5 μm in (c,d).

(1.86 eV) with a shoulder at 623 nm (1.99 eV), which agrees with excitonic peaks arising from the K point of the Brillouin zone. The PL peak position and peak width is consistent with mechanically cleaved monolayer MoS₂ (ref. 3). The Li-exfoliated monolayer sample shows a weaker PL peak, this reflects either slight doping or the presence of defects in it. The chemical purity of the Na-exfoliated MoS₂ flakes is verified by energy-dispersive X-ray spectroscopy (Supplementary Fig. S14) and its electrical property is evaluated in the form of a field effect transistor (Supplementary Fig. S15 and Supplementary Note 2). The field effect mobility of monolayer MoS₂ flake is measured to be in the range of 1–8 cm²/(V × s) while that of few layer MoS₂ flakes are in the range of 20–80 cm²/(V × s), which are comparable with those of field effect transistor made from mechanically exfoliated MoS₂ flakes³⁷.

Inkjet printing. Inkjet printing is highly promising for the high-throughput deposition of micron-sized patterns by virtue of its speed, low cost, additive and direct writing capability³⁸. The good dispersion and high viscosity of our MoS₂ dispersion render it highly suitable for jet-printing. The ink is made from 0.02 mg ml⁻¹ MoS₂ fully dispersed in ethanol/water (2:1 volume) solution (viscosity 2.64 cP and surface tension 34.3 mN m⁻¹). To print high-resolution patterns and uniform films, 10- μ m diameter printer nozzle is selected, and the wafers are heated to 60 °C before printing (Supplementary Figs S16, S17 and Supplementary Note 3). Owing to the moderate surface energy of the ink, MoS₂ inks can be directly printed on plastic, SiO₂, glass and optical fibre pigtail (Fig. 5a–d) without any chemical/physical modification. Figure 5a shows the word ‘NUS’ printed directly using the MoS₂ flakes. The AFM and SEM characterization of the MoS₂ printed thin film show that the printed MoS₂ film is continuous and uniform with a sheet thickness of 2–3 layers, as shown in Fig. 5c,d.

Discussion

In summary, we have explored the use of metal naphthalenide for the intercalation–exfoliation of metal chalcogenides (MoS₂ and WS₂) and obtained high-efficiency exfoliation of micron-sized monolayer sheet (widths in the range of 5–10 μ m). The size distribution of the flake is much better than exfoliation using organolithium salts (*n*-butyl lithium). This can be related to a reduced chemical reaction of the radical anion (C₁₀H₈⁻) with the host material, and the fact that we apply a pre-expansion procedure with hydrazine to facilitate the efficient intercalation of the metal cations. Evidence from XRD and NMR shows the existence of highly ordered ternary phase after cation intercalation. In terms of exfoliation efficiency, sodium naphthalenide (Na⁺C₁₀H₈⁻) produces higher quality monolayer flake than its lithium and potassium counterparts. This work contributes a high-yield chemical processing method for producing high-quality 2D chalcogenide monolayers with direct relevance to printable photonics.

Methods

Pre-expansion of MoS₂. Bulk MoS₂ (1.6 g; SPI, single crystal) and 20 ml hydrazine hydrate (Aldrich, 98%) are sealed in an autoclave and heated at 130 °C for 48 h. The expanded MoS₂, which has a worm-like appearance, is washed three times by water and dried at 120 °C for 10 h.

Intercalation of MoS₂. Na (0.69 g; Aldrich) (for K or Li, we used 1.08 g or 0.21 g, respectively), 1.92 g naphthalene (Aldrich) and 80 ml anhydrous tetrahydrofuran (THF) (Aldrich, fresh redistilled by Na) are stirred for 2 h in ice-water bath in argon atmosphere. Pre-expanded MoS₂ powder (1.6 g) is added to the dark blue solution and the mixture is further stirred for 5 h. After reaction, the product is washed five times by anhydrous THF. The procedures are similar for both K and Li.

Intercalation process for WS₂ is similar except that 2.48 g of WS₂ is used with the same amount of reagent above.

Caution: Li_xMoS₂ will self-heat in air, Na_xMoS₂ will self-ignite in air and K_xMoS₂ will self-explode in air.

Exfoliation. Distilled water (100 ml) is added to the intercalated sample. The mixture is sonicated in a low-power sonic bath (60 W) for 30 min to form a homogeneous suspension. The mixture is centrifuged at 8,000 r.p.m. for 15 min for several cycles to remove excess impurity, and then at 1,000 r.p.m. for 15 min in the last cycle.

Equipment. The following equipment were used: Raman (Alpha 300R), PL (equipped on Raman), SEM (Jeol JSM-6701F), AFM (Dimension Fast Scan), XPS (SPECS), UV-VIS-NIR (Shimadzu UV-3600), solid NMR (Bruker 400 MHz), powder XRD (Siemens D5005), Jet-Printer (Dimatix, 2800).

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Author contributions

J.Z. designed the work and performed the experiments. K.P.L. conceptualized the work, analysed the data and wrote the paper. H.Z., S.D., Y.P.L., C.T.N., H.S.S., H.Y.J. and B.L. performed some characterization experiments and analysed data.

Additional information

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