# Assembling a photo-active 2D puzzle: from bulk powder to large-area films of semiconducting transition metal dichalcogenide nanosheets

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ABSTRACT (Conspectus). Two-dimensional (2D) semiconducting materials are poised to revolutionize ultrathin, high-performance optoelectronic devices. In particular, transition metal dichalcogenides (TMDs) are well-suited for applications requiring robust and stable materials such as electrocatalytic, photocatalytic and photoelectrochemical devices. One of the most compelling assets of these materials is the ability to produce and process 2D TMDs in the nanosheet form using solution-based (SB) exfoliation methods. Compared to other methods, SB techniques are typically inexpensive, efficient, and more suitable for scale-up and industrial implementation. In acknowledgement of the importance of this area, much work has been done to develop various SB methods starting from the exfoliation of bulk crystalline TMD materials to the chemical modification of final devices consisting of thin films of semiconducting 2D TMD nanosheets.

diverse material and device properties. Therefore, the aim of this Account is to provide an overview of the developed SB techniques that can serve as a guide for assembling highperformance thin films of 2D TMDs. We start by introducing the most popular methods for producing 2D TMDs using liquid-phase exfoliation (LPE), discussing their working mechanisms as well as their advantages and disadvantages. Notably we highlight a recently-developed LPE technique using electro-intercalation that draws on the advantages of previously presented methods. Next, we discuss processing the as-produced 2D TMD nanosheets via SB separating techniques designed for size and morphology selection while also presenting the ongoing challenges in this area. We then examine SB methods for processing the selected 2D nano-material dispersions into semiconducting thin films. Various methods are compared and contrasted and special attention is paid to a recently developed method which carefully deposits 2D TMD nanoflakes with preferential alignment and which has been shown scalable to the meter-squared size range. Finally, we explore strategies for increasing the optoelectronic performance of the TMD films via device engineering and defect management. We scrutinize these post-treatments based on the final device application, which are explicitly discussed. In all of the discussed process we present the most promising SB techniques giving critical analysis and insight from experience. While we provide our own "best practices", we stress the use of adaptability and critical thinking when designing specifically tailored procedures. By providing examples of different uses and measured improvements in one comprehensive guide, we hope to simplify process-development and aid researchers in making their own unique photo-active 2D "puzzles".

## 1. INTRODUCTION

Since the first observations of monolayer graphene,<sup>1</sup> researchers have been captivated by twodimensional (2D) materials. Inventing preparation methods, controlling material properties, manipulating assembly, and demonstrating applications of a vast variety of 2D materials in the past decades have produced a rich research field.<sup>2–4</sup> While the prototypical graphene is a semimetal, the unique semiconducting properties of select 2D transition metal dichalcogenides (2D-TMDs) have attracted significant attention for application in next-generation ultrathin, flexible optoelectronic devices including transistors, light emitting diodes, solar cells, and photoelectrodes.<sup>5–8</sup> Given the robustness of TMDs, photoelectrochemical (PEC) applications are of particular interest, and rapid advance has been achieved in recent years.<sup>9–12</sup> However, in order to realize such applications beyond the laboratory, it is also necessary to produce 2D-TMDs using economically-viable techniques.<sup>13</sup>

Of the numerous possible preparation methods, liquid-phase exfoliation (LPE) techniques are a leading class of methods for producing high-quality 2D-TMD nanosheets in a way that readily facilitates upscaling. Coleman and coworkers laid the foundation for LPE of 2D materials by using ultrasonication to transform bulk graphite powder into graphene nanosheets.<sup>14</sup> Soon after analogous techniques were developed to demonstrate LPE on the semiconducting TMDs,<sup>15,16</sup> first with MoS<sub>2</sub>, and then with WS<sub>2</sub>, MoSe<sub>2</sub>, and WSe<sub>2</sub>.<sup>15,17–19</sup> While these reports gave promise towards scalable roll-to-roll production of 2D-TMD optoelectronic devices, developing methods to further process nanosheet dispersions in order to select/separate the desirable material dimensions and deposit them into ultrathin films for devices emerged as the next challenge. In addition, defects present in the structure of LPE-based 2D-TMDs were found to significantly hinder device performance for solar energy conversion.<sup>10,20,21</sup> To date, much progress has been made on the topics of materials processing and defect mitigation in LPE-based 2D-TMDs, however more

Author accepted manuscript (Final published version at https://doi.org/10.1021/accountsmr.2c00209) fundamental understanding and engineering advances are needed to fully enable these promising materials for commercial application.

In this Account, we aim to summarize the state-of-the-art in the scalable solution-based production via exfoliation, processing, and application of semiconducting 2D-TMDs and give a perspective towards further advancing the field.

## 2. SOLUTION-BASED EXFOLIATION METHODS

We begin with the production of 2D-TMDs via LPE-based methods, which leverage the properties of crystalline TMDs that contain layers of *X-M-X* bonded tri-atomic layers (typically M = W, Mo, and X = S, Se) held together by van der Waals (vdW) forces (see crystal structure in Figure 1a). A principal advantage of LPE-based methods is the ability to convert bulk powders of microcrystalline (3D) TMDs into to 2D materials in a liquid dispersion that can be used in subsequent processing steps. Indeed, using micron-sized powders as a starting point is significantly advantageous over competing methods for producing 2D-TMDs that employ macroscale single crystals as starting material, or physical/chemical vapor deposition methods, which require high vacuum and high temperature. With this in mind, the concept of LPE can be divided into two main classes of techniques that dominate the literature: ultrasonication and ion intercalation. These techniques are shown schematically in Figure 1b and 1c, respectively, and will be discussed below.





**Figure 1.** (a) The layered (2H) crystal structure of a semiconducting TMD material is shown schematically with a ball-and-stick model. (b) schematic of liquid phase exfoliation of bulk TMD particles (brown) *via* ultrasonication with a horn probe (gray). (c) Schematic of an intercalation-based exfoliation with cations (red spheres).

## 2.1. Ultrasonication

As mentioned in the introduction, ultrasonication (schematically shown in Figure 1b) was among the earliest techniques developed for the LPE of layered materials. The method employs ultrasonic pressure waves via an immersed probe in a solvent (e.g. N-Methylpyrrolidone, NMP) whose surface tension complements the surface energy of the layered material.<sup>19</sup> Cavitation bubbles caused by the ultrasonic waves form predominantly at the edges and in between the layers of the bulk crystal. Upon collapse, high-energy microjets are generated which overcome the interlayer

vdW forces and break apart the layered structure.<sup>19</sup> Importantly, the magnitude of the exfoliation force is difficult to control and the force also causes breaks in the tri-atomic layer plane leading to scission across the crystal lattice.<sup>16</sup> This causes two critical drawbacks: nonideal nanoflake morphology and high defect densities.<sup>16</sup> Indeed, it has been well-recorded that nanoflakes, in particular MoS<sub>2</sub> and WSe<sub>2</sub>, suffer from a lateral size-thickness dependency wherein the thinnest flakes (monolayer or few atomic layer) possess small lateral dimensions (ca. 100 nm) and only thicker multilayer flakes (>3 tri-atomic layers) possess larger dimensions (>1  $\mu$ m).<sup>10,16</sup> Due to the highly anisotropic charge carrier transport in TMDs, high quantum yields for the extraction of photogenerated charges in TMD nanoflakes can only be obtained using mono-to-few-layer flakes with large lateral dimensions,<sup>10</sup> thus yielding an intrinsic limitation for devices comprised of ultrasonicated nanoflakes. Furthermore, we note that the uneven layers create step edge defects along the basal plane of the nanoflakes.<sup>10,16,20</sup> As a result, devices made from ultrasonicated 2D TMD nanoflakes tend to perform well below their theoretical capabilities and require further treatment strategies to avoid high defect densities.<sup>10,20</sup>

## 2.2 Ion intercalation

Another class of methods for LPE is ion intercalation (shown schematically in Figure 1c), wherein an ion from solution is interpolated in between the layers of a bulk vdW material. In the prototypical chemical intercalation approach, the ion insertion occurs spontaneously (e.g. via diffusion). The presence of the ion expands the intralayer spacing, thereby weakening interlayer forces and a chemical reaction can create additional forces to separate the layers.<sup>19,22</sup> Given its small size and negative redox potential, the lithium cation Li<sup>+</sup>, is the most commonly used ion for chemical intercalation based-techniques with TMDs. While this technique produces highly concentrated dispersions, the relatively harsh chemical reaction (water reduced by Li<sup>+</sup> to make H<sub>2</sub>

gas<sup>23</sup>) causes a phase transformation from the semiconducting 2H crystal phase of the TMD to the semi-metallic 1T phase as well as high concentration of defects.<sup>22–24</sup> For electro- or thermocatalytic applications these properties are desirable and have found widespread application,<sup>23–25</sup> however for semiconducting optoelectronic applications including photoelectrochemistry, the high defect concentration leads to rapid photogenerated charge recombination and poorly performing devices.<sup>22,26,27</sup>

## 2.2.1 Electrochemical ion intercalation using single crystals

Recently a few groups have developed an ion intercalation approach that maintains the semiconducting behavior of the 2H crystal phase of TMDs, by using large molecular cations (e.g. tetra-alkyl ammonium), whose reactivity is benign.<sup>26,28,29</sup> The larger cation size increases the TMD interlayer spacing sufficiently so that only gentle agitation is subsequently necessary to transform the bulk crystals from their pre-exfoliated, intercalated state into 2D nanoflakes. However, the large ion size precludes their spontaneous intercalation and an additional driving force must be added. An electrochemical bias (e.g. applying a negative potential to a TMD-based electrode to drive in positive molecular ions) can be simply used with a bulk single crystal TMD electrode since the single crystal is sufficiently conductive. Despite the quality of the resulting 2D-TMDs, the use of use of macro-scale single crystals as starting material, which are difficult and expensive to prepare, limits its scalability and broad application.

## 2.2.2 Electrochemical ion intercalation of powders

However, our lab recently presented a preparation route starting with inexpensive, commercially available powder and—using the electro-intercalation of the large alkylammonum cations— afforded the scalable production of high-quality TMD nanosheets. A schematic of this method is shown Figure 2a and can be called electrochemical pellet intercalation (ECPI).<sup>30</sup> Briefly, commercial TMD powder is pressed into a pellet and then annealed in a sealed container with

Author accepted manuscript (Final published version at https://doi.org/10.1021/accountsmr.2c00209) excess chalcogenide powder. Annealing conditions depend on the TMD used, for example 1100 °C for 48 hours with 2.3 °C/min ramp and a natural cooling cycle for MoS<sub>2</sub> vs 1000 °C for 12 hours with 2.1 °C/min ramp for WSe<sub>2</sub>. We observed significant crystal growth after the annealing step, rendering the pellet sufficiently conductive to undergo electrochemical intercalation. In contrast, an insulating (unannealed) electrode will exhibit a large potential drop, which will reduce the electric field at the TMD-electrolyte interface, thus reducing the driving force for ion intercalation.

The annealed pellet is attached to an alligator clip and submerged in acetonitrile with 5 mg/mL tetraheptylammonium bromide (THA<sup>+</sup>Br<sup>-</sup>), where THA<sup>+</sup> is the intercalate. A bias of 10 V is applied between the TMD pellet (cathode) and a glassy carbon rod (anode), which oxidizes bromide to bromine. The pellet can be seen to visibly expand as a result of intercalation while the electrolyte becomes yellow in color due to bromine formation. Continued intercalation causes material to slough from the TMD pellet. The intercalated powder and residual pellet are retrieved, rinsed with ethanol, and agitated in NMP using a low-power ultrasonication bath for 1-2 hours or until a color change and viscosity increase are observed. Finally, the solution is centrifuged at a relatively low speed (120 ref) to remove any unexfoliated bulk material and the supernatant is collected, which can then be used (e.g. deposited into thin film for device applications) without further purification (even without any nanoparticle size selection, however, this aspect can be important for device operation, see below). Notably any remaining intact portion of the pellet can be collected, dried, and reused in subsequent rounds of ECPI. It should also be stressed that the method is highly adaptable as described in more detail in our publication in *ACS NANO*.<sup>30</sup>



**Figure 2**. (a) Simplified illustration of exfoliation using the electrochemical pellet intercalation (ECPI) technique: (1) pressing TMD bulk powder particles into a pellet, (2) annealing, (3) immersion in tetraheptylammonium bromide electrolyte, (4) electrochemical intercalation, and (5) collection of intercalated powder. HAADF-STEM pictures (b-e) for exfoliated MoS<sub>2</sub> made via ECPI (b, d) and sonication (d, e). (f) Absorbed photon-to-current conversion efficiencies for the PEC reaction  $\Gamma/I_3^-$  with an applied potential of +0.3 V vs a Pt reference electrode. Inset: schematic of PEC set-up. Reproduced from reference 30. Copyright 2022 American Chemical Society.

In that recent work<sup>30</sup> we describe ECPI-made  $MoS_2$  nanosheets in detail and demonstrate their improved optoelectronic performance compared to ultrasonication-produced  $MoS_2$  nanoflakes. It was shown that the ECPI method gives ultrathin nanosheets with high aspect ratios and lateral dimensions frequently surpassing 1  $\mu$ m as observed in the transmission electron microscope, TEM,

images in Figure 2b and 2c. Moreover, the sheets were shown to be relatively thinner for the same lateral dimensions and the basal planes appear to have few step edge defects compared to MoS<sub>2</sub> nanoflakes produced via high-powered ultrasonication alone (see TEM images in Figure 2d and 2e). These morphological differences could be correlated to differences in optoelectronic performance. When deposited into thin films (see Section 4 below) and applied as a photoanode for iodine oxidation, ECPI-made MoS<sub>2</sub> nanosheets exhibited an absorbed-photon-to-current conversion efficiency (APCE) up to 90 % as shown in Figure 2f compared to only 10-15 % with ultrasonically-exfoliated MoS<sub>2</sub>. Based on this comparison, it is clear that choosing an exfoliation method for the desired application is an important first step towards preparing scalable 2D TMD based devices with excellent performance.

## 3. LIQUID-BASED 2D NANOSHEET SIZE SELECTION

Nanosheet size selection is an important step following any liquid phase exfoliation method. Since all LPE methods produce a range of TMD nanosheet/nanoflake sizes and their optoelectronic performance is known to strongly depend on the number of atomic layers and the lateral flake size, developing scalable methods for the facile separation of nanoflakes by size is an important goal in the field. When considering scalability, centrifugation and filtration are among the most feasible, making them highly popular. These methods are shown schematically in Figure 3 and briefly discussed next.



**Figure 3**. Schematics of two commonly used methods for isolating nanoflakes according to size. (a) Illustration of centrifugation. A polydisperse blend of thin and thick nanoflakes (i) makes up the starting dispersion (left). Following centrifugation, a new dispersion (right) is obtained where thinner material remains in the supernatant (ii) while large and unexfoliated material has been sedimented (iii). (b) Illustration of sieve-based filtration. An as-obtained dispersion is fed into the top cell and is successively separated by size as the dispersion travels down the column, sequentially passing through the membranes. The membrane pore diameter progressively decreases effectively separating the nanoflakes into groups possessing different distributions of lateral dimensions. Panel (b) reproduced from reference 10. Copyright 2017 American Chemical Society. Panel (a) contains original artwork by authors and is not subject to copyright.

## 3.1. Centrifugation

Centrifugation (Figure 3a) leverages centrifugal forces to segregate particles from the dispersion according to their sedimentation velocity, which is dependent on the particle shape, size, and density. In general, the largest/heaviest particles sediment at the bottom of the dispersion, forming

a pellet (Figure 3a-iii), while smaller/lighter particles stay dispersed in the supernatant (Figure 3aii). The supernatant can be additionally processed for further size collection or purification.<sup>31</sup> For instance, the processing of ultrasonication exfoliated TMD material often requires an primary centrifugation at low speed to discard large and unexfoliated bulk material.<sup>20,31–33</sup> The supernatant can then be centrifuged at a faster speed to isolate the desired-size nanomaterial in the sedimented pellet, allowing the smallest, amorphous fragments to be removed with the remaining supernatant.<sup>20,32,33</sup>

While centrifugation is simple and easy to perform over a range of scales, its main disadvantage is the lack of precise control. Indeed, the acquisition of monodisperse nanoflake thickness samples is essentially unattainable with centrifugation.<sup>10</sup> As a result, centrifugation is best suited for applications requiring high-yield nanoflake dispersions where some liberty concerning nanoflake dimension and size dispersity can be tolerated.

#### 3.2. Sieve filtration

Another demonstrated size selection technique is sieve-based filtration (Figure 3b). Our group has developed this technique for WSe<sub>2</sub> nanoflakes and it was shown to be an effective way to separate size groups of these nanoflakes including the largest populations.<sup>10</sup> The filtration is accomplished *via* a pressure-driven liquid column containing numerous stages divided by track-etched membranes of decreasing pore size. Narrow distributions of flake lateral dimensions were demonstrated with separate fractions having average lateral dimensions of ca. 1000 nm (largest fraction) to 100 nm (smallest fraction), see TEM images of all fractions (Figure 4a-d). While there is a correlation between the lateral dimensions of the nanoflakes and their number of layers (thickness) when ultrasonication LPE is used, the sieve filtration method does not nominally

Author accepted manuscript (Final published version at https://doi.org/10.1021/accountsmr.2c00209) separate by nanoflake thickness. Centrifugation could be applied to further separate the fractions by thickness.

Overall yield of the sieve filtration technique is high because nanoflakes are not intentionally discarded during the process. Furthermore, scale-up could be reasonably attained by augmenting the surface area of the filters. Moreover, additional filters could be introduced to further refine the nanoflake distributions. However, we note that the track-etched filters with controlled pore size are still relatively expensive.



**Figure 4**. Relationship between nanoflake lateral dimensions and the nanoflake internal quantum yield. (a-d) Transmission electron microscopy photos of nanoflake films of filtered dispersions from greatest (a) to smallest (d) lateral dimensions. (e) Simulated charge carrier transport of the internal quantum efficiencies (IQE) of WSe<sub>2</sub> nanoflakes as a function of thickness and lateral dimensions. Respectively, the points labelled A-D describe the empirical results of the nanoflake films shown in (a-d). Figures reproduced from *reference* 10. Copyright 2017 American Chemical Society.

The sieve filtration method, applied in our lab with ultrasonication-exfoliated WSe<sub>2</sub>, underscored an apparent link between the average dimensions of the nanoflakes and their resulting internal quantum efficiency (IQE) as shown in Figure 4e, which plots average flake size of the different fractions produced (A-D, largest to smallest) over a contour plot of the predicted IQE of the nanoflakes as photocathodes under an applied bias.<sup>10</sup> While predictions suggest that thin, large-width flakes should dislay the highest internal quantum yields, nanoflakes of the desired thinness and large lateral dimensions are not accessible using the ultrasonicated dispersions employed in that demonstration. We note that the ECPI method described in the previous section provides exactly this class of nanosheets, and can be another factor in their excellent performance. Applying the sieve filtration on the ECPI produced flakes could represent a future opportunity to further increase the performance of 2D TMD based photoelectrodes.

## 4. SOLUTION-PROCESSABLE FILM FORMATION

Since most applications for semiconducting TMD nanomaterials use the materials in the solid state, additional methods are needed to assemble the nanosheets into thin films in a controllable fashion. There are many ways to accomplish thin film formation, but not all routes produce equally high performing devices. Moreover, the device requirements dictate the deposition methods that can be used. For large-area applications employing thin films of 2D TMD nanoflakes, excellent coverage and a film without nanoflake aggregates are generally required while preferential flake orientation may only be needed in specific cases. The next subsections present two main classes of liquid-phase film deposition methods: evaporation-based and interfacial nanoparticle self-assembly techniques.

4.1. Liquid phase evaporation-based techniques

This class of methods includes drop casting, spin coating, spray coating, dip coating, and doctor blading. Given a dispersion of 2D TMD nanosheets in a liquid phase solvent (e.g. NMP), thin films of TMDs can be simply formed via evaporating the solvent leaving the nanoparticles behind. While simple in principle, there are a number of factors that should be considered.

For example, with respect to film quality, uniformity and nanoflake orientation are crucial for the performance of the final device. While orientation is not problematic for spherical nanoparticles, the anisotropic nature of vdW nanoflakes necessitates command over their orientation in relation to the substrate to facilitate high-performing devices.<sup>32</sup> More information on evaporation-based techniques including their advantages and drawbacks can be found in the Supporting Information, which includes an overview of each technique's performance with respect to ease of operation, scalability, film uniformity, and nanoflake orientation (summarized in Table S1). Notably, none of the solvent evaporation-based methods allow for control over the orientation of the particles in relation to one another and to the substrate. This is because the inter-particle vdW forces will become increasingly important as the liquid evaporates and flake re-stacking and aggregation will result. For nanoflakes this represents a critical barrier to obtaining highperforming devices.

#### 4.2. Interfacial nanoparticle self-assembly

Employing a fluid-fluid interface as a 2D template to align the 2D nanoparticles and aid in controlled thin film deposition has brought success compared to the solvent evaporation techniques discussed above. The Langmuir-Blodgett (LB) technique is the prototypical method using a liquid-gas interface. Originally the LB method used a monolayer of surfactant at the water-air interface, which could be transferred to a flat substrate <sup>34</sup> While LB-films have been prepared with many

different types of nanoparticles, for 2D TMD nanoflakes it is complicated since, rather than aligning at the water-air interface in a monolayer fashion, the flakes restack into aggregates and eventually form sediments. In our group we used the idea of interfacial self-assembly to develop a film deposition technique based on liquid-liquid interfacial self-assembly (LLISA) (see schematic in Figure 5a) to overcome this challenge.<sup>32</sup>

## 4.2.1. Liquid-liquid interfacial self-assembly

In contrast to an air-liquid interface, the LLISA method takes advantage of the interface between two immiscible liquids that are poor solvents to disperse 2D TMDs, such as hexane and water (or ethylene glycol). A nanoflake dispersion using a good dispersant (ex., NMP) is directly inserted at the liquid-liquid interface, and nanoflakes collect at the hexane-water interface. NMP, which is soluble in hexane and miscible with water, disperses quickly away from the interface confining a single layer of flakes to the liquid-liquid boundary forcing them to orient horizontally along the interfacial plane. Following formation of a self-assembled nanoflake monolayer at the interface, the top layer (hexane) can be aspirated off, leaving a compact film on the surface of the water layer. The nanoflake film is then ready for transfer to a preferred substrate by a stamping method, or by removing the water layer thereby depositing the nanoflake film onto said substrate.





**Figure 5**. (a) Schematic of the liquid-liquid interfacial self-assembly (LLISA) technique showing the nanoflake dispersion (red) being inserted at an ethylene glycol (EG, green)-hexane (blue) interface until a compact film is formed at which point the hexane layer is removed *via* aspiration and the water layer is removed to lower the film onto the substrate. (b-e) A comparison of film morphology from liquid-air (b-c) and liquid-liquid (d-e) self-assembly is shown with false colored SEM images from top-down (b,d) and cross-sectional (c,e) perspectives. (f) Schematic of roll-to-toll (R2R) LLISA deposition system. (g) Photograph of R2R LLISA film deposited on a plastic substrate. Figures (a-e) reprinted with permission from reference 32. Copyright 2015 The Authors. Figures (f-g) reproduced from reference 33. Copyright 2019 American Chemical Society

Importantly the LLISA method leads to improved morphology control over the LB approach. This is illustrated by comparing optical and electron microscope images of WSe<sub>2</sub> nanoflake thinfilms prepared by a LB approach (Figure 5 b,c) to comparable images from the LLISA approach (Figure 5 d,e).<sup>32</sup> While the nanoflakes exhibit considerable aggregation and overlapping with the LB approach, the nanoflakes deposited by the LLISA approach self-assemble such that flake Author accepted manuscript (Final published version at https://doi.org/10.1021/accountsmr.2c00209) overlap is minimized (provided that injection of the dispersion ceases once a complete monolayer of flakes is formed at the interface). The result is a "puzzle-like" morphology of 2D TMD nanoflakes (Figure 5d, inset).

We also showed that the improved nanoflake-substrate contact afforded by the LLISA method resulted in ameliorated film conductivity and superior performance of WSe<sub>2</sub> nanoflakes as photocathodes for solar-driven water reduction (H<sub>2</sub> production). Notably, the LLISA film exhibited higher photocurrent density despite absorbing fewer photons, indicating improved absorbed photon-to-current conversion efficiency (APCE). Importantly, it was possible to tune film thickness by adding sequential layers without disrupting previous layers, thereby preserving the puzzle-like assembly.

Since our initial demonstration, this technique has been leveraged for many subsequent works<sup>10,20,35,36</sup> on 2D TMD nanoflake films as it provides superior optoelectronic and photoelectrochemical performances (compared to drop casting or spin coating).<sup>31</sup> Thus the LLISA method has opened an avenue to explore fundamental concepts related to 2D TMD nanoflake films by eliminating convolution of faulty flake-to-flake charge transfer or poor flake-substrate contact.<sup>10,36,37</sup> As a prime example: the understanding that optimal photogenerated charge harvesting occurs in laterally-large but thin flakes was established by comparing films made by the LLISA technique and subsequently motivated the work to identify new exfoliation techniques (e.g. the ECPI technique discussed above).<sup>10</sup>

## 4.2.2. Roll-to-roll continuous film deposition

While LLISA films represent an important milestone in nanoflake film formation, first demonstrations were shown on a small scale (few square-centimeter device area). Though large compared to the size of individual nanosheets, it remains insufficient for globally-relevant solar energy conversion.<sup>13</sup> Thus we next developed a modified version of the LLISA technique for

continuous, roll-to-roll (R2R) film formation (see schematic Figure 5f).<sup>33</sup> In a large deposition bath (100 mm x 100 mm) a liquid-liquid interface between two immiscible liquids is once again employed (water-heptane), and the TMD nanoflakes are dispersed in a solution of 1-butanol/tert-butanol (1:10) and injected from the bottom layer. Because of the buoyancy of the butanol solution, the nanoflake dispersion floats rapidly to the liquid-liquid interface. The butanol then dissolves in the water, leaving the flakes to assemble at the interface. As with the few-cm<sup>2</sup> batch scale, the nanoflakes assemble in a single layer with minimal overlap and oriented flat along the interface. Importantly, injecting the flakes from the bottom layer permits the dosing apparatus to be permanently fixed to the base of the bath, leaving the top layer free.

To advance the flakes towards the flexible substrate, a system of continuously moving paddlebelt-pushers is installed in the top layer. As the paddles push the film onto the advancing substrate, there is no need to remove the top liquid layer. This combined with injection from the bottom eliminates any need to remove or insert apparatus and allows for continuous film formation and deposition. A typical film of MoS<sub>2</sub> nanoflakes made from this technique is shown in Figure 5g, with an area of over 50 cm<sup>2</sup>. Moreover, the width of the films can be regulated by modifying the width of the deposition bath while the length is only limited by the length of available substrate.

Importantly, we demonstrated that our roll-to-roll films were reproducible and performed similar to batch-scale films when implemented in PEC devices.<sup>33</sup> We also showed that it was possible to use this apparatus to demonstrate a R2R deposition of a type II vdW heterojunction employing p-type WSe<sub>2</sub> and n-type MoS<sub>2</sub>. A uniform film was produced with a sharp interface between the first and second layer verifying the individual integrity of the two films. Thus, these large-scale films can be tuned not only by choice of TMD but also by number of layers and by combination of different TMDs.

#### 5. ENHANCING THIN-FILM OPTOELECTRONIC PERFORMANCE

After preparing TMD nanoflake thin-films according to the device requirements, additional modifications may be required to adjust or enhance certain aspects of the film. Indeed, defects and charge carrier separation can still be addressed. In this final section we discuss a few of the many approaches for improving the performance of TMD nanoflake thin films, namely via heterojunction formation and defect passivation techniques.

#### 5.1. van der Waals heterojunctions

Forming vdW heterojunctions (vdWHJs) is a powerful technique to not only adjust the final characteristics of the film but also to promote photogenerated charge separation in semiconducting 2D TMDs. Indeed, the vdW attractive forces experienced by 2D TMD nanosheets can facilitate their restacking via basal plane interactions, which facilitates electronic communication between the disparate atomic layers.<sup>38</sup> Of the possible semiconductor heterojunction types, a type II heterojunction with staggered conduction and valence band alignment (as shown schematically in Figure 6a) is the most promising for solar energy conversion applications.<sup>38</sup> A prime example, improved PEC performance has been demonstrated in MoS<sub>2</sub>/WS<sub>2</sub><sup>12,39</sup> and WSe<sub>2</sub>-MoS<sub>2</sub><sup>33</sup> vdWHJs the latter being demonstrated with the LLISA deposition leading to vdWHJ nanoflake films with good contact to the conducting substrate (See Figure 6b) and over large scale. Owing to the relative ease of forming high-quality 2D TMD vdWHJs with clean interfaces with the afore discussed ECPI and LLISA methods we believe that this is a compelling route towards augmenting the performance of 2D TMD-based devices and, critically, one that is solution-processable.

## 5.2. Hybrid inorganic-organic heterojunctions

In addition to purely inorganic heterojunctions, 2D TMD materials can also be combined with organic semiconductors to create desirable type II junctions. As organic semiconductors (OSs) can be easily tuned in terms of energy levels and solvent solubility, they offer a great range of possibilities in combination with inorganic semiconductors. Our group demonstrated the feasibility of hybrid organic/inorganic heterojunctions by pairing MoS<sub>2</sub> nanoflakes with a dihexanoic acid (DHA-PDI) functionalized perylene diimide OS , which was found to be essential for homogeneous film formation of the OS on the MoS<sub>2</sub> nanoflake films, deposited by an all solution processing method (see Figure 6c-e) .<sup>35</sup> Transmission electron microcopy revealed an intimate contact between the nanoflakes and the DHA-PDI, which formed fibers (Figure 6c), and optically homogeneous thin films were feasible over relatively large areas (Figure 6d).

When employed as a photoanode, the hybrid system yielded photocurrent densities 6-10 times greater than either individual film as seen by linear scanning voltammetry (Figure 6e). This behavior was explained by improved separation of photogenerated holes in the TMD by transfer to the OS, as shown schematically in Figure 6e inset. This simple demonstration underlines the versatility of semiconducting 2D TMD nanoflakes and points to still more opportunity for tunability in devices based on solution-processed 2D TMDs.



**Figure 6**. Examples of TMD based heterojunctions. (a) Illustration the band alignment and charge separation in a vdWHJ based on MoS<sub>2</sub> (green) and WSe<sub>2</sub> (purple) (b) Cross-section SEM image of an WSe<sub>2</sub>/MoS<sub>2</sub> vdWHJ prepared *via* sequential LLISA depositions. (c) Image of a hybrid MoS<sub>2</sub>/DHA-PDI film acquired with transmission electron microscopy. (e) Photographs of pure organic (left), MoS<sub>2</sub> (right), and hybrid (middle) films deposited on FTO-glass. (e) linear scanning voltammetry of hybrid and pure films subject to intermittent illumination in an  $\Gamma/I_3^-$  redox couple (inset shows suggested band alignment and mechanism of charge transfer). Figure (b) reproduced from reference 33. Copyright 2019 American Chemical Society. Figures (c-e) reproduced from reference 35. Copyright 2017 American Chemical Society.

5.3. Defect Passivation

Defect passivation is another promising way to lessen charge recombination and enhance device performance is defect passivation. This step is usually performed after film-formation and is possible via a number of viable approaches. Here we discuss defect healing using atomic layer deposition (ALD) and treatment with various surfactants.

## 5.3.1. Atomic Layer deposition

ALD is performed by alternatingly reacting gas-phase precursors with a surface to build, layerby-layer, the desired deposition material.<sup>10,40</sup> Since each reaction is self-limiting, atomically-thin films can be formed in a controllable and conformal manner. Given the low reactivity of the TMD basal planes, ALD precursors will react preferentially with edge defects or surface defects, essentially filling these defects and passivating them. In an effort to passivate edge defects, the ALD of Al<sub>2</sub>O<sub>3</sub> has been frequently used in PEC devices for water oxidation.<sup>40</sup> In our own attempts passivating WSe<sub>2</sub> with Al<sub>2</sub>O<sub>3</sub> we found that ALD preferentially took place at edge sites (as depicted schematically in Figure 7a), leaving the basal planes relatively untouched. The deposition yielded improved photocurrent and decreased dark current, as can be seen in the LSV curves in Figure 7b measured with WSe<sub>2</sub> photocathode prepared from nanoflakes with different average size (from sieve filtration).<sup>10</sup> Importantly, the observed improvement was related to the size of the nanoflakes with larger, thicker flakes benefitting the most (see "A" in Figure 7b). Improved photovoltage current was observed in open-circuit potential experiments, suggesting that photogenerated charge carrier recombination was principally suppressed. It should be noted, however, that Al<sub>2</sub>O<sub>3</sub> is less suitable for PEC in aqueous application given its poor stability in acid or base.



**Figure 7**. Examples of defect passivation strategies. (a) Schematic of passivated edge and step edge defects of a 2D TMD nanoflake using ALD. (b) Photocurrent density-voltage curves of ALD-treated WSe<sub>2</sub> nanoflake film photocathodes in organic redox chloranil under intermittent light. Gray lines indicate photocurrent density (J<sub>ph</sub>) of the untreated photoelectrodes and colored lines indicate the J<sub>ph</sub> after ALD. Lateral flake dimensions decrease from sample A to D (see Figure 4). (c) Illustration of defect healing *via* surfactant (HTS) in a WSe<sub>2</sub> nanoflake. (d) Photocurrent density-voltage curve of HTS-treated WSe<sub>2</sub> nanoflake film photocathode compared to an untreated film under intermittent light in aqueous acidic electrolyte for the H<sub>2</sub> evolution reaction (with Pt based co-catalyst). The surface potential of the WSe<sub>2</sub> films from (d) are shown in (e) and (f), respectively, from untreated and HTS-treated film. Figures (a,b) reproduced from reference 10. Copyright 2017 American Chemical Society. Figures (c-f) reproduced from reference 20. Copyright 2018 American Chemical Society.

#### 5.3.2. Chemical Functionalization

Less controllable than ALD but capable to work well in acidic conditions,<sup>20</sup> chemical functionalization works by exposing (e.g. via solution) TMD nanoflakes to a molecule possessing one functionality suitable to bind with dangling surface bonds (defects) in the TMD structure.<sup>20,21,41</sup> Silane groups are among the most frequently used chemical functional group, with alkylsilanes and bis(trifluoromethane)sulfonimide (TFSI) being common molecules. Indeed, in our own experience treating  $MoS_2$  nanoflakes with alkyltrichlorosilanes we observed that the improvement of the conductivity and charge mobility exhibited a nontrivial effect due to the electronically insulating nature of the alkyl chain.<sup>31</sup> Notably hexyltrichlorosilane (HTS) was found to perform better than butyl- or octyltrichlorilanes.<sup>31</sup> Accordingly, in subsequent work, we applied this finding to single-layer nanoflake films of WSe<sub>2</sub> (produced by ultrasonication LPE) for solardriven water reduction in acidic electrolyte.<sup>20</sup> We found that treating the WSe<sub>2</sub> photocathode with HTS passivated the Se vacancies, as shown schematically in Figure 7c. As a result, the photocurrent density doubled compared to untreated samples (as shown in Figure 7d). The effect of the passivation was also seen by Kelvin probe force microscopy imaging of the untreated and HTS treated films (Figures 7 e and f, respectively) where an average increase and homogenization of the surface potential after HTS treatment is observed. Thus, with these demonstrations it is clear that chemical functionalization is a facile and powerful technique for various materials and device applications. Successfully implementing the optimized defect passivation strategy for the material used under the intended device application represents the final step in assembling the puzzle to create high performance semiconducting 2D-TMD nanoflake thin films for large scale application.

#### 6. CONCLUSIONS AND OUTLOOK

In this Account we explored the different available routes towards constructing a thin film of semiconducting 2D TMD nanoflakes. From 2D nanomaterial production via exfoliation to sorting, deposition, and finally tuning the materials in the solid state, we have shown that there are many possibilities at each stage and that every choice has an impact on the application and performance of the final device. We placed special emphasis on methods that produce and preserve the semiconducting properties of TMD nanoflakes and that have been shown to be up-scalable. Relevant methods to produce 2D TMDs via exfoliation including ultrasonication, ionintercalation, and ECPI were examined followed by size-selection and separation techniques such as centrifugation and sieve filtration. The discussion next focused on processing the 2D TMDs into high-quality thin films using liquid-phase interfacial nanoparticle self-assembly techniques (e.g., LB and LLISA), highlighting a continuous R2R method based on LLISA. We closed our Account by discussing well-known strategies to improve the performance of the final device using heterojunctions (vdW and hybrid organic-inorganic) and defect mitigation (ALD and chemical functionalization). These methods represent the "puzzles pieces" available for the construction of photo-active 2D TMD films with unique optoelectronic properties. In each case we discussed the advantages and disadvantages and offered direction based on our own experiences and expertise, which are summarized next.

Based on the state-of-the-art and the experience of our laboratory the most promising route towards scalable and high performance semiconducting 2D TMD thin film devices is (1) exfoliation via ECPI, (2) size selection via centrifugation, (3) film deposition via LLISA, and (4) forming vdwHJs to enhance charge separation. In this way we ensure that thin nanoflakes with large lateral dimensions best suited for efficient photon energy conversion are produced. Moreover, keeping the processing and size selection simple with high yields, and using a

deposition method that ensures dense, "puzzle-like" films of nanoflakes (well-contacted with the substrate for efficient charge extraction and with continuous nanoflake coverage) are important practical aspects to prioritize. Finally, improving substrate/material contact with minimal organic contaminants and enhancing charge separation are both needed to ensure the best photogenerated charge carrier generation. Indeed, the application of the ECPI method to produce complementary 2D TMDs for heterojunction-based devices has not been explicitly demonstrated and represents a path for immediate exploitation.

The immense potential of 2D TMDs means that this field is constantly expanding and improving on itself. In particular, we envision that atomically doped and alloyed TMDs will play a larger role in the next generation of ultrathin and flexible optoelectronic devices. Indeed, several studies have already shown that atomic doping can lead to ambipolar behavior, polarity switching, and increase in catalytic behavior.<sup>42–44</sup> Similarly, alloyed TMDs have shown promise in fine tuning band gaps for precise control over optical, electronic, and optoelectronic behaviors.<sup>45–50</sup> These represent promising pathways towards expanding the range of properties accessible to 2D TMDs and increasing their tunability, thereby broadening their device application. However, to date these methods have all used energy intensive, bottom-up techniques (chemical vapor deposition, atomic layer deposition, etc.), which are not suitable for scalable applications. Thus, it is critical that future works tackle this issue by proposing scalable approaches for atomic doping and alloying of 2D TMDs.

Additionally, an ongoing challenge is the scalable separation and selection of nanoflake or nanosheet sizes. While some control can be exerted, there is consistent trade-off between the volume that can be processed and the degree of selectivity. We propose that this could take the

form of improved selectivity and operability of filtration methods, or entirely innovative methods not yet known.

In all, this account provides a step-by-step guide for assembling photo-active 2D puzzles of 2D TMDs. As it turns out, there is more than one way to assemble this puzzle and a few pieces may still be missing. So, although user discretion is required, it is our hope that this work can be used to inform those wishing to construct their own puzzles and to highlight the need to find the final missing pieces.

# ASSOCIATED CONTENT

# **Supporting Information**.

The following files are available free of charge.

A PDF file including additional discussion on solution-based deposition techniques including Table S1, which compares their suitability for processing 2D TMD nanoflake dispersions into thin films.

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