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High-yield exfoliation of 2D semiconductor monolayers and reassembly of organic/ inorganic artificial superlattices



Lin et al. describe an intercalation-based exfoliation method for the scalable production of high-purity 2D semiconductor monolayers in the liquid phase. The key to the high-yield exfoliation is the complete intercalation of layered crystal through a unique "intercalation and separation" chemistry. Re-assembling these monolayers through the facile solution-based techniques results in a wide range of artificial superlattices with tunable compositions, periodicities, and properties.



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Highlights

A solution-phase exfoliation approach to high-purity 2D semiconductor monolayers

An "intercalation and separation" chemistry achieving the complete intercalation

The facile and scalable assembly of versatile artificial superlattices

Superlattices with tunable compositions, periodicities, and physical properties

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High-yield exfoliation of 2D semiconductor monolayers and reassembly of organic/inorganic artificial superlattices

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SUMMARY

The scalable preparation of high-purity monolayers is essential for practically integrating two-dimensional (2D) semiconductors in diverse technologies but remains a persistent challenge. Previous efforts to exfoliate 2D layered crystals by the organic ammonium intercalation usually produce few-layer nanosheets owing to a self-retarding effect that hinders the complete intercalation in neighboring layers. Herein, we report a unique "intercalation and separation" chemistry with a constant self-refreshing crystal surface that mitigates the self-retarding effect to ensure a complete intercalation of the bulk crystal, ultimately enabling high-yield solution-phase exfoliation of 2D semiconductor monolayers in excellent purity (e.g., monolayer purity of >95% for In₂Se₃ and InSe). Furthermore, we have assembled large-area organic/inorganic hybrid superlattices with diverse organic molecules and inorganic 2D monolayer crystals, thus creating a family of artificial superlattice materials with atomically modulated chemical compositions, widely tunable superlattice periodicities, and specifically tailorable electronic and thermal properties.

INTRODUCTION

Two-dimensional (2D) monolayer semiconductors with dangling-bond-free surfaces allow for preserving the pristine crystal structure and associated physical/chemical properties at the ultimate thickness limit and have received enormous research interests for their broad potential in electronics, optoelectronics, magnetics, catalysis, and energy storage.¹⁻⁷ These surface-saturated monolayer crystals may function as versatile building blocks to hybridize with other inorganic⁸⁻¹⁰ or organic¹¹⁻¹⁴ components through van der Waals (vdW) interactions to create diverse superlattice structures with widely tunable structural characteristics and specifically tailorable functionalities. For the ultimate deployment in practical technologies, the scalable preparation of high-purity 2D monolayers represents the essential material foundation.^{8,15,16} For this purpose, the conventional mechanical exfoliation and chemical/physical vapor deposition techniques are generally of low throughput and facing severe challenges toward scaled-up production. Alternatively, the solution-based large-scale production of 2D nanosheets as versatile building blocks may offer an attractive pathway to a wide range of applications at an affordable cost.^{16–19}

The bigger picture

Two-dimensional (2D) semiconductor monolayers are of considerable interests as building blocks to hybridize with other inorganic or organic components for creating versatile superlattice structures. However, the scalable preparation of 2D semiconductor monolayers remains challenging to date. Here, we report a unique "intercalation and separation" chemistry that enables complete intercalation of 2D layered crystals and high-yield exfoliation of diverse 2D semiconductor monolayers in near-unity purity. Using these 2D monolayers as nanoscale building blocks, we have successfully assembled a family of organic/inorganic and inorganic/inorganic artificial superlattice materials with tunable compositions, structures, and properties. This new intercalation chemistry and the scalable solution-chemical production of 2D semiconductor monolayers and superlattices move us a significant step closer to practically integrating 2D semiconductors in diverse technologies at an affordable cost.

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However, to date, the scalable solution-phase preparation of high-purity 2D semiconductor monolayers remains a major roadblock. The absence of large-scale 2D semiconductor monolayers with the crucial thickness uniformity is hindering the next-stage development of solution-based approaches such as the assembly of long-range ordered superlattice structures beyond discrete local heterostructure domains.^{20,21} Limited successes have been achieved in the bottom-up chemical synthesis.²²⁻²⁴ In parallel, the top-down solution-phase exfoliation of freestanding 2D nanosheets from bulk crystals has been widely explored for the fabrication of thinfilm electronics^{17,18} and energy storage^{25,26} devices. Among diverse exfoliation techniques, the well-established liquid-phase exfoliation (LPE) strategy employing high-power sonication or high-shear mixing is a straightforward and general approach,^{17,27–30} but usually yields nanosheets with a broad thickness distribution with limited selectivity toward monolayer materials. On the other hand, the intercalation-based exfoliation using alkali metals may be a viable method for selectively producing pure monolayers.^{4,31–34} However, during the fast and spontaneous intercalation process and subsequent violent hydration reaction, the highly reactive and energetic alkali metal may damage the atomically thin 2D crystals and result in a large number of defects^{33,34} or cause undesired phase transition into metallic phase (e.g., 1T MoS₂) through the injection of excessive electrons.³⁵ By contrast, the electrochemically driven intercalation of organic ammonium cations into 2D layered semiconductors may be finely tuned by the molecular size and external potential, allowing for a milder reaction to retain the desired structural phase with minimum structural damage to the resulting monolayers.^{12,36,37}

However, previous attempts to exfoliate ammonium-intercalated layered crystals mostly produce few-layer nanosheets with a mixed thickness (e.g., typically 2-6 nm or 3-10 layers for exfoliated MoS₂) owing to the incomplete intercalation of bulk crystals.^{18,38,39} At the initial stage of reaction, the outer layers near the crystal surface were first intercalated and greatly expanded. The large-size ammonium cations already intercalated within the vdW gap exert large elastic and electrostatic interlayer repulsions to retard the continued intercalation in the neighboring layers (i.e., self-retarding effect) (Figure 1A), which thus prevents the complete intercalation in every vdW gap (as manifested in the well-known staging phenomenon of graphite intercalation compounds^{4,40-42}). Applying an excessive overpotential could overcome the self-retarding effect, but inevitably leads to violent reactions and disintegration of bulk crystals before reaching complete intercalation. This phenomenon has been widely observed in many 2D layered crystals such as MoS₂, especially when starting with centimeter-scale bulk crystals.^{18,38,39} As a result, exfoliating these incompletely intercalated crystals has usually produced multi-layer nanosheets with a statistically mixed layer thickness (Figure 1A).

Herein, we report a unique "intercalation and separation" process that mitigates the self-retarding effect and ultimately enables the complete intercalation throughout the entire bulk crystal without excessive overpotential that may cause undesired structural damage or phase transition (Figure 1B). In particular, we hypothesize that when the intercalation-induced mechanical strain exceeds the in-plane yield strain of 2D crystals, the initially intercalated layers on the outer surface may naturally break off from the bulk, exposing underlying fresh layers for the continued intercalation and eliminating the self-retarding effect from previously intercalated layers. Using In₂Se₃ as a model system, we show the crystal surface is constantly refreshed for a continued "intercalation and separation" process from the surface to core until the entire bulk crystal is consumed, allowing for complete intercalation and high-yield exfoliation of solution-dispersed 2D semiconductor monolayers *en masse*.



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Figure 1. The intercalation and exfoliation behavior of different layered crystals

(A) Schematic illustration of the intercalation of large-size ammonium cations that exert elastic/ electrostatic interlayer repulsions to retard the continued intercalation in neighboring layers, preventing the complete intercalation in every vdW gap. Exfoliating these incompletely intercalated crystals produces mostly multi-layer nanosheets with mixed thickness.
(B) For layered crystals with sufficiently high intercalation-induced strain, the intercalated parts may break off from the bulk owing to the excessive strain accumulated, exposing underlying lattices for continued intercalation. Such a continued intercalation and separation process enables the complete intercalation of the entire bulk crystal and subsequent exfoliation into pure monolayers.

This unique self-refreshing process is general and can produce high-purity 2D monolayers from large-size bulk layered crystals with high intercalation-induced strain (e.g., ln₂Se₃, lnSe, and Bi₂Se₃). Taking a step further, we show the exfoliated 2D semiconductor monolayers can serve as versatile building blocks for assembling ordered molecule/2D hybrid superlattices with alternating molecular layers and inorganic 2D monolayers, thus creating a family of versatile artificial superlattices with atomically modulated chemical compositions, widely tunable structural periodicities, and specifically tailored electron and phonon transport characteristics. Together, our study presents unique intercalation chemistry that offers a viable low-cost chemical approach to high-purity 2D semiconductor monolayers and large-area hybrid superlattice materials with tunable structures and functionalities.

RESULTS AND DISCUSSION

Intercalation and separation process

The intercalation of large tetraalkylammonium cations generates considerable mechanical strain in the host layered crystal that may be accumulated at the interface between expanded and pristine lattices. Such intercalation-induced strain depends on the size of intercalated cations and the rigidity of the 2D crystal itself. If the intercalation-induced strain does not exceed the breaking limit of the 2D lattice, the bulk crystal can maintain its integrity during the insertion of ammonium cations. As discussed earlier, the steric and electrostatic repulsion of intercalated cations could hinder further intercalation in adjacent layers of already intercalated regions (self-retarding effect), leading to incompletely intercalated bulk crystals (e.g., MoS₂) (Figure 1A).¹⁸ On the other hand, if the intercalation-induced mechanical strain exceeds the breaking limit of 2D lattices, the intercalated crystals may bend, fracture, and separate from the bulk during the intercalation process, which continually exposes new underlying surface for the intercalation and thus effectively avoids the self-retarding effect (Figure 1B). Expectedly, such intercalation and exfoliation tend to occur in crystals with higher intercalation-induced mechanical strain. Previous studies suggest that crystals with larger monolayer thickness, such as five-atomiclayer In₂Se₃ and four-atomic-layer InSe, typically exhibit higher strain energy toward lattice deformation (e.g., caused by intercalation) than three-atomic-layer MoS₂ and WSe₂ crystals.^{43,44} Indeed, theoretical calculations show these thicker monolayer crystals experience much higher mechanical strain upon structural deformation

CellPress Chem Article -2.0 Α С detachment saturatio pre-intercalatio ntercalatio Current (mA) -1.5 Current (mA) -1.0 -0.5 0.0 -1 -2 -3 -4 Potential *vs.* Ag/AgCI (V) ō 10 20 30 40 50 Elapsed time (min) RT 100 °C 200 °C 300 °C 400 °C D 1.3 nm 1.6 nm 1.9 nm 1.8 nm 1.0 nm î 1 1 F G H 0.8 RT In 3d_{3/2} RT In 3d_{5/2} 400 °C 100 °C \$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$ 400 °C 200 °C Intensity (a.u.) Absorbance 0.6 300 °C Probability 300 °C 1.0 nm 400 °C 0.4 200 °C 100 °C 0.2 >1.0 nm RT

Figure 2. Complete intercalation of In₂Se₃ crystal and high-yield exfoliation of high-purity 2D semiconductor monolayers

2.0

(A and B) Linear sweep voltammetry (A) and constant potential amperometry (B) profiles of the alkylammonium intercalation of In₂Se₃ crystal. The current spikes (pointed out by blue arrows) signify periodic detachments of intercalated layers and exposure of fresh surface, whereas the regions between spikes indicated the continuous intercalation process. Inset photographs show the crystal intercalated for a different time. (C) The photograph of In₂Se₃ monolayers in DMF produced *en masse* (in 2-liter-volume bottles) through the continued intercalation of large-size bulk

455

450

Binding Energy (eV)

445

440

0.0

400

500 600

Wavelength (nm)

700

800

crystals. The two monolayer dispersions are in different concentrations. (D) AFM images of In_2Se_3 nanosheets at room temperature (RT) and those annealed at 100°C to 400°C, respectively. Some regions appearing thicker are where two monolayers overlap. The thickness scales of all AFM images are identical. Scale bars are 300 nm.

(E) Schematic illustration of pristine In₂Se₃ monolayer (thickness ≈ 1.0 nm) and surface-functionalized monolayer (thickness > 1.0 nm).

(F) Statistical analysis of the thickness of nanosheets annealed at different temperatures, showing a small thickness variation for all samples (standard deviation ≈ 0.1 nm).

(G and H) XPS analysis (G) and UV-vis optical absorption spectra (H) of In₂Se₃ annealed at different temperatures, both suggesting a well-retained structure after thermal annealing.

(Figure S1), particularly for the intercalation of bulky-size cations (e.g., \approx 10–20 Å for organic tetraalkylammonium comparing with \approx 1 Å for inorganic lithium).

Using ln_2Se_3 semiconductor crystal as a model system, we have thoroughly studied this unique intercalation behavior that differs from what is commonly seen in MoS₂, WSe₂, and others. The chemical intercalation of organic ammonium cations, such as tetrabutylammonium bromide (TBAB) and tetraheptylammonium bromide (THAB), into ln_2Se_3 bulk crystal was conducted in an electrochemical cell with the oxidation of Br⁻ on anode and the formation of (THA⁺)_x(ln_2Se_3)^{x-} on cathode (Figure S2).^{18,36} The electrochemical intercalation of ammonium cations typically occurs at a certain electrochemical potential threshold before which the intercalation is nearly not observable ("pre-intercalation" region in Figure 2A).³⁶ The onset potential of THA⁺ intercalation starts at around -1.2 V versus Ag/AgCl as evidenced by the rising

surface-functionalized

In₂Se₃ monolayers

0.8

1.2

1.6

Thickness (nm)

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current ("intercalation" region in Figure 2A). Further increasing the applied potential leads to a nearly linear increase in the current. Beyond -2.1 V versus Ag/AgCl, the electrochemical current stays nearly constant, probably indicating the saturation of all accessible intercalation surfaces on the In₂Se₃ crystal ("saturation" region in Figure 2A). In the meantime, periodic current spikes were superimposed on the saturated base current. These unique current spikes were not previously observed in electrochemical intercalation of other 2D layered crystals such as MoS₂ and black phosphorus,^{12,36} which suggests an "intercalation and separation" and periodic self-refreshing process in In₂Se₃, as further investigated below.

The unique "intercalation and separation" process was monitored by the constant potential amperometry (Figure 2B). For the intercalation at a constant electrochemical potential of -4 V, the time-resolved current profile consists of a relatively stable but gradually reducing base current along with a series of superimposed periodic current spikes (pointed by blue arrows). The base current is mainly contributed by the continuous intercalation process, whereas the spikes signify a sudden increase and recovery of current. They were attributed to the exposure of fresh In₂Se₃ surface for new intercalation reactions after the detachment of surface intercalated layers from bulk crystal. In particular, the formed hybrid $(THA^+)_x(In_2Se_3)^{x-}$ causes significant crystal volume expansion that generates sufficient mechanical strain between pristine In₂Se₃ and intercalated THAB/In₂Se₃ lattices to drive periodic detachment of intercalated layers from bulk crystal (photograph insets in Figure 2B). Such a unique intercalation behavior mainly arises from the much larger intercalationinduced mechanical strain in In₂Se₃ crystal (e.g., under the same structural deformation, the strain in In₂Se₃ lattice is approximately 4 times larger than that in MoS₂; see Figure S1), whereas the yield strain values of these 2D crystals are rather similar (Figure S3). The high intercalation-induced strain naturally breaks the intercalated In₂Se₃ crystals from the bulk and exposes the next fresh layers for subsequent intercalation reactions, resulting in a rapid current increase, which then returns to the base value (a spike) once newly exposed crystal layers are again saturated.

In particular, a likely scenario is that each intercalated monolayer is microscopically separated from the surface so that it does not produce a self-retarding effect for the subsequent intercalation, thus enabling the complete intercalation (Figures 1B and S4). However, such microscopic separation of a single intercalated surface monolayer does not generate sufficient strain to induce the complete detachment. Instead, the intercalated surface layers remain loosely connected to the bulk crystals (Figure S5). With the continued intercalation process, the number of intercalated and loosely connected monolayers increases, eventually accumulating sufficient strain that induces the detachment of loosely connected monolayer materials from the electrode. Such detachment suddenly exposes the underlying fresh surface to the electrolyte and reduces diffusion barriers, thus leading to a large intercalation current spike in the constant potential amperometry. Indeed, our experiments show that material detachments always occur concurrently with current spikes. The base current gradually decreases over time owing to the shrinking crystal size as the reaction proceeds. Upon the consumption of the entire bulk crystal, the current abruptly drops to zero (flat region of current profile and the last photograph in Figure 2B).

Together, the abovementioned experimental observations demonstrate a unique "intercalation and separation" process (Figure 1B). The high intercalation-induced strain represents the key to the automatic separation of the intercalated layer from pristine one, which effectively mitigate the self-retarding effect. Through periodic

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material detachment, the self-refreshed crystal surface allows for the continued intercalation process. It ultimately enables the complete intercalation throughout the entire bulk crystal and subsequent exfoliation into high-purity 2D monolayers *en masse*. Furthermore, we have demonstrated that this "intercalation and separation" process is general for 2D layered crystals of high intercalation-induced strain including ln_2Se_3 , lnSe, and Bi_2Se_3 , which will be discussed later.

High-yield exfoliation of 2D semiconductor monolayers

The completely intercalated THAB/ln₂Se₃ with organic molecules in vdW gaps may be decoupled through mild sonication, allowing for the near-unity-yield exfoliation into high-purity 2D semiconductor monolayers *en masse* (monolayer purity of >95%) (Figures 2C and 2D). The as-exfoliated ln₂Se₃ monolayers are capped with ammonium molecules, exhibiting a thickness larger than the pristine single vdW layer (Figures 2D–2F).⁴⁵ The existence of organic molecules on the exfoliated ln₂Se₃ monolayers is confirmed by the infrared absorption for C-H stretching vibration (Figure S6). In particular, atomic force microscope (AFM) studies show the THAB-capped ln₂Se₃ monolayer nanosheets exhibit an average thickness of 1.9 \pm 0.1 nm (Figure 2F). It is noted that some regions that appear thicker are where two or three monolayers stack up and match a double or triple thickness. Based on large-area AFM analyses (Figures 2D and S7), nearly all the ln₂Se₃ nanosheets are monolayers. Such a narrow thickness distribution indicates a high monolayer uniformity that is previously difficult to achieve in intercalation-based exfoliation or direct LPE.^{17,18}

After thermal annealing in an inert gas environment (Ar/H₂: 95/5), the organic ammonium layers decompose and are eventually volatilized from the surface of inorganic In₂Se₃ monolayers. Increasing the annealing temperature up to 400°C gradually reduces the thickness from the initial 1.9 to 1.0 nm (Figures 2D and 2F). Notably, all samples exhibit excellent thickness uniformity with a small standard deviation of 0.1 nm (Figure 2F), which is critical for the subsequent assembly of ordered superlattice structures with high-degree and broad-area uniformity. According to X-ray photoelectron spectroscopy (XPS) analyses (Figure 2G), all the as-exfoliated and thermally annealed In_2Se_3 monolayers share the same valence state of In^{3+} and Se²⁻ and identical chemical composition (\approx 2:3 for In:Se), suggesting negligible material degradation during the removal of organic components. Similarly, UV-vis optical absorption spectra reveal no obvious change in light absorbance characteristics for the materials gone through thermal annealing processes (Figure 2H). Scanning/ transmission electron microscopy (S/TEM) studies show the similar contrast among different nanosheets (Figure S8A), further confirming the thickness uniformity of In₂Se₃ monolayers. The 6-fold symmetric electron diffraction pattern (Figure S8B) matches the hexagonal In₂Se₃ (001) crystal lattice. Energy dispersive spectroscopy (EDS) analysis also reveals an In:Se atomic ratio of approximately 2:3 (Figure S9), consistent with the XPS results. All these structural and compositional characterizations unambiguously confirm the exfoliation of high-purity In₂Se₃ monolayers in liquid phase with an unprecedented thickness uniformity.

Assembly of versatile organic/inorganic hybrid superlattices

By assembling 2D semiconductor monolayers building blocks into multi-layer stacking thin film, the high-purity ammonium-capped In_2Se_3 monolayers enable the creation of an organic/inorganic hybrid superlattice structure (Figure 3A). The inorganic In_2Se_3 monolayer crystals alternate with organic THAB molecular layers, exhibiting a superlattice periodicity of ≈ 17 Å as confirmed by powder X-ray diffraction (XRD) studies (Figure 3B). Eliminating organic molecules from the thin film transforms the THAB/In_2Se_3 hybrid superlattice into pure In_2Se_3 semiconductor lattice. In

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Figure 3. Reassembly of versatile artificial molecule/In₂Se₃ hybrid superlattices

(A) Schematic illustration of the assembly process of THAB/In_2Se_3 organic/inorganic hybrid superlattices by stacking multiple layers of THAB-capped In_2Se_3 monolayers through a simple spin-coating approach.

(B and C) XRD patterns (B) and Raman spectra (C) of THAB/In₂Se₃ hybrid superlattices annealed at a temperature of up to 400°C. All XRD patterns were calibrated by the internal Si reference peak (red dashed line). The shift of the first peak indicates the change of the interlayer distance *d* in the material, whereas the peak at ~19° indicates the existence of In₂Se₃ lattice in the annealed samples.

(D and E) Reciprocal space map by 2D GIWAXS of the THAB/In_2Se_3 superlattice (D) and that annealed at 400°C (E), respectively. The presence of diffraction peaks only in the out-of-plane or q_z direction confirms highly oriented thin-film structures in the horizontal plane.

(F and G) Cross-sectional TEM images of the assembled THAB/In₂Se₃ hybrid superlattice before (F) and after (G) 400°C thermal annealing. The interlayer distance of THAB/In₂Se₃ superlattice (d \approx 17 Å) and pure In₂Se₃ after thermal annealing (d \approx 9.7 Å) match the XRD and 2D GIWAXS data. Insets are proposed crystal structures from experimental data. Scale bars are 2 nm. (H) A summary of selected organic and inorganic ligands used for constructing artificial superlattice.

(I and J) XRD patterns of assembled molecule/ In_2Se_3 superlattices incorporating various organic or inorganic ions (I) and PVP polymer molecules (J). The diffraction peaks in (I), from left to right, correspond to the interlayer spacing of 18, 17, 15, 14, 13, and 12 Å, respectively.

particular, peak shift and intensity weakening of the superlattice diffraction peak (d \approx 17 Å, 20 \approx 5.1°) was observed when the hybrid superlattice material is thermally annealed, indicating the gradual removal of organic components and the shrink of interlayer distance. Meanwhile, both In₂Se₃ (002) (d \approx 9.7 Å, 20 \approx 9.0°) and (004) (d \approx 4.8 Å, 20 \approx 18.5°) peaks appear and grow more prominent at higher annealing temperatures. The annealing at 400°C completely volatilized the molecular layers and converted the THAB/In₂Se₃ hybrid superlattice into the pure In₂Se₃ lattice with a retained [001] orientation. Therefore, removing organic components from hybrid superlattices does not cause significant structural damages to the In₂Se₃ monolayer crystals, and the ordered stacking structure is well preserved. The collapse of hybrid superlattice and concurrent formation of pure In₂Se₃ crystal lattice was further confirmed by the Raman spectra (Figure 3C). The A₁(LO +TO), A₁(TO), and A₁(LO) phonon modes of In₂Se₃ are not fully visible in the as-deposited thin

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film. However, all three peaks grow stronger and can be identified in the thin film after annealing at 400°C, confirming the formation of crystalline multi-layer In_2Se_3 crystal lattice.⁴⁶

It should also be noted that no diffraction peaks for intrinsic In₂Se₃ (00*)* series (e.g., 002 at d \approx 9.7 Å, 20 \approx 9.0°, and 004 at d \approx 4.8 Å, 20 \approx 18.5°) were observed in the XRD pattern of as-assembled THAB/In₂Se₃ superlattice structure before thermal annealing. Instead, only the THAB/In₂Se₃ superlattice periodicity (d \approx 17 Å and high order diffraction peaks) exists that combines the thickness of both organic THAB molecular layer and inorganic In₂Se₃ monolayer. These results unambiguously demonstrated the monolayer characteristics of In₂Se₃ nanosheets because the intrinsic (00*)* series diffraction peaks are expected in bi-layer or thicker material but not in the monolayer structure that lacks in layer repeating along the [001] direction. Together, the completely vanished (00*)* series XRD peaks of intrinsic 2D layered crystals are strong evidence of high-purity monolayer materials, which was previously difficult in conventional intercalation-based exfoliation or direct LPE approaches.

The 2D grazing incidence wide-angle X-ray scattering (GIWAXS) studies were conducted to further probe the overall uniformity and orientation of superlattice structures (Figures 3D and 3E). The 2D diffraction data show scattering peaks only in the out-of-plane or q_z direction, which confirms the oriented alignment of all nanosheets in the plane of the film and excludes the possibility of random out-of-plane orientation. Moreover, in the q_{xy} direction, the 2D layers in the superlattice structure are not registered to each other. It suggests negligible structural or orientational disorders in the superlattice, robustly demonstrating the ordered superlattice consisting of alternating In₂Se₃ monolayer and organic layers. The solutionbased assembly of superlattice can be readily scaled up by simply increasing the number of spin-coating cycles, in stark contrast to the conventional vapor-phase method that requires repeated and arduous layer-by-layer growth to achieve multiple superlattice periods.^{8,9} The periodicity values suggested by GIWAXS and XRD are slightly smaller than the monolayer thickness measured by AFM (Figure S10). This may originate from the thickness overestimation in AFM owing to the impurity at the material/substrate interface and the absence of compression force from neighboring nanosheets as widely observed in thin 2D crystals.^{4,47} TEM analyses reveal the significantly expanded interlayer distance of the as-assembled THAB/ In_2Se_3 superlattice (d \approx 17 Å, Figure 3F) comparing with the intrinsic In_2Se_3 after 400°C annealing (d \approx 9.7 Å, Figure 3G), matching XRD (Figure 3B) and GIWAXS (Figures 3D and 3E) analyses. The reassembled THAB/In₂Se₃ superlattice, despite the distinct formation pathway, shares a similar structure with the previous ammonium-intercalated MoS₂ and black phosphorus.¹² Notably, both XRD and GIWAXS collect average signals from large-area thin-film samples (typical area >1 mm²). Therefore, these data suggest high material uniformity of monolayers and superlattices at the macroscopic scale, which is essential for the scalable production toward practical technologies.

We can further modulate the chemical composition and geometric configuration of organic molecules, thus generating a new family of hybrid superlattices with a tunable structural periodicity (Figure 3H). In particular, by replacing THAB (4 × C₇) with smaller molecules such as TBAB (4 × C₄) and cetyltrimethylammonium bromide (CTAB, 3 × C₁ + C₁₆) or larger molecules such as tetradecylammonium bromide (TDAB, 4 × C₁₀), the In₂Se₃ crystal can be electrochemically intercalated in a similar way and further exfoliated into monolayers with surface functionalized by diverse

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molecules (Figure S6). To this end, the periodicity of the reassembled ammonium/ In₂Se₃ superlattice structure can be adjusted from ≈ 17 Å (THAB) to ≈ 18 Å (TDAB), ≈ 15 Å (TBAB), and ≈ 14 Å (CTAB) (Figures 3I and S11A). The variation in the periodicity is attributed to the geometric configuration of intercalated organic molecules. Furthermore, after the assembly of the THAB/In₂Se₃ hybrid superlattice, the organic ammonium molecules may be further replaced with some inorganic species such as NaCl and NH₄SCN through a post-assembly ligand exchange process. In analog to the well-studied surface chemistry in quantum dots, exchanging long-chain ligands with compact inorganic species shrinks the distance between adjacent crystal layers and reduces the superlattice periodicity to ≈ 13 Å with NaCl and ≈ 12 Å with NH₄SCN, respectively (Figure 3I).^{48,49} In addition, we have successfully used many alkali metal halides (KCI, NaI, etc.), ammonium salts (NH₄F, NH₄NO₃, etc.), and even organic molecules (ethanedithiol, etc.) to replace the organic components in the hybrid superlattices.

As previously shown in the colloidal quantum dots based thin films,⁵⁰ the compact inorganic ligands in the superlattice material require lower annealing temperatures (i.e., lower input energy) to remove interlayer species and transform into pure In_2Se_3 semiconductor crystal (Figure S12). This is favorable for the low-temperature processing of thin-film materials for diverse applications to manage the thermal budget and reduce the manufacturing cost. In addition, capping In_2Se_3 monolayers with an even thicker organic layer such as polymer (polyvinylpyrrolidone [PVP]) can further expand the interlayer distance to ≈ 33 Å (Figures 3J and S11B). Besides these organic or inorganic ligands shown here, many other functional molecules or ions may be utilized for constructing a wide range of exotic superlattice structures with atomically modulated chemical compositions and widely tunable structural configurations for flexible manipulation of the physical (electronic, optical, magnetic, etc.) and chemical (reactivity, thermal stability, etc.) properties.

Exfoliation of diverse 2D layered crystals

We have further explored the feasibility to use the "intercalation and separation" process for producing 2D monolayers of other layered crystals. It was discovered that not all layered materials may be fully intercalated and exfoliated into pure monolayers like In₂Se₃. In particular, ammonium-intercalated MoS₂, MoSe₂, and WSe₂ were exfoliated into mostly multi-layer nanosheets (e.g., 3–15 layers), with XRD patterns showing the intrinsic (00*I*) series peaks (Figures 4A–4C). On the other hand, some other crystals may be exfoliated into high-purity monolayers including InSe (>95%) and Bi₂Se₃ (>70%). In analog to In₂Se₃, these crystals also followed the gradual "intercalation and separation" process. Furthermore, THAB/InSe (Figure 4D) or PVP/Bi₂Se₃ (Figure 4E) hybrid superlattices can be reassembled from the exfoliated high-purity monolayers with organic ligands on surface. Other layered crystals including NbSe₂ and PtS₂ also show a reasonable exfoliation selectivity toward monolayers (≈ 50%).

For layered crystals that can be exfoliated into high-purity monolayers through the continued "intercalation and separation" process, it was noticed that they generally exhibit low Young's modulus of in-plane crystal lattice besides the high intercalation-induced strain (i.e., In₂Se₃, InSe, and Bi₂Se₃). According to the calculated elastic data (Figure 4F),⁵¹ In₂Se₃, InSe, and Bi₂Se₃ all exhibit much lower in-plane Young's modulus along [100] direction (E₁₀₀ < 80 GPa) than other typical 2D crystals such as MoS₂, MoSe₂, and WSe₂ (E₁₀₀ ≈ 200 GPa). Because 2D crystals with lower inplane Young's modulus usually possess smaller lattice breaking strength as well,⁵² it may favor the separation of intercalated materials. From the perspective of lattice



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Figure 4. Exfoliation of diverse 2D crystals in different thickness

(A–E), XRD patterns of the exfoliated MoS₂ (A), MoSe₂ (B), and WSe₂ (C), InSe (D), and Bi₂Se₃ (E), respectively. Red vertical lines refer to the intrinsic XRD peaks of each crystal. MoS₂, MoSe₂, and WSe₂ are exfoliated into mostly multi-layer nanosheets exhibiting intrinsic (00*I*) series diffraction peaks. InSe monolayers capped with ammonium molecules assemble the InSe/THAB superlattice. Bi₂Se₃ monolayers capped with PVP polymer produce Bi₂Se₃/PVP superlattice. Insets are the corresponding crystal structures.

(F) The plot of calculated Young's modulus in [100] and [001] direction of various crystals. The three materials marked as star can be exfoliated into high-purity monolayers, whereas others have a lower monolayer yield. The error bars indicate the range of calculated values for each crystal.

breaking during the alkylammonium cation intercalation, In_2Se_3 , InSe, and Bi_2Se_3 are more likely to undergo an "intercalation and separation" process than other 2D crystals (e.g., MoS_2 , $MoSe_2$, and WSe_2). At this stage, the fundamental mechanism that governs this intercalation and exfoliation process is not yet fully clear. We hope the values of intercalation-induced strain and Young's modulus may provide some hints for the following investigations of this unique intercalation chemistry and its applicability to other 2D materials.

Electronic and thermal characteristics of superlattices

Within the superlattice structure, the insulating organic molecular layers between inorganic 2D semiconductor layers naturally serve as a transport barrier for both electrons and phonons. To this end, we have first investigated the electron transport behavior along the vertical direction of the superlattices (Figures 5A and 5B). At low bias, the assembled THAB/In₂Se₃ superlattice is rather insulating owing to the relatively thick organic ammonium molecular layer (superlattice d \approx 1.7 nm, gap distance ≈ 0.7 nm) between the 2D semiconductor sheets (Figure 5C). The current rises exponentially after surpassing a certain threshold voltage, suggesting typical tunneling characteristics.⁵³ Increasing the thickness of the molecular layer by adding PVP results in a wider tunneling barrier (superlattice d \approx 3.3 nm, gap distance \approx 2.3 nm), which thus requires a higher threshold voltage to tunnel through the barrier and delivers a lower current level. On the contrary, replacing THAB molecules with compact inorganic NH₄SCN (superlattice d \approx 1.2 nm, gap distance \approx 0.2 nm) substantially shifts the turn-on threshold voltage to a smaller value by reducing the tunneling barrier width and height. For all three superlattice materials, the turn-on threshold voltage is proportional to the thickness of the thin film (Figure 5D), which

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Figure 5. Tailored electronic and thermal properties of the superlattices

(A) Schematic illustration of the electronic measurement of superlattices along the vertical direction.

(B) Optical (top) and AFM image (bottom) of the vertical device with thin-film superlattice on Au electrode. Scale bars are 10 μ m (top) and 0.5 μ m (bottom).

(C) Measured I-V profile for three types of superlattice materials in similar thickness (\approx 90 nm). (D) The turn-on threshold voltage (defined as the voltage required to reach 0.5 nA) for all three superlattices at different thickness.

(E) Plot of ln (I/V^2) versus 1/V for three superlattice materials. The dashed lines indicate the transition point of each curve.

(F) The thermal conductivity of single-crystal In₂Se₃, annealed In₂Se₃ from superlattice, NH₄SCN/ In₂Se₃ superlattice, THAB/In2Se₃ superlattice, and PVP/In₂Se₃ superlattice. The error bars indicate the standard deviation of the measured thermal conductivity values. Inset is the schematic illustration of TDTR thermal conductivity measurement.

resembles the linear relationship between the breakdown voltage and thickness of dielectric materials. $^{\rm 54}$

Predicted by the tunneling model through a rectangular barrier, a plot of ln (I/V²) against 1/V exhibits a logarithmic growth in the low-bias regime (high 1/V regime). Tunneling in the high-bias regime (low 1/V regime) is considered as crossing a triangular barrier, defined as Fowler-Nordheim tunneling, which suggests a linear decay of $\ln (I/V^2)$ against 1/V. Therefore, when the applied bias approaches the barrier height (from high to low 1/V regime), a transition from logarithmic growth of ln (I/V^2) against 1/V to linear decay will be observed, corresponding to the transformation of the trapezoidal barrier to triangular shape.⁵⁵ The transition voltage is the highest for PVP/In₂Se₃ superlattice and the lowest for NH₄SCN/In₂Se₃ superlattice (Figure 5E), suggesting the barrier height of bulky-size PVP is qualitatively higher than that of the small NH₄SCN species. However, the measured I-V profile may combine the tunneling current through the molecular layer and the semiconducting 2D inorganic nanosheets.⁵⁶ As a result, the exact measure of the barrier height may be challenging to obtain by simply fitting the I-V curve and would require further investigations. Besides, although the molecule/In₂Se₃ superlattice itself is rather insulating, the recovered In₂Se₃ thin films after thermal annealing and removal of interlayer organic components exhibit typical semiconductor behaviors. The fabricated In_2Se_3 thin-film transistors deliver an on/off ratio of more than 10^5 and electron mobility of 0.2 cm²·V⁻¹·s⁻¹, slightly lower than values from In_2Se_3 nanosheets synthesized using CVD methods (Figure S13).^{45,57} Prominent photocurrent generation was also observed upon the light irradiation (Figure S14). This may offer a viable route to

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solution-processable 2D semiconductor thin films toward diverse large-area electronic and optoelectronic applications.

In addition, the phonon transport may be effectively modulated at the interface between material layers with distinct chemical compositions and structural configurations. Those superlattice structures consisting of periodically alternating layers of distinct materials have been demonstrated to dramatically lower down the thermal conductivity through the creation of a large quantity of such heterointerface.^{11,58,59} Indeed, a low out-of-plane thermal conductivity of $\approx 0.07-0.08 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ was obtained for the three superlattice structures (Figure 5F), representing a significant reduction from the value of single-crystal ln₂Se₃ (0.53 ± 0.06 W \cdot \text{m}^{-1} \cdot \text{K}^{-1}). In addition, the ln₂Se₃ thin film obtained by thermally annealing the hybrid THAB/In₂Se₃ superlattice also exhibits a greatly reduced thermal conductivity (0.12 ± 0.01 W \cdot \text{m}^{-1} \cdot \text{K}^{-1}), which may be ascribed to the fragmented crystal domains and rotational disorders between neighboring ln₂Se₃ layers. Therefore, the thermal transport characteristics of hybrid superlattice materials may be tailored through the chemical modulation of diverse interlayer materials for creating an adjustable heterointerface.

Conclusions

In summary, we have reported a unique intercalation and exfoliation approach for scalable preparation of 2D semiconductor monolayers in the liquid phase with exceptionally high monolayer purity (>95% for In₂Se₃ and InSe). Through the "intercalation and separation" chemistry, the crystal surface is constantly refreshed, which mitigates the self-retarding effect and ensures the complete intercalation throughout the entire bulk crystal for the subsequent exfoliation of pure 2D semiconductor monolayers en masse in near-unity yield. This approach is general for layered crystals with high intercalation-induced strain including In₂Se₃, InSe, and Bi₂Se₃. The robust and scalable preparation of solution-processable 2D semiconductor monolayers with highly uniform thickness enables the assembly of artificial organic/2D and inorganic/2D hybrid superlattices with alternating organic molecules or inorganic ions and 2D monolayers, creating a series of versatile artificial superlattices with widely tunable chemical compositions and structural periodicities. The chemical manipulation of interlayer molecules readily modulates the physical properties of the superlattices including electron and phonon transport characteristics. Together, the scalable chemical production of high-purity 2D semiconductor monolayers in the solution phase defines a versatile material platform for solution-processable 2D-semiconductor-based electronics and optoelectronics.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Professor Xiangfeng Duan (xduan@chem. ucla.edu).

Materials availability

All materials generated in this study are available from the lead contact.

Data and code availability

All data supporting this study are available in the manuscript and supplemental information.

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Electrochemical intercalation of 2D crystals and LPE

To conduct an intercalation reaction, a three-electrode electrochemical cell was used with a thin piece of 2D crystal (e.g., In_2Se_3 and MoS_2) as the cathode, graphite rod as the anode, and Ag/AgCl as the reference electrode. Quaternary alkylammonium molecules (e.g., CTAB, TBAB, THAB, and TDAB) were dissolved in acetonitrile as the electrolyte solution (10 mg/mL). The intercalation duration of In_2Se_3 is approximately 1–2 h depending on the size of the initial crystal. Two half-cell reactions are as follows:

$$xBr^{-} - xe^{-} \rightarrow x/2Br_{2}$$
 anode (Equation 1)

 $xTHA^+ + In_2Se_3 + xe^- \rightarrow (THA^+)_x(In_2Se_3)^{x-}$ cathode (Equation 2)

Upon completion, the intercalated In_2Se_3 materials were collected and transferred into DMF liquid for exfoliation with mild sonication of 3–30 min. For PVP-functionalized 2D nanosheets, the intercalated material was exfoliated in 0.2 M PVP/DMF solution for 30 min. The lateral dimension of In_2Se_3 monolayers may be adjusted by the sonication time (e.g., shorter time produces nanosheets of larger size). Exfoliated materials were washed by repeated centrifugation to remove any organic residues.

Superlattice assembly and ligand exchange

The In_2Se_3 monolayers were dispersed in DMF as ink materials for assembling thinfilm superlattices by spin coating. The ink concentration was monitored by UV-vis optical absorption. The used SiO₂/Si substrate was pre-cleaned with acetone and isopropanol wash before oxygen plasma or piranha solution etching. The coating speed and duration were 2,000 rpm and 60 s. The ink concentration and spincoating speed/cycle numbers together determine the thickness of the thin films. For NH₄SCN in DMF solution, the concentration is in the range of 0.1–1 M. For alkali metal halide (NaCl, KBr, etc.) in methanol solution, the concentration is 0.01 M. The ligand exchange processes usually last for 3 h. The ligand-exchanged thin films were rinsed and dried for the following characterizations.

Device fabrications

The vertical tunneling devices were fabricated on standard SiO₂/Si substrate (300 nm oxide layer) by E-beam lithography/e-beam evaporation of Ti/Au (5/ 30 nm) bottom electrode, spin-coating superlattice thin films, and E-beam lithography/E-beam evaporation of Au (40 nm) top electrode. Thin-film transistors were fabricated on the substrate (such as 70 nm Si₃N₄ on conductive Si substrate) following the standard photolithography, wet etching, and E-beam evaporation of Ti/Au or Cr/Au (30/50 nm) source/drain electrodes. The oxygen plasma treatment of the substrate was performed before spin coating.

GIWAXS

Films for 2D GIWAXS measurements were prepared on 1.5 × 1.5 cm substrates. Measurements were performed at the Stanford Synchrotron Radiation Lightsource on beamline 11–3 using a wavelength of 0.9742 Å with an incidence angle of 2°. Samples were placed in a helium chamber to increase signal-to-noise with a sample to detector distance of 250 mm. The IgorPro macro, Nika, was used to calibrate the GIWAXS data.

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DFT calculations

DFT calculations implanted in CASTEP packages were performed. The generalized gradient approximation and Perdew-Burke-Ernzerhof were chosen to describe the exchange-correlation energy. The cutoff energy of the plane-wave basis set was set to be 380 eV with ultrasoft pseudopotentials. The coarse quality has been applied in the k-points for the energy minimization based on the Broyden-Fletcher-Goldfarb-Shanno algorithm. The convergence thresholds are set as 5 × 10^{-5} eV per atom for the total energy and 0.005 Å per atom for the inter-ionic displacement.

Characterizations

Structural and compositional characterizations were performed using scanning electron microscopy (SEM, JEOL JSM-6700F FE-SEM) with EDS, S/TEM, and electron diffraction (TEM, FEI T12 Quick CryoEM and CryoET; acceleration voltage, 120 KV. FEI Titan TEM; acceleration voltage, 300 KV. JEOL JEM-ARM300F Grand ARM STEM; acceleration voltage, 300 KV), XRD (PANalytical X'Pert Pro X-ray powder diffractometer), AFM (Bruker Dimension Icon Scanning Probe Microscope), UV-vis-NIR spectroscopy (Shimadzu 3100 PC), FT-IR spectroscopy (Jasco 420), Raman spectroscopy (Horiba, 488 nm laser), and XPS (Kratos AXIS Ultra DLD). The transport characteristic measurements on transistors were conducted at room temperature under ambient conditions (in vacuum and dark) with a probe station and a computer-controlled analog-to-digital converter. The photoresponse of thin-film devices was measured using a similar electrical setup coupled with 473 nm laser or regular yellow light.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.chempr. 2021.03.022.

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AUTHOR CONTRIBUTIONS

X.D. conceived the research. X.D. and Z.L. designed the experiments. Z.L. developed the intercalation/exfoliation method, characterized the materials, fabricated electronic devices, and performed device measurements and data analyses. Z.W., F.S., C.J., Q.Q., L.P., J.Z., Z.S., I.S., and Z.A. contributed to material preparation,



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device fabrication, and data analyses. B.H. performed the DFT calculations. Z.L., X.Y., C.W., and X.P. collected SEM, TEM, and STEM images. Y.W., Z.L., and S.T. collected and analyzed the 2D GIWAXS data. J.S.K., Z.L., and Y. Hu performed the TDTR thermal conductivity measurement and data analysis. X.D. and Y. Huang supervised the research. Z.L. and X.D. wrote the manuscript. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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