

Supplementary Information for

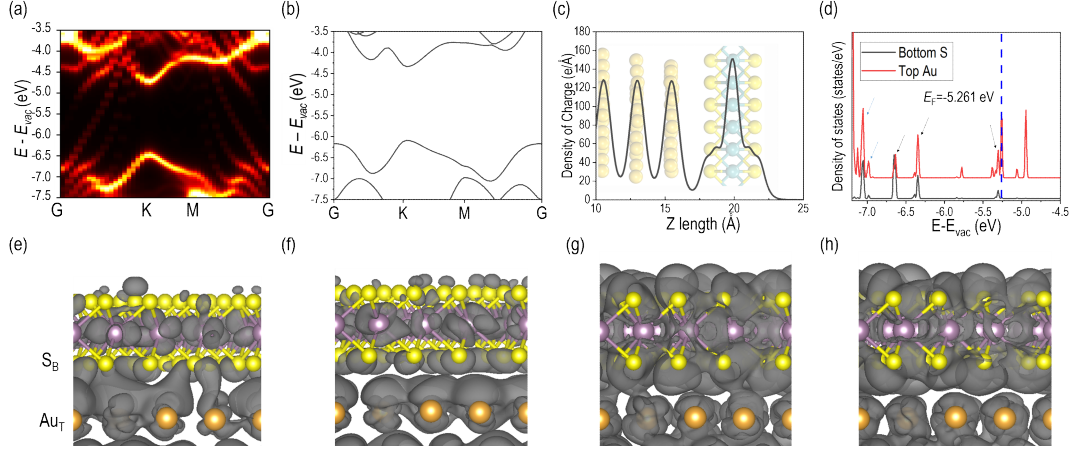
Universal mechanical exfoliation of large-area 2D crystals

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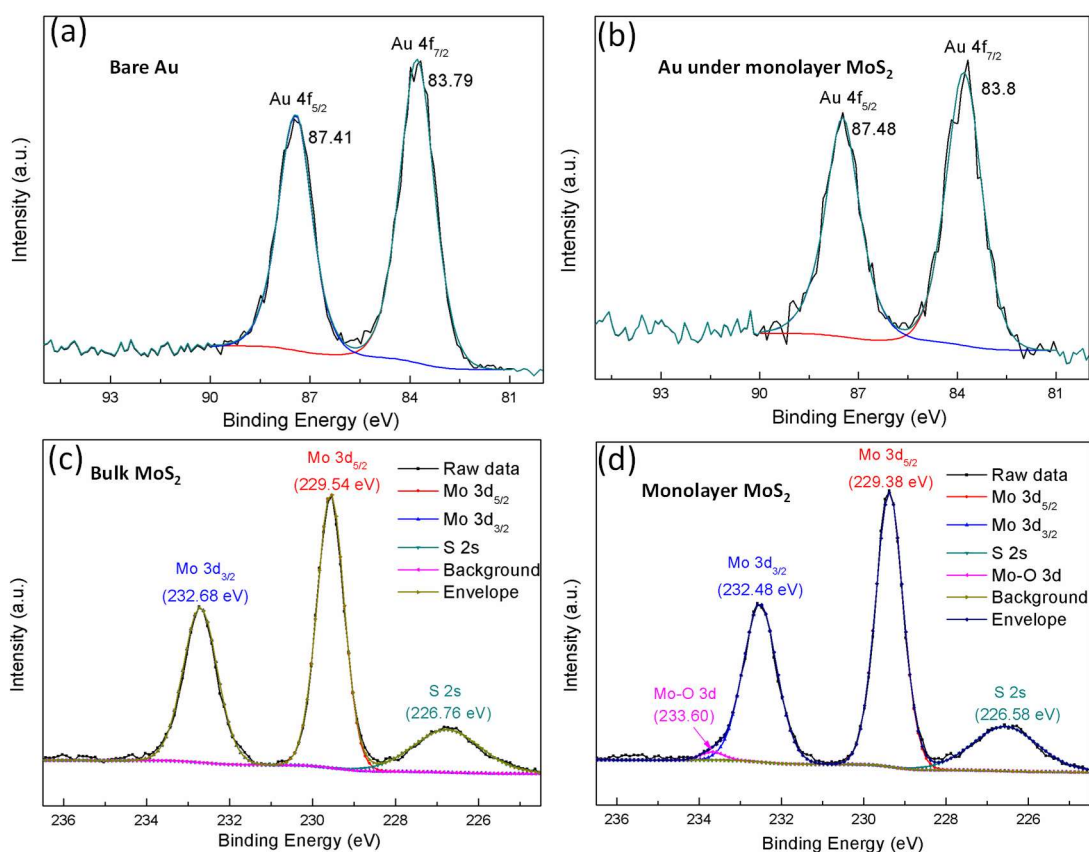
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Supplementary Figures

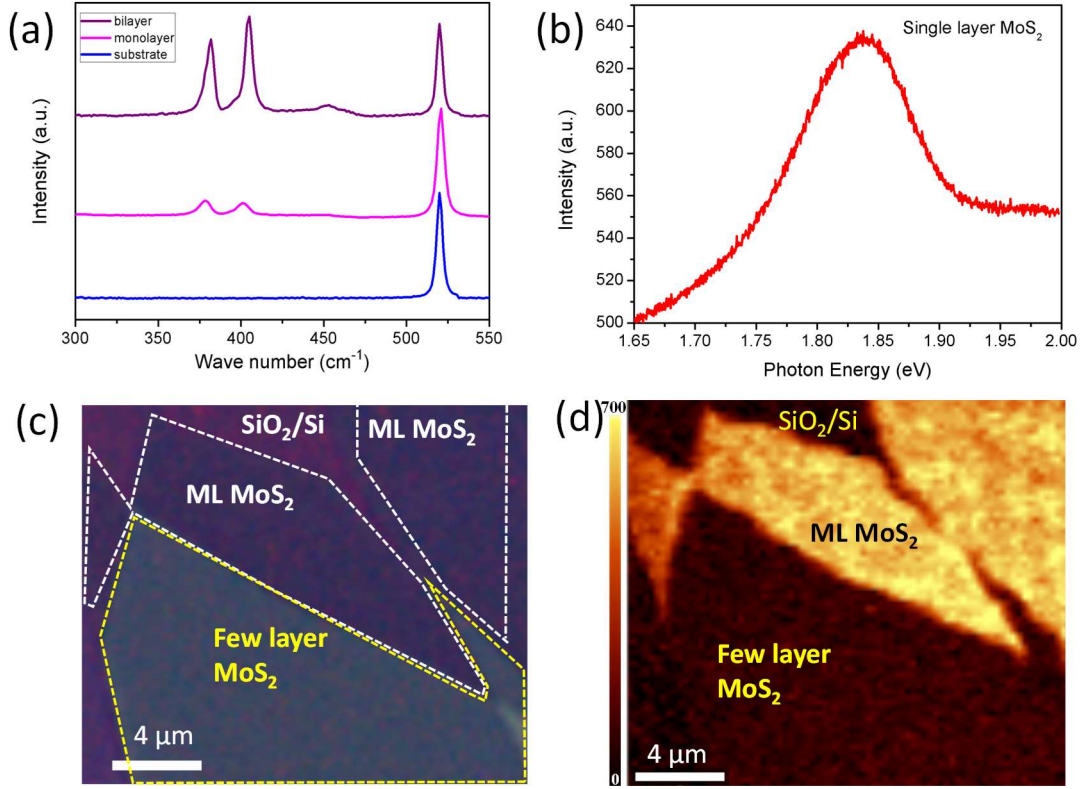


Supplementary Figure 1. Electronic structures of an Au (111) supported monolayer MoS₂ (1L-MoS₂), a typical 2D material, interface. Here, MoS₂ was chosen in consideration of that it has a moderate $R_{LA/IL}$ of 1.51 and group 16 (VIA) elements are the major portion of non-metal elements in all considered 2D layers. The vacuum energy was set as energy zero in both bandstructures and DOS plots. **(a)** Unfolded bandstructure of the interface, which was calculated using the KPROJ program based on the $\mathbf{k}$ -projection method^{1, 2}. **(b)** Bandstructure of freestanding 1L-MoS₂. The bandgap of 1.76 eV and the shape of valence (VB) and conduction (CB) bands remain nearly unchanged after the free-standing layer in contact with the Au substrate while the positions of VB and CB shift downward by ~ 0.5 eV. This shift is a result of vertical electric dipole moments (~ 0.75 e $\cdot\text{\AA}$) formed at the interface upon contact, which were illustrated by the DCD in Fig. 1e and a layer-averaged line profile associated with total electronic charge density, as plotted in **(c)**. Dipole moment $\mathbf{p}$ here is defined as $\mathbf{p} = -e \sum_l Z_l \mathbf{R}_l + \int \mathbf{r} \rho(\mathbf{r}) d\mathbf{r}$, where e is the electron charge, the l summation is over Mo and S ionic sites, and $\rho(\mathbf{r})$ is the electronic charge density in the MoS₂ interlayer. Both VB and CB of the intact MoS₂ were perturbed by some Au states, as depicted in **(a)**, which indicates Au states electronically hybridize with states of MoS₂. We plotted local density of states (LDOS) of the interface in **(d)** in order to reveal the interactions between MoS₂ and Au (111). Only the Gamma point was used for clarity. Grey and red lines represent the LDOSs of an interfacial S atom (denote S_B) and an interfacial Au atom (denote Au_T). The hybrid states of S_B and Au_T were marked by black and light blue arrows. Each of those peaks contains six states while some of those states were representatively visualized in **(e)** to **(h)**. Panels **(e)** and **(f)** plot the isosurface contours of wavefunction norms for the bonding and anti-bonding states sitting at ~ -5.3 eV with an isosurface value of 1×10^{-4} e Bohr⁻³, while those for the states at ~ -7.0 eV were shown in **(g)** and **(h)** with an isosurface value of 3×10^{-5} e Bohr⁻³,

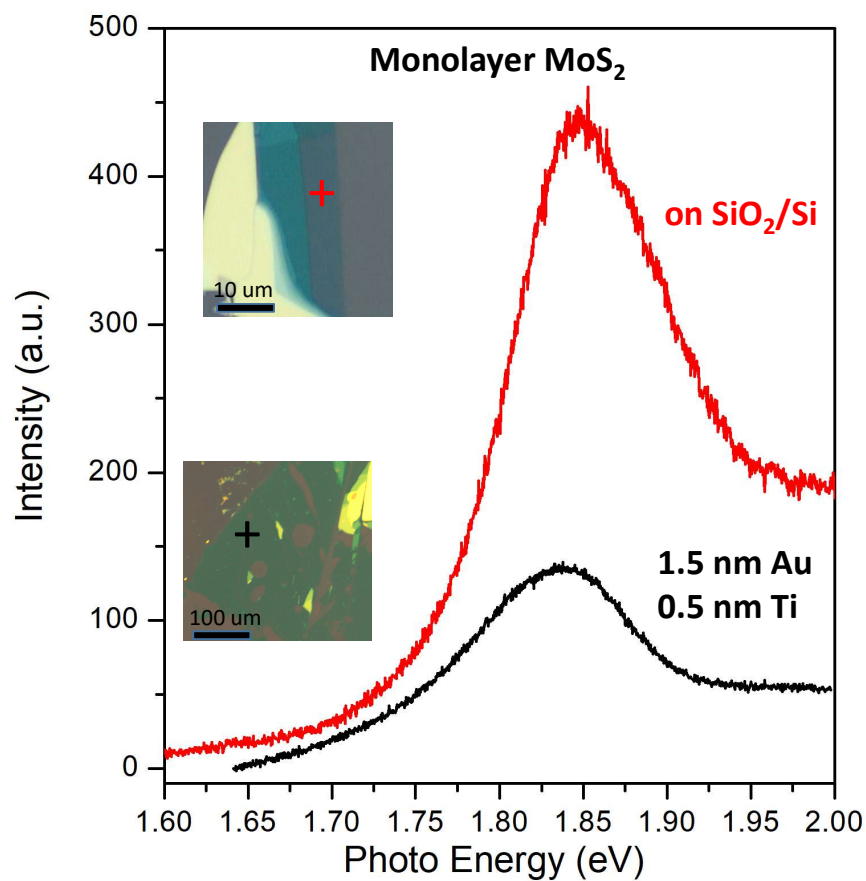
respectively. The hybridization between them is, however, not as strong as a typical covalent bond. The energy splitting of bonding-states and anti-bonding states is only few meV for those states marked by the black arrows and is up to 86 meV for those states marked by the light-blue arrows. While both the bonding and anti-bonding states are all fully occupied, together with the rather small energy splitting, we conclude the interaction between Au and MoS₂ is not covalent bonding, but an interaction type called covalent-like quasi-bonding, as we discussed in the main text and recently identified in 2D layers.



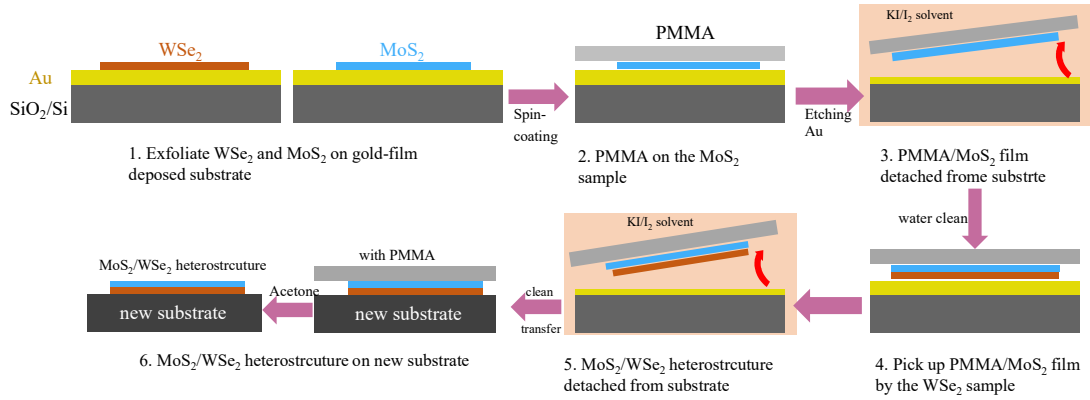
Supplementary Figure 2. XPS analysis was employed to obtain the core-level XPS spectra for the comparison of exfoliated single layer MoS₂ and bulk MoS₂ flakes. **(a, b)** XPS spectra of Au 4f from bare Au surface and the Au beneath a monolayer MoS₂ flake. They do not show noticeable difference of the binding energies but with a slightly decreased intensity for the Au spectra under MoS₂ flake due to the screening effect. **(c, d)** Mo 3d and S 2s spectra and the corresponding fitting curves of a bulk MoS₂ flake and of an exfoliated single layer MoS₂ flake. The core-level Mo 3d and S 2s spectra of the exfoliated MoS₂ show a small redshift (around 0.2 eV) when compared with the bulk MoS₂ bulk flakes, suggesting a possible charge transfer between the single layer MoS₂ flake and the underlying Au film^{3, 4}. In addition, the consistence of the shape and peak width of the Mo 3d spectra of the exfoliated single layer MoS₂ with the bulk MoS₂ flake indicates that the single layer MoS₂ is clean and retains its chemical identity after exfoliation. This XPS result demonstrates the important role of Au for the successful exfoliation of large single layer MoS₂ flake.



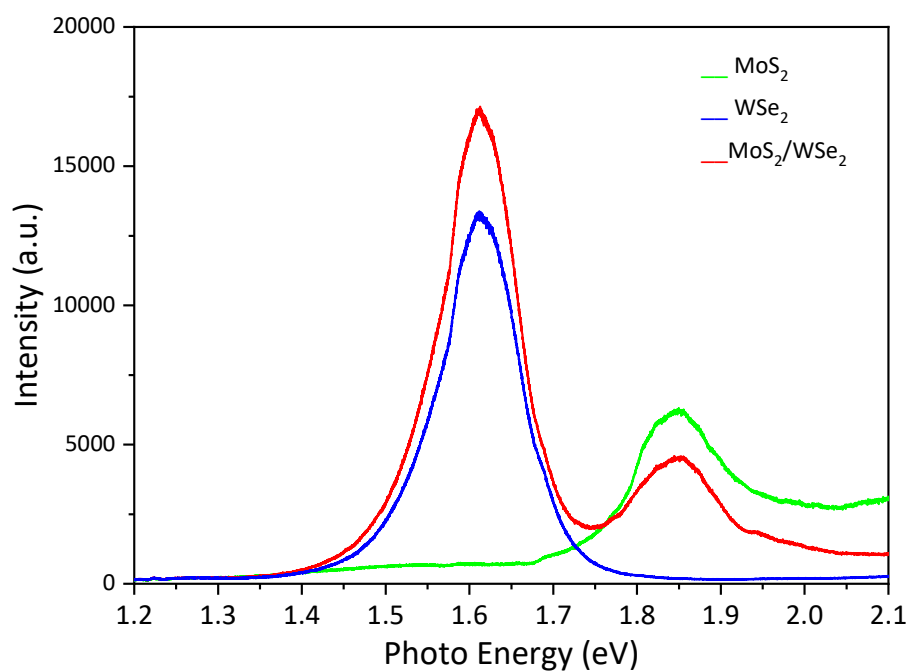
Supplementary Figure 3. Raman and PL spectra of MoS₂ exfoliated with Au/Ti adhesion layer (nominally 1.5 nm/0.5 nm). (a) Raman spectra of monolayer and bilayer MoS₂, normalized by the intensity of the Si peak at 520 cm⁻¹. **(b)** PL spectrum of monolayer MoS₂ exfoliated onto the ultrathin Au/Ti adhesion layer. **(c)** Optical image of a MoS₂ flake with coexisting monolayer and few-layer areas. **(d)** PL mapping image of the MoS₂ flake shown in **(c)**, with PL intensity in the monolayer area substantially higher than in few-layer and substrate regions. Raman peaks of E_{2g}¹ and A_{1g} are at 386 and 406 cm⁻¹, respectively. From the Raman result, we can determine the following: first, the space between the two peaks (Δ) is ~ 20 cm⁻¹, suggesting that the as-exfoliated material is monolayer; second, the Raman peaks show no split, suggesting that the crystal quality of the as-grown MoS₂ film is good. The PL peak of A exciton is at 1.83 eV. These features are in good agreement with the data seen previously for monolayer MoS₂.



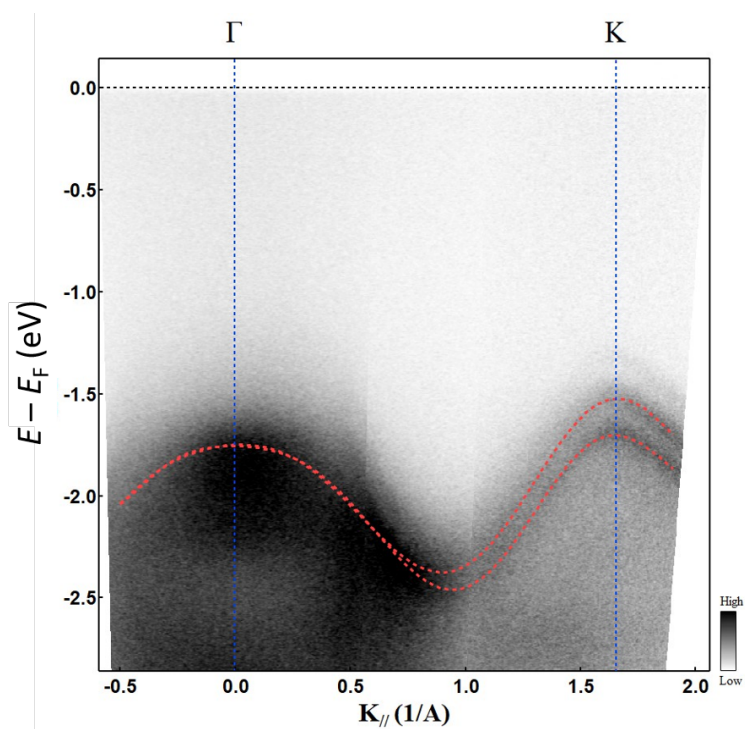
Supplementary Figure 4. Comparison of PL spectra between MoS₂ monolayers exfoliated on the SiO₂/Si substrate using the common tape method (red curve) and on the Au/Ti film using the present gold-assisted method (black curve), respectively.



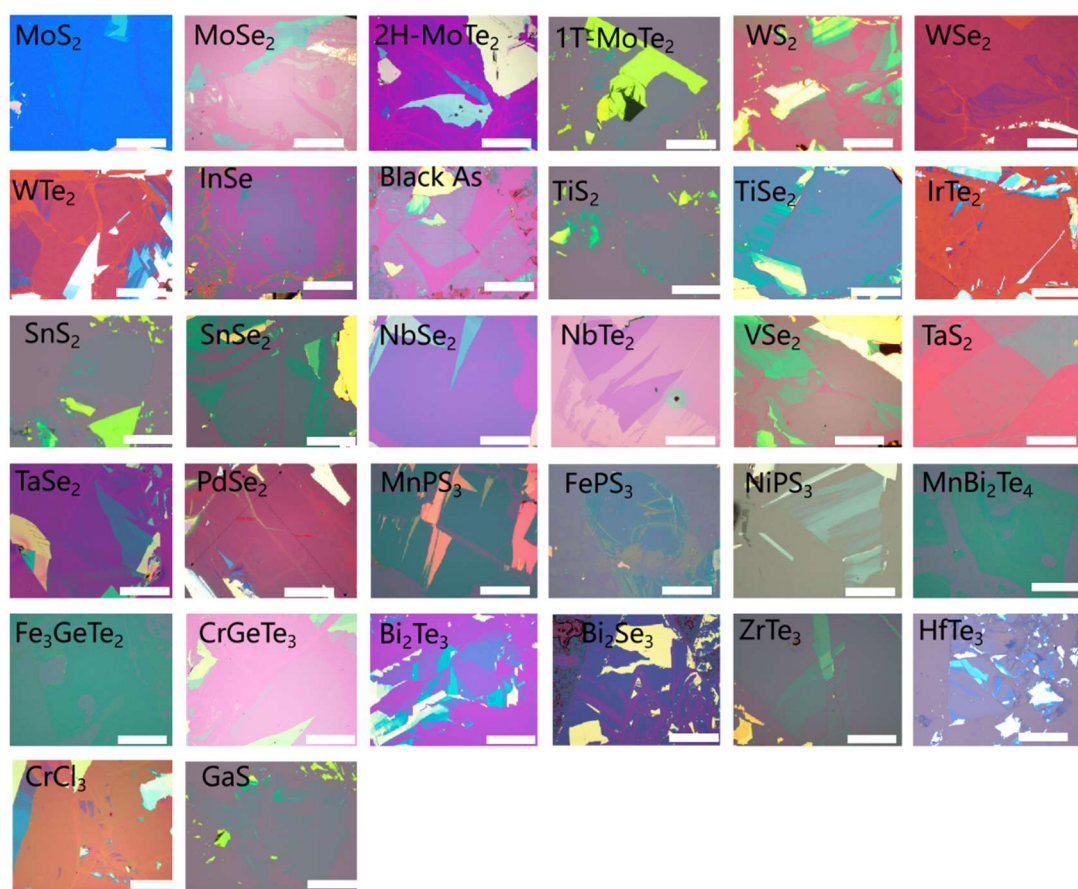
Supplementary Figure 5. Fabrication process of the MoS₂/WSe₂ heterostructure. Firstly, we exfoliated large area MoS₂ and WSe₂ monolayers on two separate Au/Ti/SiO₂/Si substrates, respectively. Then, PMMA was spin-coated onto the MoS₂ monolayer and then the sample was put into KI/I₂ solution. After roughly 10 hours of etching, the gold film was removed and the PMMA film together with the MoS₂ flake detached from the SiO₂/Si substrate. In order to clean the ion residual, the PMMA film was washed three times using DI water. The next step lies in using the WSe₂ sample to pick up the PMMA/MoS₂ film from water. Since both MoS₂ and WSe₂ flakes are several millimeters in size, no special alignment is need in this step if the twisting angle between these two layers is not specified. Additional baking at ~ 100 °C ensures the contact between these two layers. Next, we employed the same procedure, i.e. etching in KI/I₂ solution and three times washing using DI water, to remove the Au film from WSe₂. A new substrate, e.g. SiO₂/Si was used to pick up the hetero-bilayer from Di water. Finally, we removed the PMMA layer using acetone.



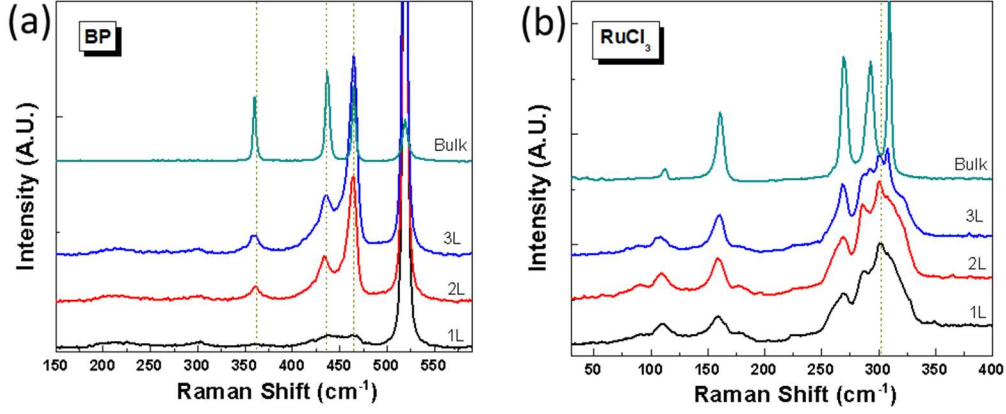
Supplementary Figure 6. PL spectra of MoS₂/WSe₂ heterostructure.



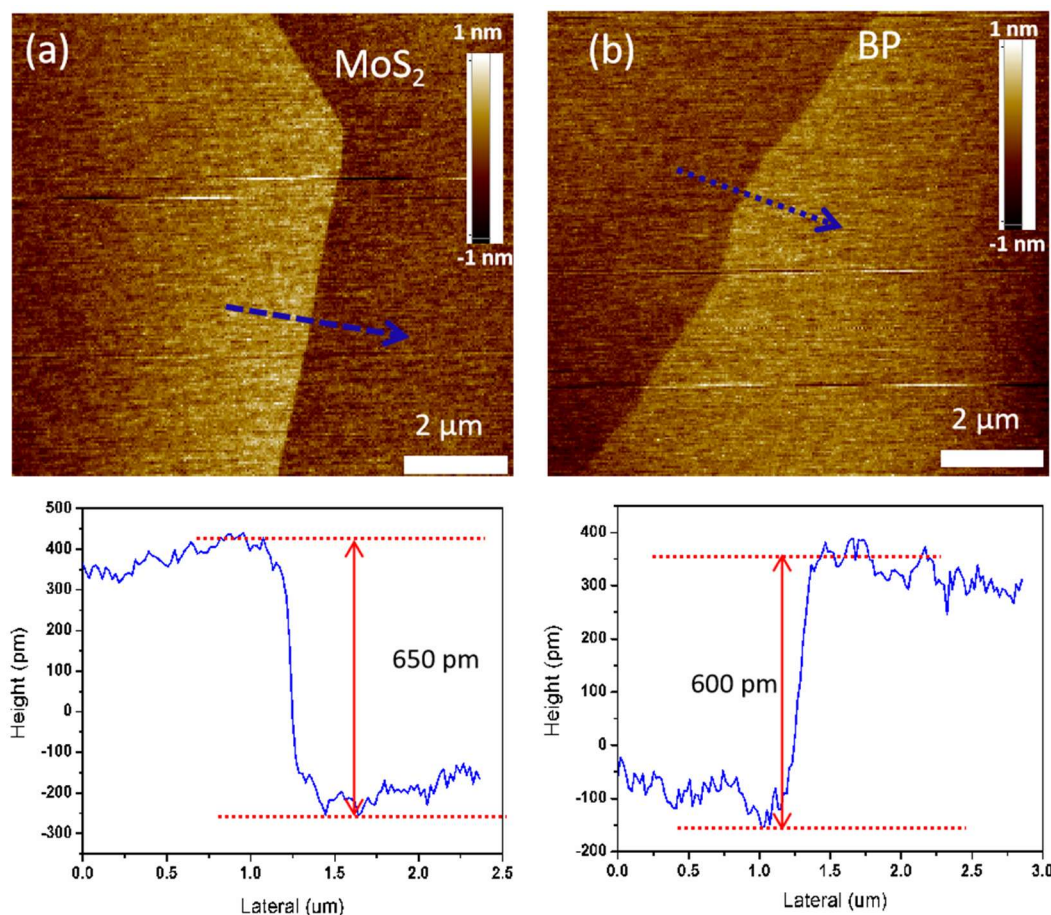
Supplementary Figure 7. Band structure of monolayer MoS₂ flake exfoliated on Au/Ti adhesion layer (5 nm/1 nm).



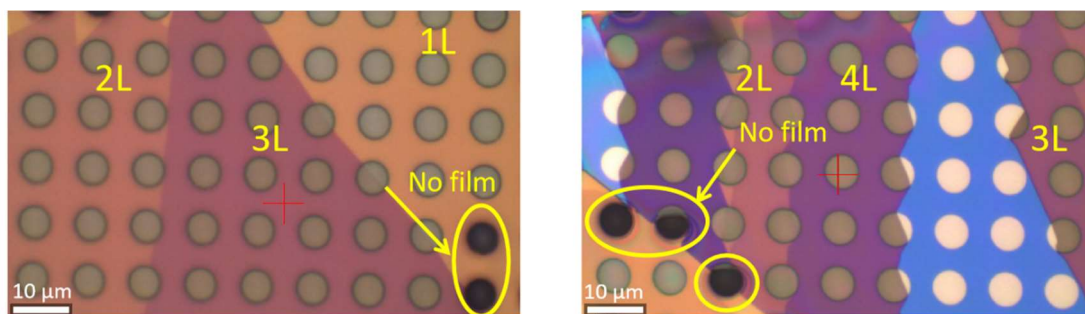
Supplementary Figure 8. Optical images of 2D materials exfoliated using Au adhesion layers. Some of materials shown are obtained here for the first time in monolayer form, for example, IrTe₂, ZrTe₃, PtSe₂. Scale bars: 500 μ m.



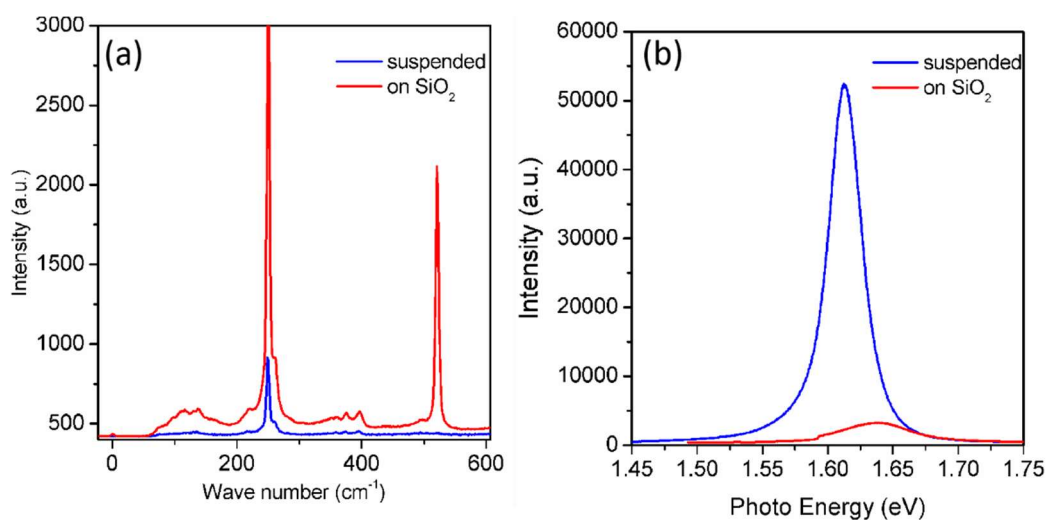
Supplementary Figure 9. Raman spectra of exfoliated black phosphorus (BP) **(a)** and RuCl₃ **(b)** crystals with different thickness, in comparison with the corresponding layered bulk crystals. In close analogy to bulk, three typical Raman peaks are resolved at 360, 436, and 465 cm⁻¹ for the monolayer and few-layer BP samples shown in panel **(a)**. It can be seen that the phonon intensity decreases with layer numbers. The evolution of Raman intensity versus the number of layers is attributed to the multilayer interference occurring for both the incident light and the emitted Raman radiation, being akin to the case of graphene⁵ and MoS₂^{6, 7}. As for monolayer and few-layer α -RuCl₃ samples, five strong and sharp phonon modes are resolved at 117, 164, 270, 296 and 312 cm⁻¹, respectively, in panel **(b)**. It should be noted that the two lowest energy phonons in α -RuCl₃ show asymmetric Fano line shape stemmed from the coupling between the discrete optical phonons and the magnetic scattering, as we have discussed before⁸. For all thicknesses, it can be seen that the energies of all phonons are independent on the number of layers, as indicated by the dashed vertical lines. This is in marked contrast to TMDC⁹ and indicates that the van der Waals interlayer interactions in BP and α -RuCl₃ are extremely weak and have tiny effects on phonon energy.



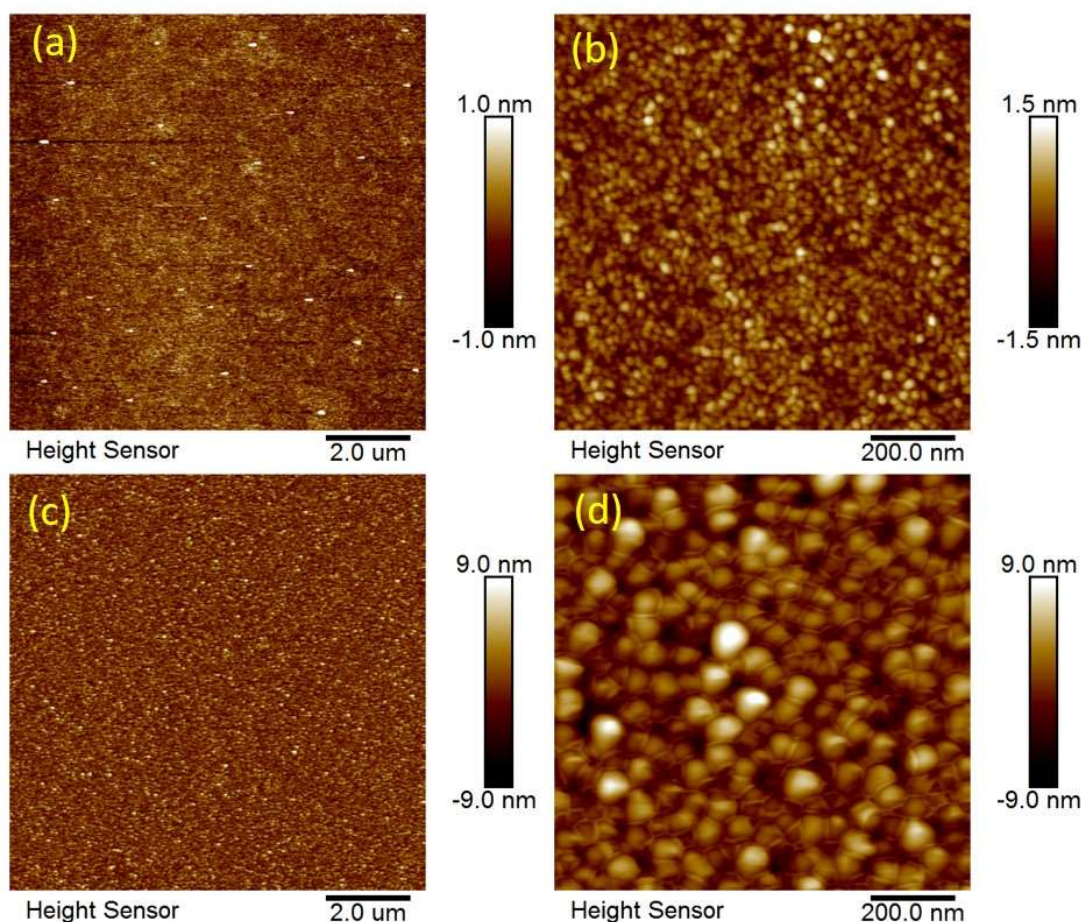
Supplementary Figure 10. AFM images of as-exfoliated 2D MoS₂ **(a)** and black phosphorus/phosphorene (BP) **(b)**. Given the the morphology of the freshly exfoliated samples at the nanometer scale, there is no evidence of structural irregularity or bubbles on the surfaces. The height profiles taken along the blue lines in AFM images are depicted in the lower parts of panels **(a)** and **(b)**. It is noted that the heights of monolayer MoS₂ and BP on the SiO₂/Si substrate are ~0.65 nm and ~0.60 nm, respectively, slightly larger than their theoretical thicknesses. Such deviation might imply that there are some absorbents at the interface between the MoS₂ or BP layer and the SiO₂/Si substrate^{6, 10}.



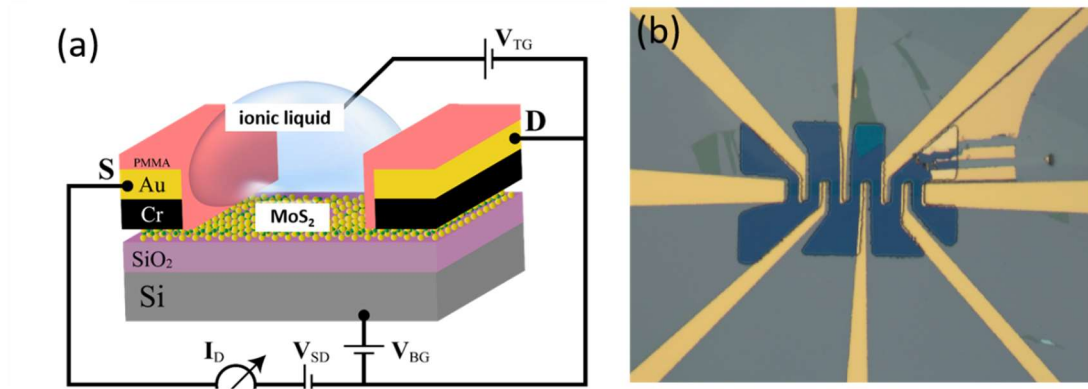
Supplementary Figure 11. Suspended WSe₂ samples with suspended coverage of 97% and 93%, respectively.



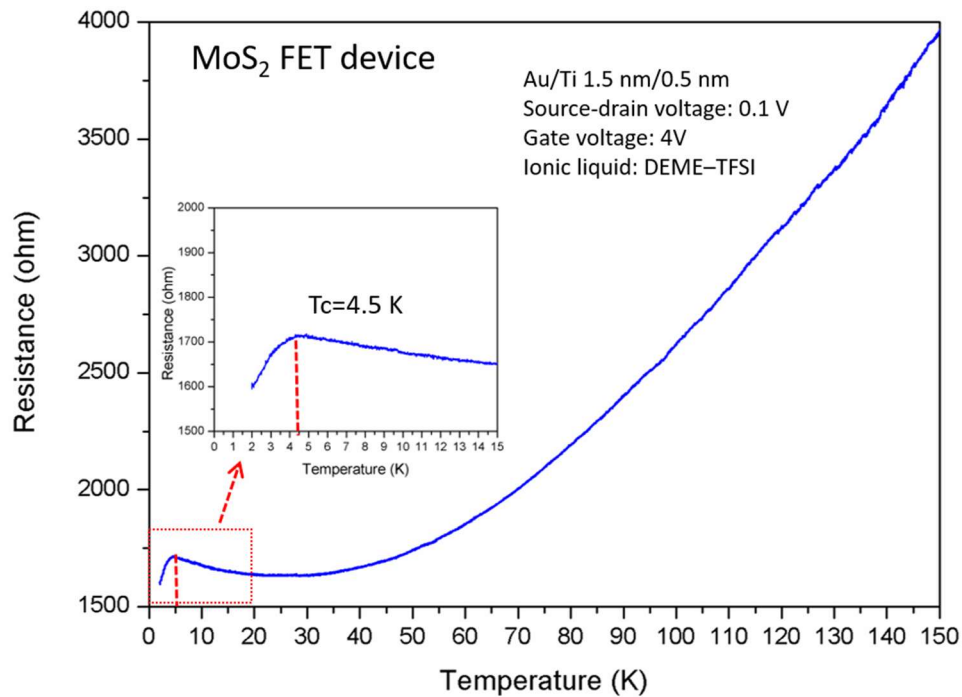
Supplementary Figure 12. Raman (a) and PL (b) spectra of suspended monolayer WSe₂ (blue) in comparison with monolayer WSe₂ exfoliated on a SiO₂/Si substrate (red), which explicitly show a roughly 10 times enhancement of PL intensity for suspended samples.



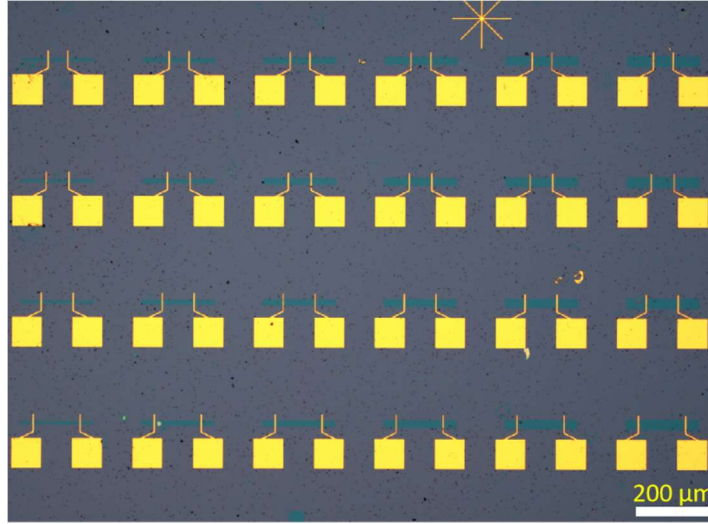
Supplementary Figure 13. AFM images of Au/Ti (1.5 nm/ 0.5 nm) film before (a and b) and after (c,d). annealing at 250 °C for 2h. (a) and (b) are large-scale and zoom-in AFM images of an as-prepared metal thin-film sample, respectively. The size of metal grains appreciably increases after annealing, as shown in panels (c) and (d). These AFM images demonstrate that the metals (Au/Ti) deposited on SiO₂/Si substrate is not a continuous film but some metal clusters with boundaries, which can become more obvious after annealing. Therefore, the substrate surface is still not conductive even an ultrathin metal layer was deposited on it.



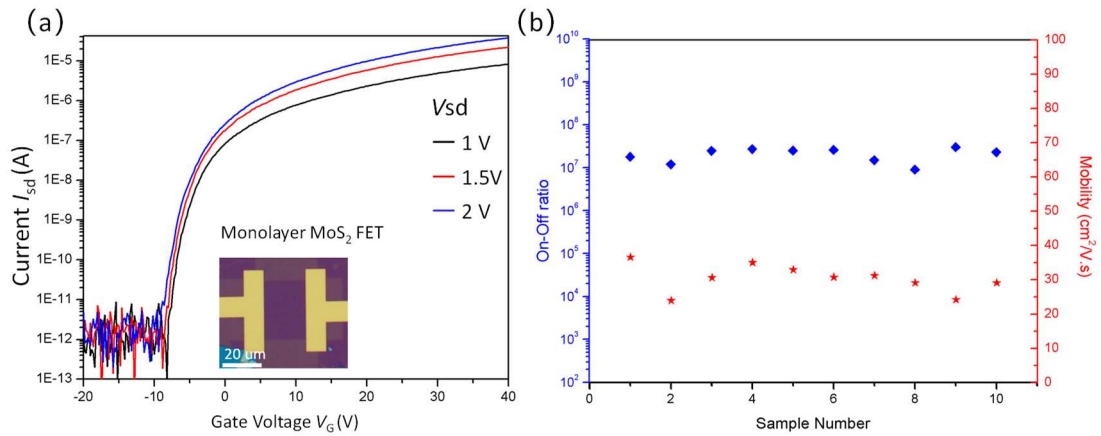
Supplementary Figure 14. (a) Monolayer field-effect transistor (FET) device structure with ionic liquid top gate. (b) Optical micrograph of an actual FET device with monolayer MoS₂ channel, and an insulating PMMA coating with window for the ionic liquid top gate.



Supplementary Figure 15. Temperature dependent I - V curve of a monolayer MoS₂ device gated by ionic liquid (DEME-TFSI) at 4 V. The measurement temperature ranges from 2 K to 150 K. The inset is a zoom-in I - V curve at temperature from 2 to 15 K, from which a superconducting transition is indicated at $T_c = 4.5$ K.



Supplementary Figure 16. Optical image of UV-patterned MoS₂ device arrays fabricated from a single large monolayer MoS₂ flake exfoliated onto an ultrathin Au/Ti adhesion layer.



Supplementary Figure 17. Electrical measurements of monolayer MoS₂ back-gated FET devices. **(a)** Relationship between source-drain current I_{sd} and back gate voltage V_g for source-drain voltage V_{sd} ranging from 1 to 2 V. **(b)** Statistics of on-off ratio (blue) and mobility (red) of ten monolayer MoS₂ back-gated FET devices. The monolayer MoS₂ flakes were transferred to Si wafer (with 300 nm SiO₂ layer) by etching gold film in KI/I₂ solvent and DI water cleaning, as demonstrated in Supplementary Fig. 5. Then, the FET devices were fabricated by patterning, metal deposition and lift-off procedures.

Supplementary Tables

Supplementary Table 1. Calculated energies of all 58 considered 2D materials

2D-Materials	Ads. Energy on Au(111) (eV per unit cell)	Interlayer Coupling Energy (eV per unit cell)	Ads. Energy on Au(111) (eV Å ⁻²)	Interlayer Coupling Energy (eV Å ⁻²)	Ads. Energy on Au(111) (eV per bottom atom)	Interlayer Coupling Energy (eV per bottom atom)	R_{LAI}	Space Group	Magnetic Structure*
h-BN	0.146	0.136	0.0268	0.0250	0.073	0.068	1.07	P -6 m 2	NM
Gr	0.147	0.118	0.0279	0.0225	0.073	0.059	1.24	P 63/m m c	NM
P(Black)	0.801	0.484	0.0556	0.0334	0.400	0.242	1.67	C m c a	NM
As(Black)	1.014	0.584	0.0597	0.0350	0.507	0.292	1.71	C m c a	NM
W ₂ N ₃	0.520	0.230	0.0716	0.0316	0.520	0.230	2.26	P 63/m m c	NM
TiS ₂	1.087	0.542	0.0547	0.0273	0.543	0.271	2.00	P -3 m l	NM
VS ₂	0.412	0.265	0.0476	0.0305	0.412	0.265	1.56	P -3 m l	FM
NbS ₂	0.605	0.264	0.0632	0.0276	0.605	0.264	2.29	R 3 m H	NM
TaS ₂ -2H	0.549	0.249	0.0575	0.0262	0.549	0.249	2.19	P 63/m m c	NM
TaS ₂ -1T	0.457	0.278	0.0469	0.0286	0.457	0.278	1.64	P -3 m l	NM
MoS ₂	0.345	0.229	0.0397	0.0263	0.345	0.229	1.51	P 63/m m c	NM
WS ₂	0.329	0.227	0.0371	0.0261	0.329	0.227	1.42	P 63/m m c	NM
ReS ₂	1.128	0.856	0.0312	0.0211	0.282	0.214	1.48	P -1	NM
CoPS ₃	4.883	1.433	0.0829	0.0211	1.221	0.358	3.35	C1 2/m l	FM
NiPS ₃	1.946	1.354	0.0336	0.0233	0.486	0.339	1.44	C1 2/m l	FM
PdS ₂	1.479	0.889	0.0494	0.0290	0.739	0.445	1.71	P b c a	NM
PtS ₂	0.457	0.292	0.0421	0.0262	0.457	0.292	1.60	P -3 m l	NM
GaS	0.388	0.218	0.0347	0.0196	0.194	0.109	1.78	P 63/m m c	NM
InS	1.093	1.025	0.0718	0.0588	0.547	0.512	1.22	P m n n	NM
GeS ₂	0.316	0.273	0.0262	0.0223	0.316	0.273	1.17	P 42/n m c Z	NM
SnS	0.90	0.617	0.0534	0.0365	0.451	0.309	1.46	P n m a	NM
SnS ₂	0.488	0.243	0.0418	0.0207	0.488	0.243	2.02	P -3 m l	NM
TiSe ₂	0.483	0.289	0.0454	0.0270	0.483	0.289	1.68	P -3 m l	NM
VSe ₂	0.476	0.261	0.0502	0.0272	0.476	0.261	1.85	P -3 m l	FM
NbSe ₂	0.607	0.304	0.0590	0.0295	0.607	0.304	2.00	P 63/m m c	NM
MoSe ₂	0.414	0.243	0.0441	0.0258	0.414	0.243	1.71	P 63/m m c	NM
WSe ₂	0.384	0.241	0.0409	0.0256	0.384	0.241	1.60	P 63/m m c	NM
ReSe ₂	1.458	0.906	0.0373	0.0232	0.364	0.227	1.61	P -1	NM
FeSe	0.565	0.381	0.0424	0.0285	0.565	0.381	1.49	C m m a	AFM
PdSe ₂	1.284	1.117	0.0388	0.0288	0.642	0.559	1.34	P b c a	NM
PtSe ₂	0.641	0.341	0.0537	0.0276	0.641	0.341	1.95	P -3 m l	NM
GaSe	0.352	0.228	0.0285	0.0185	0.176	0.114	1.54	P 63/m m c	NM
InSe	0.519	0.267	0.0369	0.0188	0.259	0.133	1.97	P 63/m m c	NM
GeSe ₂	0.411	0.335	0.0304	0.0242	0.411	0.335	1.25	P 42/n m c Z	NM
SnSe	1.033	0.658	0.0560	0.0353	0.516	0.329	1.58	P n m a	NM
SnSe ₂	0.621	0.275	0.0488	0.0214	0.621	0.275	2.24	P -3 m l	NM

Sb ₂ Se ₃	0.630	0.340	0.0448	0.0239	0.630	0.340	1.88	R -3 m H	NM
Bi ₂ Se ₃	0.618	0.336	0.0416	0.0224	0.618	0.336	1.86	R -3 m H	NM
ZrTe ₃	1.283	0.633	0.0554	0.0274	0.428	0.211	2.02	P1 21m/m l	NM
ZrTe ₅	2.378	1.088	0.0431	0.0186	1.189	0.544	2.32	C m c m	NM
HfTe ₃	1.307	0.637	0.0567	0.0279	0.436	0.212	2.03	P1 21m/m l	NM
HfTe ₅	1.538	1.078	0.0280	0.0186	0.308	0.216	1.51	C m c m	NM
VTe ₂	0.658	0.295	0.0585	0.0262	0.658	0.295	2.23	P -3 m l	FM
MoTe ₂	0.490	0.281	0.0456	0.0261	0.490	0.281	1.75	P 63/m m c	NM
WTe ₂	1.026	0.516	0.0471	0.0235	0.513	0.258	2.00	P m n 21	NM
MnBi ₂ Te ₄	0.791	0.368	0.0497	0.0229	0.791	0.368	2.17	R -3 m H	FM
FeTe	0.654	0.329	0.0461	0.0232	0.654	0.329	1.99	C m m a	AFM
IrTe ₂	0.870	0.683	0.0680	0.0503	0.870	0.683	1.35	P -3 m l	NM
PtTe ₂	0.865	0.479	0.0631	0.0334	0.865	0.479	1.89	P -3 m l	NM
Sb ₂ Te ₃	0.773	0.404	0.0489	0.0256	0.773	0.404	1.91	R -3 m H	NM
Bi ₂ Te ₃	0.842	0.397	0.0508	0.0235	0.842	0.397	2.16	R -3 m H	NM
CrCl ₃	0.800	0.550	0.0300	0.0180	0.267	0.183	1.67	R -3 H	FM
RuCl ₃	1.111	0.574	0.0356	0.0184	0.370	0.191	1.94	P 31 l 2	AFM
CdCl ₂	0.260	0.203	0.0204	0.0158	0.260	0.203	1.29	R -3 m H	NM
CrBr ₃	1.693	1.207	0.0245	0.0175	0.282	0.201	1.40	R -3 H	FM
CdBr ₂	0.323	0.222	0.0234	0.0160	0.323	0.222	1.47	R -3 m H	NM
CrI ₃	1.425	0.715	0.0344	0.0175	0.475	0.119	1.96	R -3 H	FM
CdI ₂	0.387	0.247	0.0248	0.0157	0.387	0.247	1.57	R -3 m H	NM

*NM: Non-magnetic; FM: Ferromagnetic; AFM: Antiferromagnetic

Supplementary References

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