ACCOUNTS of chemical research

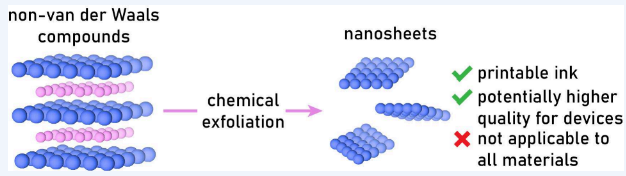
pubs.acs.org/accounts Article

Friends not Foes: Exfoliation of Non-van der Waals Materials

Published as part of Accounts of Chemical Research special issue "2D Materials".

Mulan Yang and Leslie M. Schoop*

Cite This: *Acc. Chem. Res.* 2024, 57, 2490−2499 Read Online



CONSPECTUS: Two-dimensional materials have been a focus of study for decades, resulting in the development of a library of nanosheets made by a variety of methods. However, many of these atomically thin materials are exfoliated from van der Waals (vdW) compounds, which inherently have weaker bonding between layers in the bulk crystal. Even though there are diverse properties and structures within this class of compounds, it would behoove the community to look beyond these compounds toward the exfoliation of non-vdW compounds as well. A particular class of non-vdW compounds that may be amenable to exfoliation are the ionically bonded layered materials, which are structurally similar to vdW compounds but have alkali ions intercalated between the layers. Although initially they may have been more difficult to exfoliate due to a lack of methodology beyond mechanical exfoliation, many synthesis techniques have been developed that have been used successfully in exfoliating non-vdW materials. In fact, as we will show, in some cases it has even proven to be advantageous to start the exfoliation from a non-vdW compound.

The method we will highlight here is chemical exfoliation, which has developed significantly and is better understood mechanistically compared to when it was first conceived. Encompassing many methods, such as acid/base reactions, solvent reactions, and oxidative extractions, chemical exfoliation can be tailored to the delamination of non-vdW materials, which opens up many more possibilities of compounds to study. In addition, beginning with intercalated analogues of vdW materials can even lead to more consistent and higher quality results, overcoming some challenges associated with chemical exfoliation in general. To exemplify this, we will discuss our group's work on the synthesis of a 1T'-WS_2 monolayer ink. By starting with $K_{0.5}WS_2$, the exfoliated 1T'-WS_2 nanosheets obtained were larger and more uniform in thickness than those from previous syntheses beginning with vdW materials. The crystallinity of the nanosheets was high enough that films made from this ink were superconducting. We will also show how soft chemical methods can be used to make new phases from existing compounds, such as H_xCrS_2 from $NaCrS_2$. This material was found to have alternating amorphous and crystalline layers. Its biphasic structure improved the material's performance as a battery electrode, enabling reversible Cr redox and faster Na-ion diffusion. From these and other examples, we will see how chemical exfoliation of non-vdW materials compares to other methods, as well as how this technique can be further extended to known compounds that can be deintercalated electrochemically and to quasi-one-dimensional crystals.

■ KEY REFERENCES

- Song, X.; Singha, R.; Cheng, G.; Yeh, Y.-W.; Kamm, F.; Khoury, J. F.; Hoff, B. L.; Stiles, J. W.; Pielnhofer, F.; Batson, P. E.; Yao, N.; Schoop, L. M. Synthesis of an aqueous, air-stable, superconducting 1T'-WS_2 monolayer ink. *Sci. Adv.* **2023**, *9*, eadd6167.[1] *Chemical exfoliation of $K_{0.5}WS_2$ was used to make high-quality, superconducting monolayer 1T'-WS_2 nanosheets. These nanosheets were stable as an ink and formed high-quality films when deposited on both rigid and flexible substrates.*
- Song, X.; Cheng, G.; Weber, D.; Pielnhofer, F.; Lei, S.; Klemenz, S.; Yeh, Y.-W.; Filsinger, K. A.; Arnold, C. B.; Yao, N.; Schoop, L. M. Soft Chemical Synthesis of H_xCrS_2: An Antiferromagnetic Material with Alternating Amorphous and Crystalline Layers. *J. Am. Chem. Soc.* **2019**, *141*, 15634−15640.[2] *$NaCrS_2$ was proton-exchanged to make H_xCrS_2, which was shown to have alternating amorphous and crystalline layers, and could be further exfoliated to make CrS_xnanosheets.*
- Stiles, J. W.; Soltys, A. L.; Song, X.; Lapidus, S. H.; Arnold, C. B.; Schoop, L. M. Unlocking High Capacity and Fast Na^+ Diffusion of H_xCrS_2 by Proton-Exchange Pretreatment. *Adv. Mater.* **2023**, *35*, 2209811.[3] *H_xCrS_2 was used as an electrode material to reach a record capacity for a noncomposite transition metal chalcogenide. This is*

Received: May 16, 2024
Revised: July 24, 2024
Accepted: August 5, 2024
Published: August 16, 2024

https://doi.org/10.1021/acs.accounts.4c00295
Acc. Chem. Res. 2024, 57, 2490−2499

enabled by the alternating amorphous and crystalline layers in the material generated by proton-exchanging $NaCrS_2$.

1. INTRODUCTION TO TWO-DIMENSIONAL MATERIALS

The study of low-dimensional materials has grown rapidly in popularity since the first exfoliation of graphene from graphite in 2004.[4] Until then, it was believed that a truly two-dimensional (2D) graphene sheet — only one layer of atoms thick — could not be isolated; because carbon can be found in many polymorphs, a single sheet of carbon atoms would be expected to crumple into another structure.[5] However, simply by using tape, Novoselov and Geim were able to mechanically exfoliate graphite to obtain monolayers of graphene.[4] This is made possible by the van der Waals (vdW) nature of graphite's structure, in which the out-of-plane bonding is much weaker than the in-plane bonding, to the extent that even using tape can interrupt the vdW forces to peel the layers apart.

Graphene has been shown to have remarkable properties due to its 2D structure. The facile synthesis method has enabled a multitude of experimental studies, including ones showing that "magic-angle" twisted bilayer graphene, in which two layers of graphene are stacked with a small angle (approximately 1.1°) between them, is an unconventional superconductor.[6] Graphene also shines in applications, including energy storage,[7] sensors,[8] and wearable electronics.[9] For instance, graphene electronic tattoos[10] that can be directly applied to skin are being developed to perform the same function as electrocardiograms, as well as to measure other physiological parameters.[11] These graphene-based tattoos are flexible enough to move with human skin, making them significantly more comfortable than currently available measurement devices.

Although, in some ways, the field has expanded greatly, the actual material focus has remained quite narrow, with many studies concentrating on characterizing the same known set of materials as opposed to developing methods to synthesize new ones. This is surprising considering that just one computational study put forth approximately 1000 materials that could be "easily exfoliated",[12] which has recently been updated to include another 1000 compounds falling into this category.[13] Part of the difficulty in synthesizing new nanomaterials may be due to a lack of established methods; materials that cannot be mechanically exfoliated can require significant trial and error before a suitable method for exfoliation is found. If a larger quantity of material is the goal, then the method development becomes even more finicky.

Thus, with this perspective, we aim to describe the utility of an alternative synthesis route both in addressing less easily exfoliated materials, as well as in overcoming common drawbacks of chemical exfoliation. When beginning with a vdW material, common liquid exfoliation methods include either intercalating ions to separate the layers or directly exfoliating in a solvent (Figure 1). We highlight here how beginning with a non-vdW counterpart of a known vdW material can lead to higher-quality nanosheets. This method can also be used to synthesize nanosheets of metastable phases that do not have vdW bulk structures. In general, the main class of non-vdW compounds we will discuss herein are ionically bonded layered materials. We also compare this synthesis strategy to chemical vapor deposition, another common synthesis technique, which targets up-scaling and produces high-quality nanosheets.

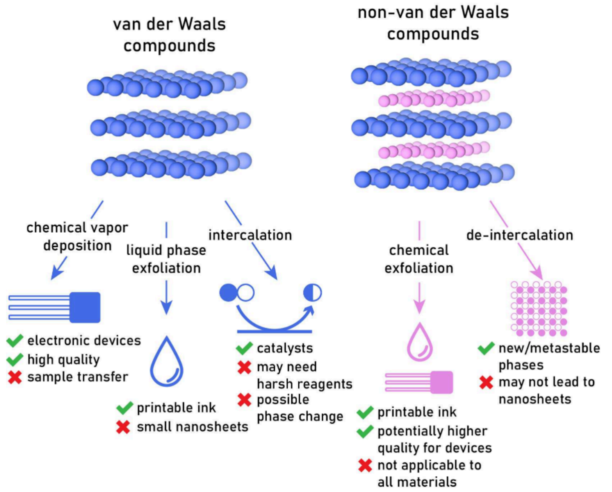


Figure 1. Possible synthesis routes of nanosheets from van der Waals and non-van der Waals compounds. Blue spheres represent a layered structure, with pink spheres representing alkali ions intercalated between the layers. Common applications (first checkmark under each image) as well as possible advantages (green checkmarks) and disadvantages (red x's) of each method are listed. Although each method can be used to produce nanosheets for multiple applications, we are highlighting one application per method that requires the highest possible quality nanosheets derived using that method.

2. SYNTHESIS OF 2D MATERIALS

Various approaches have been developed for synthesizing nanosheets, which we can categorize as being bottom-up or top-down. Mechanical exfoliation, as mentioned above, is a top-down exfoliation method because the bulk version of the target nanosheet is first synthesized. This method produces the highest quality monolayers, but they cannot be reliably obtained in bulk due to the inherent imprecision of the process. In addition, its reliance on individually exfoliating sheets means it is not scalable for industrial use.[14] Below, we will discuss some of the major synthesis methods for these materials that are also more readily upscaled. These can help to enable the use of 2D materials in applications beyond the lab.

2.1. Chemical Vapor Deposition

After mechanical exfoliation, chemical vapor deposition (CVD) is one of the best routes for growing wafer-scale films of high enough quality for use in devices. This is a bottom-up method in which the synthesis proceeds from the constituent starting materials. CVD has many advantages, particularly the crystallinity and homogeneity of the films produced.[15] Significant progress has also been made in the growth of single crystal transition metal dichalcogenide (TMD) monolayers,[16] for instance, by adapting the step-edge-guided strategy previously used for graphene and boron nitride to grow single-crystalline, monolayer films of WS_2,[17] MoS_2,[18] and $MoSe_2$[19] on sapphire substrates.

CVD also has a few drawbacks, such as the need for the instruments to be operated at high temperatures, which may be a deterrent for industrial use.[20] The established methodologies tend to be individualized per class of compounds, which complicates their application to other materials, with focus particularly lacking in the synthesis of nonlayered crystals.[20] CVD also struggles with the growth of heterostructures and

https://doi.org/10.1021/acs.accounts.4c00295
Acc. Chem. Res. 2024, 57, 2490−2499

with postgrowth wrinkling of the films in cases where the thermal expansion of the material and substrate differ.[15] In addition, once the film is grown, the process of transferring it to a substrate suitable for devices can potentially induce strain, cause damage, or add contamination. To circumvent these issues, the direct growth of films on the target substrate is being pursued, but these films tend to be polycrystalline due to being grown at lower temperatures, which introduces grain boundaries.[21] Despite these challenges, CVD remains one of the foremost techniques for obtaining device-quality nanosheets.

2.2. Liquid Exfoliation

Unlike CVD, liquid exfoliation is a top-down synthesis method. It involves first growing the bulk material and then choosing the right solvent, reactants, and other experimental conditions to exfoliate it. Liquid exfoliation has some advantages over CVD, particularly that it is a more versatile method that can be applied to a greater variety of materials. However, the produced nanomaterials are usually of a lower quality than those made using CVD[15,16,22] and thus are often used for applications such as catalysts, batteries, and sensors; in general, those that may benefit from defects or inhomogeneity, instead of being negatively impacted. For electronics, optoelectronics, and spintronics, nanosheets synthesized by CVD or mechanical exfoliation are preferred due to the higher likelihood of defect-free and evenly thick results.[15] Liquid exfoliation also suffers from inefficiency, with a significant portion of the bulk material usually left over once the nanomaterials are isolated, as well as difficulty in controlling the number of layers in the exfoliated materials.[15]

2.2.1. Liquid and Chemical Exfoliation Strategies. To suit all manner of materials, a multitude of methods for chemical exfoliation have been developed (Figure 2). When starting from a vdW material, there are two main routes for exfoliation: directly from the bulk or by first intercalating alkali ions. Harsher solvents or more aggressive physical agitation (i.e., sonication) can often be necessary if exfoliating the vdW material as is, which can lower the nanosheet quality. Thus, it is also common to intercalate alkali ions first using a reducing agent, which forces the layers further apart. From here, there are also more options for exfoliation methods. Sometimes, the intercalated compounds are readily exfoliable in solvents such as water, ethanol, isopropyl alcohol, etc. The best solvent system for a given material needs to be optimized for each case, but it has been shown that the best solvent systems generally have surface tensions within a specific range.[23] However, further reacting the intercalated material, for instance by performing acid/base reactions and oxidative extractions, can add impetus for the layers to delaminate. To enable an acid–base reaction to occur, the alkali ions are first exchanged with protons using an acidic solution. Then, the proton-exchanged material is reacted with bulky organic ions in a basic solution to insert large cations in between the layers of the material, further increasing the interlayer spacing and thus decreasing the interactions between layers.[24] An alternative method is reacting an oxidant (often iodine in acetonitrile) with the compounds. This is especially useful when the target material is metastable, as it can enable deintercalation potentially without disturbing the structure. However, there is a risk that the oxidation of the layers will induce an unwanted phase change.[24]

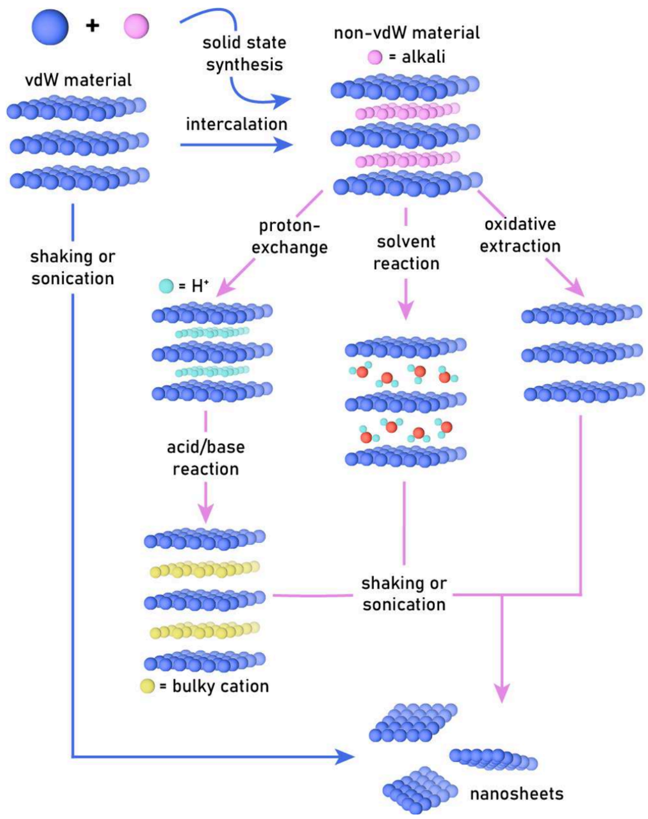


Figure 2. Possible liquid and chemical exfoliation strategies when starting with either a vdW material, which is often intercalated with an alkali ion, or a non-vdW material made directly by solid state synthesis. Acid/base reaction, solvent reaction, or oxidative extraction are strategies that can be used to expand the interlayer distance. The final step of physical agitation by either shaking or sonication delaminates the material to make the nanosheets.

2.2.2. Triumphs and Tribulations of Lithium Intercalation. We want to highlight Li-intercalation as a very common chemical exfoliation route for vdW compounds, often using *n*-butyllithium (*n*-BuLi) as the main reactant. As Li ions are intercalated between the layers, the interlayer spacing increases and the layers themselves become negatively charged to compensate.[25,26] When water is used as the solvent, lithium hydroxide can be formed, which causes hydrogen gas to evolve. These gas bubbles also assist in pushing the layers further apart.[27] Furthermore, the Li ions may be solvated, which can cause the layers to separate further than expected when they are intercalated.[28,29] Li-intercalation has been used effectively in many cases, such as the exfoliation of oxychlorides.[30,31]

Although *n*-BuLi is gentle compared to some other reducing agents, in many instances, the lithiation process can still greatly affect the structure and properties of the resulting material.[14] For instance, MoS_2 can exist as a number of polymorphs, the most thermodynamically stable one being the 2H phase (trigonal prismatic), which is semiconducting (Figure 3a,c).[32] Intercalating with Li ions expands the interlayer spacing and makes it possible to exfoliate the bulk crystal down to nanosheets.[33] However, reacting with *n*-BuLi transforms 2H-MoS_2 into the metastable 1T (octahedral) or 1T' phase (distorted octahedral), which are metallic (Figure 3b,c).[34] During this process, many defects form because the S atoms migrate (Figure 3d),[35] and the reaction temperature is not elevated enough to allow these defects to heal, resulting in

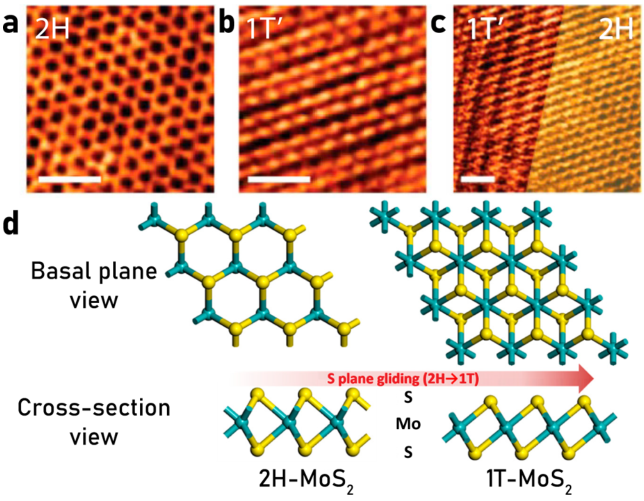


Figure 3. a−c) Scanning transmission electron microscopy images of 2H, 1T', and 1T'/2H interface regions, respectively. Scale bar is 1 nm. d) Structures of 2H-MoS_2 and 1T-MoS_2. The cross-section view shows the necessary S migration that transforms the 2H phase into the 1T phase. Reproduced from (a−c) ref 39 (d) ref 35. Copyright 2018, American Chemical Society (refs 39 and 35).

lower crystallinity.[36] The metallic properties and increase in active sites make 1T-MoS_2 a better candidate for catalytic[37] or energy storage applications.[38] However, this phase transformation does negate the usefulness of chemically exfoliated 2H-MoS_2 in electronic applications and decreases the viability of this chemical exfoliation pathway as a method to synthesize these monolayers in a large quantity.[32]

2.3. Exfoliation of Non-vdW Materials

Compared to the body of literature focused on vdW materials, much less has been done to study the exfoliation of non-vdW materials.[40] The computational study of Mounet et al. identified many "easily exfoliable" materials using the criteria of layered compounds with weak interlayer interactions.[12] It is harder to determine a simple pattern showing which non-vdW materials can be exfoliated. Thus, amidst the fervor of exfoliating vdW materials, non-vdW materials were often overlooked. Some studies on chemical exfoliation of non-vdW oxides and hydroxides to nanosheets were performed by the Sasaki group even before the 2004 study on mechanical exfoliation of graphene,[41,42] but as a whole, this area of study lacked widespread interest.[43] The popularity of graphene and TMDs helped reinvigorate activity in this field. In 2017, Guan et al. used liquid phase exfoliation to synthesize 2D WO_3 nanosheets.[44] In 2018, hematite was shown to be chemically exfoliable to nanosheets as well. Exemplifying the change in properties that can occur after exfoliating, the antiferromagnetism of hematite was converted to ferromagnetism in the hematene sheets.[45] These two examples highlight the exfoliation of nonlayered non-vdW materials, which are not the main focus of this Account, but nevertheless are a valuable class of compounds for study.[40] There has also been a push toward developing exfoliation methods for MXenes, the family encompassing transition metal carbides, nitrides, and carbonitrides.[46−48]

Overall, there is some reluctance, especially in device-oriented communities, in studying the exfoliation of non-vdW materials because the mechanism by which the exfoliation occurs is not always well-understood, particularly in the case of isotropic materials.[40] However, our group has sought to see these materials in a more positive light, especially focusing on ionically bonded layered materials that are reminiscent of their vdW counterparts. These non-vdW materials enable us to not only synthesize 2D nanosheets that are otherwise unattainable but also to improve upon the quality of even those nanosheets that can be obtained using other methods.

3. 2D TRANSITION METAL DICHALCOGENIDES (TMDs)

Significant emphasis has been placed on the exfoliation of transition metal dichalcogenides (TMDs), MX_2 where M = transition metal and X = S, Se, Te, due to their wide variety in structure and properties, especially for applications where graphene is less suitable.[14] One advantage of many 2D TMDs over graphene is their semiconducting nature (as opposed to semimetallic), enabling them to be used in place of silicon in transistors that could allow further miniaturization of devices. Two-dimensional TMDs also show promise in optoelectronic and valleytronic applications.[49] In addition, they maintain the flexibility of graphene, allowing them to be deposited on flexible substrates.[50] Many commonly studied TMDs, such as MoS_2 and WS_2, are also air stable, which simplifies their integration in devices. However, this is not always the case, as many TMDs, particularly those containing Te, are prone to oxidation.[51]

In 2011, Coleman et al. showed that chemical exfoliation could be used to exfoliate certain TMDs, including MoS_2 and WS_2.[23] Liquid exfoliation methods are well-suited for making inks, which Kelly et al. took advantage of to make thin-film transistors completely through printing (Figure 4a).[52] This

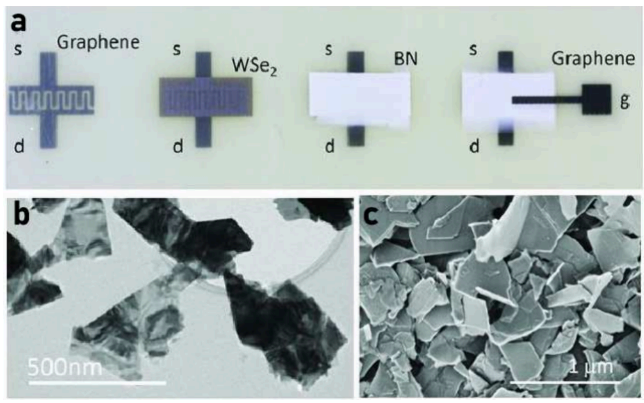


Figure 4. a) Photographs showing each step of printing a transistor, beginning with a graphene source (s) and drain (d) electrode, then a WSe_2 channel, a BN separator, and a graphene gate. b) Representative transmission electron microscopy image of WSe_2 nanosheets made by sonicating bulk WSe_2 in NMP. c) Representative scanning electron microscopy image of a network of WSe_2 nanosheets made by spraying the nanosheet containing ink. Reprinted with permission from AAAS from ref 52. Copyright 2017, American Association for the Advancement of Science.

proof of concept was a great first step but also showed that there was still a long way to go in terms of the quality of 2D TMD inks.[22] The performance of the transistors suffered due to the lack of uniformity and quality of the TMD nanosheets (Figure 4b,c), caused by the harsh synthesis method of directly sonicating the bulk crystals in *N*-methyl-2-pyrrolidone (NMP). The resulting nanosheets averaged 330−380 nm in length and

https://doi.org/10.1021/acs.accounts.4c00295
Acc. Chem. Res. 2024, 57, 2490−2499

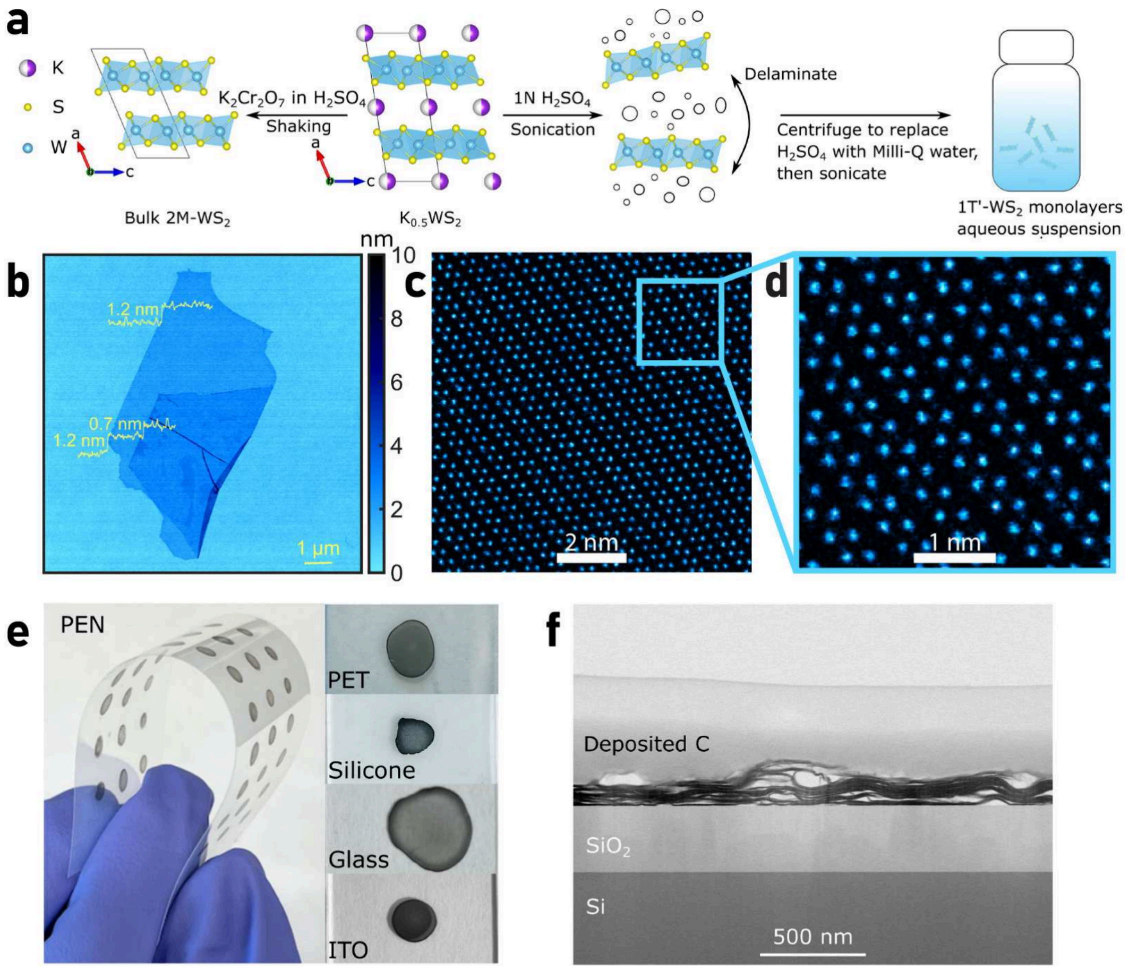


Figure 5. a) By exfoliating directly from $K_{0.5}WS_2$, a 1T'-WS$_2$ nanosheet suspension can be made. Bulk 2M-WS$_2$ can be synthesized instead by deintercalating the K ions. b) Atomic force microscopy image of a representative nanosheet, showing the monolayer thickness of the sample. c) Atomic resolution scanning transmission electron microscopy (AR-STEM) of a monolayer, with W atoms in blue. d) Expanded image of a small area in (c) to show the high quality of the sample. e) 1T'-WS$_2$ monolayer films deposited on a variety of substrates, highlighting the ink performance on a flexible substrate. f) Cross-sectional SEM image of a 1T'-WS$_2$ film. Reproduced from ref 1.

13−17 layers in thickness; however, 15% of the nanosheets had fewer than six layers and therefore may not have exhibited bulk electronic behavior. Because the band gap of TMD nanosheets is very sensitive to thickness, even this much variation impaired the network mobility of the deposited ink due to issues such as trapped charges.[52] These problems could be partially alleviated by using inks of nanosheets that are more uniform in thickness and larger laterally, which would decrease the amount of internanosheet transport required.

4. BEGINNING WITH AN ALKALI-INTERCALATED MATERIAL

4.1. Monolayer 1T'-WS$_2$ Ink

Of the known TMDs, WS$_2$ has been one of the most studied subjects due to the ease with which it can be exfoliated and the variation in its properties depending on its phase. For example, bulk 2H-WS$_2$ is a semiconductor, but 2M-WS$_2$ was found to be a superconductor with a transition temperature of 8.8 K, one of the highest among all TMD materials.[53] Unfortunately, bulk crystals of 2M-WS$_2$ cannot be made directly using conventional solid-state methods because this phase is metastable.[54] Instead, 2M-WS$_2$ is made by deintercalating $K_{0.7}WS_2$.[53] The structure of bulk 2M-WS$_2$ is essentially stacked layers of 1T'-WS$_2$, which makes this a viable starting material to exfoliate down to 1T'-WS$_2$. Previously, 1T'-WS$_2$ nanosheets have been successfully made using the conventional chemical exfoliation method of first Li-intercalating bulk 2H-WS$_2$ and then exfoliating, but this process does not result in a phase-pure solution of metallic WS$_2$ nanosheets.[55] Using mechanical exfoliation, a monolayer of 1T'-WS$_2$ was isolated and shown to be potentially superconducting, but the resistivity never reached zero, unlike the thicker samples measured, making it somewhat unclear whether 1T'-WS$_2$ remained superconducting down to the monolayer limit.[54] Thus, our group was interested in synthesizing inks of 1T'-WS$_2$ monolayers via liquid exfoliation to cast films of high enough quality to be definitively superconducting.

To accomplish this, Song et al. used chemical exfoliation from an alkali-intercalated precursor material.[1] Instead of synthesizing a bulk crystal that was essentially a stacked version of the nanosheets, they started with a bulk crystal that contained the nanosheet structure separated by alkali ions. During solid-state synthesis, the alkali ions are incorporated at a high temperature, resulting in better quality crystals without damage or defects introduced by using harsher reagents.

https://doi.org/10.1021/acs.accounts.4c00295
Acc. Chem. Res. 2024, 57, 2490−2499

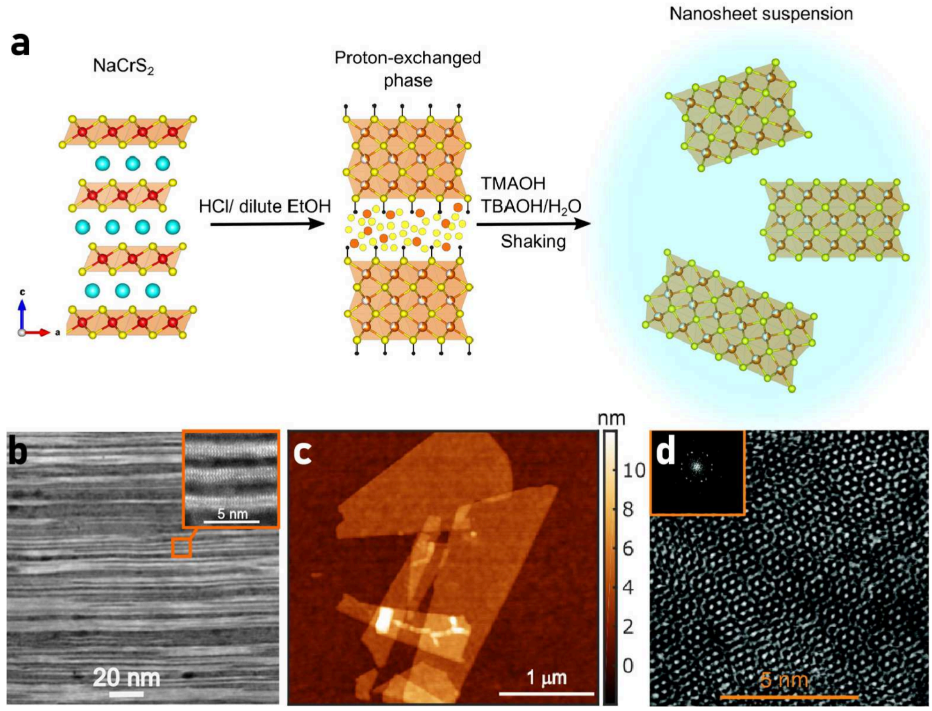


Figure 6. a) Synthesis of H_xCrS_2 crystals and acid/base exfoliation of CrS_x nanosheets. Bulk $NaCrS_2$ is shaken in a dilute HCl/ethanol solution to produce H_xCrS_2. This proton-exchanged phase is then shaken in tetramethylammonium hydroxide (TMAOH) solution followed by shaking in tetrabutylammonium hydroxide (TBAOH) solution to make CrS_x nanosheets. b) Cross section of H_xCrS_2 showing crystalline (bright) and amorphous (dark) layers. c) Atomic force microscopy of CrS_x nanosheets. d) CrS_x nanosheets stacked in a Moiré pattern, with inset showing selected area electron diffraction of the nanosheets. Reproduced from (a−c) ref 2 and reprinted with the permission of AIP Publishing from (d) ref 56. Copyright 2019, American Chemical Society (ref 2). Copyright 2021, Song et al. (ref 56).

Although it might seem counterintuitive to introduce ionic bonding between the layers, the ions open up avenues for further reactions and subsequent chemical exfoliation. In this case, the researchers were able to synthesize a superconducting ink of 1T'-WS_2 monolayers directly from $K_{0.5}WS_2$ by sonicating the crystals in 0.5 M H_2SO_4, followed by further sonication in water (Figure 5a).

One of the most impressive results from this process was that the 1T'-WS_2 nanosheets produced were primarily monolayers, as opposed to a mixture of thicknesses that is a common result of liquid exfoliation. Out of 228 nanosheets measured by atomic force microscopy, 205 were monolayers, with the majority of thicker nanosheets being bilayers (Figure 5b). Characterization of over 50 nanosheets using localized techniques, including atomic resolution-scanning transmission electron microscopy (AR-STEM) (Figure 5c,d) and selected area electron diffraction (SAED), showed that all areas measured were highly crystalline, unlike the results from mechanical or Li-intercalated exfoliations. Thus, we see that by starting with an already intercalated starting material, it is possible to obtain uniform and high-quality results from chemical exfoliation, contrary to what is generally understood. In addition, the nanosheets were air-stable and dispersed readily in water, thus negating the need for harsher solvents or storage under nonambient conditions. They could deposit the ink on a variety of substrates, both flexible and rigid (Figure 5e), and the resulting printed films were still metallic. This was mainly due to the good contact between nanosheets and their large size, which lowered the number of inter-nanosheet junctions. This can be seen in the SEM image in Figure 5f and shows how this ink is an improvement over, for example, the ink for the printed transistor referenced earlier.[52] Electronic transport measurements show that the resulting nanosheet films are also superconducting below 7.3 K. From this example, we see that the quality of chemically exfoliated nanosheets can be significantly improved when starting with a preintercalated material, increasing the viability of their usage in more exacting applications. If so, the convenience of being able to print the nanosheets directly onto substrates would be very beneficial.

4.2. Happy Accidents - Proton-Exchange of $NaCrS_2$ to H_xCrS_2 and CrS_x Nanosheets

Of course, using preintercalated materials will not always result in better quality nanosheets than can be obtained by other methods. However, attempting to exfoliate a preintercalated material can lead to unexpected and advantageous results that would have been much harder to achieve with normal intercalation methods. Such was the case in the development of H_xCrS_2, which Stiles et al. showed can be used in Na-ion batteries to reach a record capacity for noncomposite electrodes of 728 mAh g^{-1}.[3] This material was discovered as an intermediate in the exfoliation process from $NaCrS_2$ to CrS_x nanosheets.[2]

First, $NaCrS_2$ was synthesized using solid-state methods. To begin an acid/base-type exfoliation, this material was shaken in a solution of 1 M HCl in 25 vol % water/ethanol for 3 days, with the solution replaced daily, to proton-exchange the Na ions (Figure 6a). Careful characterization using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) after this step revealed the very interesting biphasic structure of H_xCrS_2 (Figure 6b). The process of proton-exchange transformed the fully crystalline structure into one composed of alternating crystalline and amorphous layers.

https://doi.org/10.1021/acs.accounts.4c00295
Acc. Chem. Res. 2024, 57, 2490−2499

After shaking H_xCrS_2 in alkylammonium solutions to complete the acid/base reaction, nanosheets were obtained measuring 2−3 nm thick (Figure 6c), approximately matching the height of the crystalline layers in the intermediate structure.[2] The resulting CrS_x nanosheets retained the crystallinity of the intermediate material, as seen in selected area electron diffraction (SAED) patterns of two nanosheets stacked in a Moiré pattern (Figure 6d).[56] However, these did not match the quality of the 1T'-WS_2 nanosheets discussed previously, showing that it can be difficult to obtain high-quality sheets of some materials, even with preintercalation. This result was not entirely surprising, as CrS_2 does not exist as a bulk vdW crystal, unlike WS_2, which may indicate that CrS_x nanosheets are relatively unstable.

Focusing instead on the electrochemical performance of the intermediate H_xCrS_2 compound led to surprising results. Stiles et al. showed that the amorphous layers are critical in achieving a higher capacity than had been seen before in transition metal sulfide electrodes, enabling the Cr ion to participate reversibly in a redox reaction that allowed for greater Na ion intercalation.[3] The amorphous layers also result in significantly faster Na ion diffusion. Amorphous electrodes may undergo large volume changes during electrochemical cycling,[57] but the inclusion of crystalline layers helped to mitigate this issue. Creating a biphasic structure out of the electrode material also adds disorder to the system, which can be beneficial for limiting the detrimental effects of transition metal migration.[58] Although this was not the initial goal, by starting with the stable $NaCrS_2$ structure, this unpredictable but useful material was found.

5. CONCLUSIONS AND DIRECTIONS FOR FUTURE STUDIES

TMDs hold significant promise for many applications due to the wide variety of interesting properties they host. However, their incorporation into devices is hindered by the lack of large-scale syntheses to make nanosheets that are defect-free enough to be used for these applications. Mechanical exfoliation remains the cleanest method for making single monolayers, with CVD being the best scalable alternative currently. In contrast, liquid exfoliation does not produce the cleanest nanosheets but results in a suspension that can be used as ink for printed electronics, simplifying the process of transferring the nanosheets to a substrate, as well as enabling all-printed transistors.[52] Unfortunately, the small lateral size of the nanosheets produced by directly sonicating the bulk crystals prevents the nanosheets from forming good contacts with each other, lowering the mobility of the film significantly compared to that of a single nanosheet. By instead starting with the already intercalated material $K_{0.5}WS_2$, Song et al. could make an ink of high-quality, monolayer 1T'-WS_2 using chemical exfoliation. These nanosheets were large enough to form nice contacts with each other and made films that were superconducting at 7.3 K.

5.1. Extending to One Dimension

Lacking though the library of 2D nanosheets is, it still greatly exceeds the number of 1D nanomaterials made using liquid exfoliation. These materials are interesting for many of the same reasons as their 2D counterparts but are still mainly synthesized using CVD methods.[59] One interesting development by Cordova et al. in the CVD synthesis of 1D crystals in particular shows how the inherent anisotropy in vdW interactions between chains in 1D and quasi-1D compounds can be taken advantage of for the controllable, directional growth of nanowires, as well as nanoribbons and nanosheets.[60] Density functional theory calculations have determined certain classes of quasi-1D compounds with vdW bonding between the chains that is comparable in strength to that in exfoliable 2D materials, suggesting that they are likely exfoliable as well.[61] Zhu et al. have used machine-learning to predict over 10,000 new vdW quasi-1D compounds, which greatly increases the number of 1D exfoliation candidates.[62] For further studies on 1D and quasi-1D materials, we point interested readers to work from the Salguero,[62−64] Arguillo,[60,65] Balandin,[59,62,64] and Reed[62,66] groups.

Work on exfoliating vdW compounds to 1D is slim but growing; on the other hand, exfoliating alkali-ion containing compounds such as we have discussed remains rare.[67] If researchers studying 1D materials also consider using this synthesis method, the mechanism behind it could be better understood and a wider array of materials could potentially be exfoliated. There have been a few proofs of concept showing how chemical exfoliation can be applied to make nanowires from vdW materials, including KP_{15},[68] $Ta_2Pd_3Se_8$,[69] and $CrSbSe_3$.[67] This last example not only showed that chemically exfoliated nanowires can still show magnetic behavior but also how the increased anisotropy and nanoscale size can alter the magnetic properties. Our group then showed that it is possible to obtain nanoribbons from a non-vdW starting material, $KFeS_2$.[70] The bulk crystal has FeS_4 chains ionically bonded by K^+ and can be exfoliated in a mixture of water and isopropyl alcohol using sonication. The resulting nanomaterials are the same structure and also retain similar magnetism to the bulk crystal. Compounds that may be worthy of study in future include $NaFeS_2$[71] and $KSbS_2$,[70,72] which are also quasi-1D materials of chains bonded by alkali ions.

5.2. Addressing Known AMX_2 Compounds

Many AMX_2 compounds, where A = Li, Na, K, and MX_2 is a TMD, can be partially deintercalated electrochemically but have not been studied as potentially exfoliable materials. Although transition metal migration often occurs before complete deintercalation and prevents it, the implied ease of deintercalation up to that point makes these strong candidates for exfoliation, as well as likely to result in nanosheets that would be useful for applications in energy storage. It is possible that chemical exfoliation will be a better route that allows the compound to be completely deintercalated. However, even if a compound cannot be exfoliated down to the monolayer limit, the intermediates in the exfoliation process can be valuable energy storage materials, as we discussed earlier. Possible materials for study include $KCrS_2$,[73] $NaCrO_2$,[74] and $LiTiS_2$.[75]

If we consider an example compound, $LiSnS_2$,[76] we can see how this logic can be used to point toward good non-vdW candidates for chemical exfoliation. Kuhn et al. showed that exfoliation of $Li_{4x}Sn_{1-x}S_2$ in water produces nanosheets that form SnS_2 upon annealing.[77] Yuan et al. were inspired by this work and extended it by exfoliating $K_{2x}Mn_xSn_{1-x}S_2$ to form magnetic $Mn_xSn_{1-x}S_2$ nanosheets. They realized that codoping K with Mn in the parent compound could assist in the exfoliation process and the retention of Mn in the final nanosheets.[78] The inclusion of Mn itself may have also aided in exfoliation by introducing site disorder that can inhibit transition metal migration.[58,79] From these studies, we see

https://doi.org/10.1021/acs.accounts.4c00295
Acc. Chem. Res. 2024, 57, 2490−2499

how these AMX_2 compounds can be a good starting point for choosing non-vdW materials for exfoliation.

5.3. Outlook

We have shown how chemical exfoliation from a preintercalated material can lead to better results than either directly exfoliating from the bulk compound or exfoliating after intercalating an ion. By discussing the usefulness of exfoliating alkali-intercalated counterparts of vdW materials, we hope that others see the utility and benefits that can come from chemically exfoliating a non-vdW material. Even in instances where the resulting nanosheets are not superior to those made using other methods, using a preintercalated material can lead to other surprising results, such as the discovery of an intermediate state when proton-exchanging. There are few downsides to trying this alternative synthesis method and much to gain.

■ AUTHOR INFORMATION

Corresponding Author

Leslie M. Schoop − *Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States;* orcid.org/0000-0003-3459-4241; Email: lschoop@princeton.edu

Author

Mulan Yang − *Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States;* orcid.org/0000-0002-0122-3818

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.accounts.4c00295

Author Contributions

CRediT: **Mulan Yang** conceptualization, visualization, writing-original draft, writing-review & editing; **Leslie M. Schoop** conceptualization, supervision, validation, writing-review & editing.

Notes

The authors declare no competing financial interest.

Biographies

Mulan Yang is a chemistry and material science Ph.D. candidate in the Schoop lab at Princeton University. She received her B.S. in chemistry from Northeastern University in 2016. Her research focuses on the chemical exfoliation of 2D and 1D materials from non-vdW compounds.

Leslie M. Schoop received her Diploma in Chemistry from Johannes Gutenberg University and PhD in Chemistry from Princeton University. She then went on to work as a Minerva fast-track fellow under Professor Bettina Lotsch at the Max Planck Institute for Solid State Research. Leslie joined the Princeton University Department of Chemistry Faculty in 2017 and was tenured in 2022. The Schoop Lab is working at the interface of chemistry and physics, using chemical principles to find new materials with exotic physical properties.

■ ACKNOWLEDGMENTS

The authors were supported by the DOD's Office for Naval Research (ONR), Award No. N00014-21-1-2733, the Princeton Center for Complex Materials, a Materials Research and Engineering Center and a National Science Foundation (NSF)-MRSEC program (DMR-2011750), and the Princeton Catalysis Initiative.

■ REFERENCES

(1) Song, X.; Singha, R.; Cheng, G.; Yeh, Y.-W.; Kamm, F.; Khoury, J. F.; Hoff, B. L.; Stiles, J. W.; Pielnhofer, F.; Batson, P. E.; Yao, N.; Schoop, L. M. Synthesis of an aqueous, air-stable, superconducting 1T'-WS2 monolayer ink. *Science Advances* **2023**, *9*, eadd6167.

(2) Song, X.; Cheng, G.; Weber, D.; Pielnhofer, F.; Lei, S.; Klemenz, S.; Yeh, Y.-W.; Filsinger, K. A.; Arnold, C. B.; Yao, N.; Schoop, L. M. Soft Chemical Synthesis of HxCrS2: An Antiferromagnetic Material with Alternating Amorphous and Crystalline Layers. *J. Am. Chem. Soc.* **2019**, *141*, 15634−15640.

(3) Stiles, J. W.; Soltys, A. L.; Song, X.; Lapidus, S. H.; Arnold, C. B.; Schoop, L. M. Unlocking High Capacity and Fast Na+ Diffusion of H_xCrS_2 by Proton-Exchange Pretreatment. *Adv. Mater.* **2023**, *35*, 2209811.

(4) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666−669.

(5) Shenderova, O. A.; Zhirnov, V. V.; Brenner, D. W. Carbon Nanostructures. *Critical Reviews in Solid State and Materials Sciences* **2002**, *27*, 227−356.

(6) Cao, Y.; Fatemi, V.; Fang, S.; Watanabe, K.; Taniguchi, T.; Kaxiras, E.; Jarillo-Herrero, P. Unconventional superconductivity in magic-angle graphene superlattices. *Nature* **2018**, *556*, 43−50.

(7) Raccichini, R.; Varzi, A.; Passerini, S.; Scrosati, B. The role of graphene for electrochemical energy storage. *Nat. Mater.* **2015**, *14*, 271−279.

(8) Liu, J.; Bao, S.; Wang, X. Applications of Graphene-Based Materials in Sensors: A Review. *Micromachines* **2022**, *13*, 184.

(9) 15 years of graphene electronics. *Nature Electronics* **2019**, *2*, 369−369.

(10) Kabiri Ameri, S.; Ho, R.; Jang, H.; Tao, L.; Wang, Y.; Wang, L.; Schnyer, D. M.; Akinwande, D.; Lu, N. Graphene Electronic Tattoo Sensors. *ACS Nano* **2017**, *11*, 7634−7641.

(11) Kireev, D.; Ameri, S. K.; Nederveld, A.; Kampfe, J.; Jang, H.; Lu, N.; Akinwande, D. Fabrication, characterization and applications of graphene electronic tattoos. *Nat. Protoc.* **2021**, *16*, 2395−2417.

(12) Mounet, N.; Gibertini, M.; Schwaller, P.; Campi, D.; Merkys, A.; Marrazzo, A.; Sohier, T.; Castelli, I. E.; Cepellotti, A.; Pizzi, G.; Marzari, N. Two-dimensional materials from high-throughput computational exfoliation of experimentally known compounds. *Nat. Nanotechnol.* **2018**, *13*, 246−252.

(13) Campi, D.; Mounet, N.; Gibertini, M.; Pizzi, G.; Marzari, N. Expansion of the Materials Cloud 2D Database. *ACS Nano* **2023**, *17*, 11268−11278.

(14) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem.* **2013**, *5*, 263−275.

(15) Choi, S. H.; Yun, S. J.; Won, Y. S.; Oh, C. S.; Kim, S. M.; Kim, K. K.; Lee, Y. H. Large-scale synthesis of graphene and other 2D materials towards industrialization. *Nat. Commun.* **2022**, *13*, 1484.

(16) Dai, Y.; He, Q.; Huang, Y.; Duan, X.; Lin, Z. Solution-Processable and Printable Two-Dimensional Transition Metal Dichalcogenide Inks. *Chemical Reviews* **2024**, *124*, 5795.

(17) Wang, J. Dual-coupling-guided epitaxial growth of wafer-scale single-crystal WS2 monolayer on vicinal a-plane sapphire. *Nature Nanotechnology* **2022**, *17*, 33−38.

(18) Li, T.; et al. Epitaxial growth of wafer-scale molybdenum disulfide semiconductor single crystals on sapphire. *Nat. Nanotechnol.* **2021**, *16*, 1201−1207.

(19) Li, T.; Yang, Y.; Zhou, L.; Sun, W.; Lin, W.; Liu, L.; Zou, X.; Gao, S.; Nie, Y.; Shi, Y.; Wang, X. Halide vapor phase epitaxy of monolayer molybdenum diselenide single crystals. *National Science Open* **2023**, *2*, 20220055.

(20) Qin, B.; et al. General low-temperature growth of two-dimensional nanosheets from layered and nonlayered materials. *Nat. Commun.* **2023**, *14*, 304.

(21) Wu, P.; Zhang, T.; Zhu, J.; Palacios, T.; Kong, J. 2D materials for logic device scaling. *Nat. Mater.* **2024**, *23*, 23−25.

(22) Rhee, D.; Jariwala, D.; Cho, J. H.; Kang, J. Solution-processed 2D van der Waals networks: Fabrication strategies, properties, and scalable device applications. *Applied Physics Reviews* **2024**, *11*, 021310.

(23) Coleman, J. N. Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. *Science* **2011**, *331*, 568−571.

(24) Bae, J.; Kim, M.; Kang, H.; Kim, T.; Choi, H.; Kim, B.; Do, H. W.; Shim, W. Kinetic 2D Crystals via Topochemical Approach. *Adv. Mater.* **2021**, *33*, 2006043.

(25) Schwarzburger, N. I.; Behrens, H.; Horn, I.; Binnewies, M. On the Mechanisms of Chemical Intercalation of Lithium in Electrode Materials. *Zeitschrift für Physikalische Chemie* **2017**, *231*, 1345−1359.

(26) Zhu, X.; Su, Z.; Wu, C.; Cong, H.; Ai, X.; Yang, H.; Qian, J. Exfoliation of MoS2 Nanosheets Enabled by a Redox-Potential-Matched Chemical Lithiation Reaction. *Nano Lett.* **2022**, *22*, 2956−2963.

(27) Ramakrishna Matte, H. S. S.; Gomathi, A.; Manna, A. K.; Late, D. J.; Datta, R.; Pati, S. K.; Rao, C. N. R. MoS2 and WS2 Analogues of Graphene. *Angew. Chem., Int. Ed.* **2010**, *49*, 4059−4062.

(28) Horwitz, N. E.; Shevchenko, E. V.; Park, J.; Lee, E.; Xie, J.; Chen, B.; Zhong, Y.; Filatov, A. S.; Anderson, J. S. Synthesis, modular composition, and electrochemical properties of lamellar iron sulfides. *Journal of Materials Chemistry A* **2020**, *8*, 15834−15844.

(29) Xie, J.; Pan, J.-A.; Cheng, B.; Ma, T.; Filatov, A. S.; Patel, S. N.; Park, J.; Talapin, D. V.; Anderson, J. S. Presynthetic Redox Gated Metal-to-Insulator Transition and Photothermoelectric Properties in Nickel Tetrathiafulvalene-Tetrathiolate Coordination Polymers. *J. Am. Chem. Soc.* **2022**, *144*, 19026−19037.

(30) Ferrenti, A. M.; Klemenz, S.; Lei, S.; Song, X.; Ganter, P.; Lotsch, B. V.; Schoop, L. M. Change in Magnetic Properties upon Chemical Exfoliation of FeOCl. *Inorg. Chem.* **2020**, *59*, 1176−1182.

(31) Villalpando, G.; Ferrenti, A. M.; Singha, R.; Song, X.; Cheng, G.; Yao, N.; Schoop, L. M. Chemical Exfoliation toward Magnetic 2D VOCl Monolayers. *ACS Nano* **2022**, *16*, 13814−13820.

(32) Janica, I.; Iglesias, D.; Ippolito, S.; Ciesielski, A.; Samorì, P. Effect of temperature and exfoliation time on the properties of chemically exfoliated MoS2 nanosheets. *Chemical Communications* **2020**, *56*, 15573−15576.

(33) Joensen, P.; Frindt, R. F.; Morrison, S. R. Single-layer MoS2. *Mater. Res. Bull.* **1986**, *21*, 457−461.

(34) Liu, L.; Wu, J.; Wu, L.; Ye, M.; Liu, X.; Wang, Q.; Hou, S.; Lu, P.; Sun, L.; Zheng, J.; Xing, L.; Gu, L.; Jiang, X.; Xie, L.; Jiao, L. Phase-selective synthesis of 1T' MoS2 monolayers and heterophase bilayers. *Nat. Mater.* **2018**, *17*, 1108−1114.

(35) Gan, X.; Lee, L. Y. S.; Wong, K.-y.; Lo, T. W.; Ho, K. H.; Lei, D. Y.; Zhao, H. 2H/1T Phase Transition of Multilayer MoS2 by Electrochemical Incorporation of S Vacancies. *ACS Applied Energy Materials* **2018**, *1*, 4754−4765.

(36) Khan, M.; Kedia, S. K.; Mishra, A.; Avasthi, D. K.; Tripathi, A. Investigation of the annealing temperature for few-layer MoS2 and ion-beam induced athermal annealing/purification behaviour by in-situ XRD. *Appl. Surf. Sci.* **2023**, *639*, 158106.

(37) Peng, R.; Liang, L.; Hood, Z. D.; Boulesbaa, A.; Puretzky, A.; Ievlev, A. V.; Come, J.; Ovchinnikova, O. S.; Wang, H.; Ma, C.; Chi, M.; Sumpter, B. G.; Wu, Z. In-Plane Heterojunctions Enable Multiphasic Two-Dimensional (2D) MoS2 Nanosheets As Efficient Photocatalysts for Hydrogen Evolution from Water Reduction. *ACS Catal.* **2016**, *6*, 6723−6729.

(38) Acerce, M.; Voiry, D.; Chhowalla, M. Metallic 1T phase MoS2 nanosheets as supercapacitor electrode materials. *Nat. Nanotechnol.* **2015**, *10*, 313−318.

(39) Tan, S. J. R.; Sarkar, S.; Zhao, X.; Luo, X.; Luo, Y. Z.; Poh, S. M.; Abdelwahab, I.; Zhou, W.; Venkatesan, T.; Chen, W.; Quek, S. Y.; Loh, K. P. Temperature- and Phase-Dependent Phonon Renormalization in 1T'-MoS2. *ACS Nano* **2018**, *12*, 5051−5058.

(40) Kaur, H.; Coleman, J. N. Liquid-Phase Exfoliation of Nonlayered Non-Van-Der-Waals Crystals into Nanoplatelets. *Adv. Mater.* **2022**, *34*, 2202164.

(41) Omomo, Y.; Sasaki, T.; Wang; Watanabe, M. Redoxable Nanosheet Crystallites of MnO2 Derived via Delamination of a Layered Manganese Oxide. *J. Am. Chem. Soc.* **2003**, *125*, 3568−3575.

(42) Liu, Z.; Ma, R.; Ebina, Y.; Takada, K.; Sasaki, T. Synthesis and Delamination of Layered Manganese Oxide Nanobelts. *Chem. Mater.* **2007**, *19*, 6504−6512.

(43) Ma, R.; Sasaki, T. Two-Dimensional Oxide and Hydroxide Nanosheets: Controllable High-Quality Exfoliation, Molecular Assembly, and Exploration of Functionality. *Acc. Chem. Res.* **2015**, *48*, 136−143.

(44) Guan, G.; Xia, J.; Liu, S.; Cheng, Y.; Bai, S.; Tee, S. Y.; Zhang, Y.-W.; Han, M.-Y. Electrostatic-Driven Exfoliation and Hybridization of 2D Nanomaterials. *Adv. Mater.* **2017**, *29*, 1700326.

(45) Puthirath Balan, A.; et al. Exfoliation of a non-van der Waals material from iron ore hematite. *Nat. Nanotechnol.* **2018**, *13*, 602−609.

(46) Mashtalir, O.; Naguib, M.; Mochalin, V. N.; Dall'Agnese, Y.; Heon, M.; Barsoum, M. W.; Gogotsi, Y. Intercalation and delamination of layered carbides and carbonitrides. *Nature Communications* **2013**, *4*, 1716.

(47) Han, F.; Luo, S.; Xie, L.; Zhu, J.; Wei, W.; Chen, X.; Liu, F.; Chen, W.; Zhao, J.; Dong, L.; Yu, K.; Zeng, X.; Rao, F.; Wang, L.; Huang, Y. Boosting the Yield of MXene 2D Sheets via a Facile Hydrothermal-Assisted Intercalation. *ACS Appl. Mater. Interfaces* **2019**, *11*, 8443−8452.

(48) Wei, Y.; Zhang, P.; Soomro, R. A.; Zhu, Q.; Xu, B. Advances in the Synthesis of 2D MXenes. *Adv. Mater.* **2021**, *33*, 2103148.

(49) Mueller, T.; Malic, E. Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors. *npj 2D Materials and Applications* **2018**, *2*, 1−12.

(50) Choi, W.; Choudhary, N.; Han, G. H.; Park, J.; Akinwande, D.; Lee, Y. H. Recent development of two-dimensional transition metal dichalcogenides and their applications. *Mater. Today* **2017**, *20*, 116−130.

(51) Dong, C.; Lu, L.-S.; Lin, Y.-C.; Robinson, J. A. Air-Stable, Large-Area 2D Metals and Semiconductors. *ACS Nanoscience Au* **2024**, *4*, 115−127.

(52) Kelly, A. G.; Hallam, T.; Backes, C.; Harvey, A.; Esmaeily, A. S.; Godwin, I.; Coelho, J.; Nicolosi, V.; Lauth, J.; Kulkarni, A.; Kinge, S.; Siebbeles, L. D. A.; Duesberg, G. S.; Coleman, J. N. All-printed thin-film transistors from networks of liquid-exfoliated nanosheets. *Science* **2017**, *356*, 69−73.

(53) Fang, Y.; et al. Discovery of Superconductivity in 2M WS2 with Possible Topological Surface States. *Adv. Mater.* **2019**, *31*, 1901942.

(54) Lai, Z.; et al. Metastable 1T'-phase group VIB transition metal dichalcogenide crystals. *Nat. Mater.* **2021**, *20*, 1113−1120.

(55) Voiry, D.; Yamaguchi, H.; Li, J.; Silva, R.; Alves, D. C. B.; Fujita, T.; Chen, M.; Asefa, T.; Shenoy, V. B.; Eda, G.; Chhowalla, M. Enhanced catalytic activity in strained chemically exfoliated WS2 nanosheets for hydrogen evolution. *Nat. Mater.* **2013**, *12*, 850−855.

(56) Song, X.; Yuan, F.; Schoop, L. M. The properties and prospects of chemically exfoliated nanosheets for quantum materials in two dimensions. *Applied Physics Reviews* **2021**, *8*, 011312.

(57) Tapia-Ruiz, N. 2021 roadmap for sodium-ion batteries. *Journal of Physics: Energy* **2021**, *3*, 031503.

(58) Huang, J.; Ouyang, B.; Zhang, Y.; Yin, L.; Kwon, D.-H.; Cai, Z.; Lun, Z.; Zeng, G.; Balasubramanian, M.; Ceder, G. Inhibiting collective cation migration in Li-rich cathode materials as a strategy to mitigate voltage hysteresis. *Nat. Mater.* **2023**, *22*, 353−361.

(59) Balandin, A. A.; Kargar, F.; Salguero, T. T.; Lake, R. K. One-dimensional van der Waals quantum materials. *Mater. Today* **2022**, *55*, 74−91.

(60) Cordova, D. L. M.; Chua, K.; Huynh, R. M.; Aoki, T.; Arguilla, M. Q. Anisotropy-Driven Crystallization of Dimensionally Resolved Quasi-1D Van der Waals Nanostructures. *J. Am. Chem. Soc.* **2023**, *145*, 22413−22424.

(61) Zhu, Y.; Rehn, D. A.; Antoniuk, E. R.; Cheon, G.; Freitas, R.; Krishnapriyan, A.; Reed, E. J. Spectrum of Exfoliable 1D van der

Waals Molecular Wires and Their Electronic Properties. *ACS Nano* **2021**, *15*, 9851−9859.
(62) Zhu, Y.; Antoniuk, E. R.; Wright, D.; Kargar, F.; Sesing, N.; Sendek, A. D.; Salguero, T. T.; Bartels, L.; Balandin, A. A.; Reed, E. J.; da Jornada, F. H. Machine-Learning-Driven Expansion of the 1D van der Waals Materials Space. *J. Phys. Chem. C* **2023**, *127*, 21675−21683.
(63) Formo, E. V.; Hachtel, J. A.; Ghafouri, Y.; Bloodgood, M. A.; Salguero, T. T. Thermal Stability of Quasi-1D NbS3 Nanoribbons and Their Transformation to 2D NbS2: Insights from in Situ Electron Microscopy and Spectroscopy. *Chem. Mater.* **2022**, *34*, 279−287.
(64) Geremew, A.; Bloodgood, M. A.; Aytan, E.; Woo, B. W. K.; Corber, S. R.; Liu, G.; Bozhilov, K.; Salguero, T. T.; Rumyantsev, S.; Rao, M. P.; Balandin, A. A. Current Carrying Capacity of Quasi-1D ZrTe3 Van Der Waals Nanoribbons. *IEEE Electron Device Lett.* **2018**, *39*, 735−738.
(65) Allison, S. J.; Cordova, D. L. M.; Hasib, M.; Aoki, T.; Arguilla, M. Q. Nanoparticle-directed bimodal crystallization of the quasi-1D van der Waals phase, Bi4I4. *Chemical Science* **2024**, *15*, 4811−4823.
(66) Cheon, G.; Duerloo, K.-A. N.; Sendek, A. D.; Porter, C.; Chen, Y.; Reed, E. J. Data Mining for New Two- and One-Dimensional Weakly Bonded Solids and Lattice-Commensurate Heterostructures. *Nano Lett.* **2017**, *17*, 1915−1923.
(67) Qu, Y.; Arguilla, M. Q.; Zhang, Q.; He, X.; Dincă, M. Ultrathin, High-Aspect Ratio, and Free-Standing Magnetic Nanowires by Exfoliation of Ferromagnetic Quasi-One-Dimensional van der Waals Lattices. *J. Am. Chem. Soc.* **2021**, *143*, 19551−19558.
(68) Tian, N.; Liu, D.; Zhou, B.; Yang, Y.; Zhang, G.; Zhang, D.; Zhang, Y. Nanowires of KP15 produced by liquid exfoliation. *Mater. Lett.* **2018**, *228*, 89−91.
(69) Liu, X.; Liu, S.; Antipina, L. Y.; Zhu, Y.; Ning, J.; Liu, J.; Yue, C.; Joshy, A.; Zhu, Y.; Sun, J.; Sanchez, A. M.; Sorokin, P. B.; Mao, Z.; Xiong, Q.; Wei, J. High yield production of ultrathin fibroid semiconducting nanowire of Ta2Pd3Se8. *Nano Research* **2020**, *13*, 1627−1635.
(70) Yang, M.; Cheng, G.; Mathur, N.; Singha, R.; Yuan, F.; Yao, N.; Schoop, L. M. Chemical exfoliation of 1-dimensional antiferromagnetic nanoribbons from a non-van der Waals material. *Nanoscale Horizons* **2024**, *9*, 479−486.
(71) Konnert, J. A.; Evans, H. T. The crystal structure of erdite, NaFeS2·$2H_2O$. *Am. Mineral.* **1980**, *65*, 516−521.
(72) Graf, H. A.; Schäfer, H. Darstellung und Kristallstruktur von KSbS2. *Zeitschrift für anorganische und allgemeine Chemie* **1975**, *414*, 211−219.
(73) Naveen, N.; Park, W. B.; Singh, S. P.; Han, S. C.; Ahn, D.; Sohn, K.-S.; Pyo, M. KCrS2 Cathode with Considerable Cyclability and High Rate Performance: The First K+ Stoichiometric Layered Compound for Potassium-Ion Batteries. *Small* **2018**, *14*, 1803495.
(74) Komaba, S.; Nakayama, T.; Ogata, A.; Shimizu, T.; Takei, C.; Takada, S.; Hokura, A.; Nakai, I. Electrochemically Reversible Sodium Intercalation of Layered NaNi < sub > 0.5 < /sub > Mn < sub > 0.5 < /sub > O2 and NaCrO2. *ECS Trans.* **2009**, *16*, 43.
(75) Dahn, J.; Haering, R. R. Lithium intercalation in TiS2. *Mater. Res. Bull.* **1979**, *14*, 1259−1262.
(76) Glibo, A.; Eshraghi, N.; Surace, Y.; Mautner, A.; Flandorfer, H.; Cupid, D. M. Comparative study of electrochemical properties of SnS and SnS2 as anode materials in lithium-ion batteries. *Electrochim. Acta* **2023**, *441*, 141725.
(77) Kuhn, A.; Holzmann, T.; Nuss, J.; Lotsch, B. V. A facile wet chemistry approach towards unilamellar tin sulfide nanosheets from Li4xSn1-xS2 solid solutions. *Journal of Materials Chemistry A* **2014**, *2*, 6100−6106.
(78) Yuan, F.; Song, X.; Cheng, G.; Yao, N.; Mozharivskyj, Y.; Schoop, L. M. Magnetic Nanosheets via Chemical Exfoliation of K2xMnxSn1-xS2. *Chem. Mater.* **2022**, *34*, 5084−5093.
(79) Chu, S.; Kim, D.; Choi, G.; Zhang, C.; Li, H.; Pang, W. K.; Fan, Y.; D'Angelo, A. M.; Guo, S.; Zhou, H. Revealing the Origin of Transition-Metal Migration in Layered Sodium-Ion Battery Cathodes: Random Na Extraction and Na-Free Layer Formation. *Angew. Chem., Int. Ed.* **2023**, *62*, e202216174.