SI

Large variations in both dark- and photoconductivity in nanosheet networks as nanomaterial is varied from MoS_2 to WTe_2

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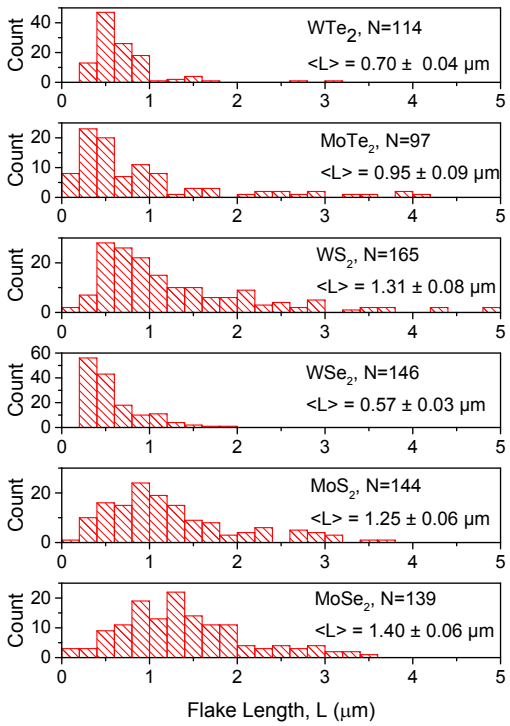

Figure S1: Flake length statistics measured using TEM. The length is defined as the longest dimension of the flake. The quoted errors are standard errors of the distribution. The mean length scales approximately inversely with density suggesting the variation in size occurs during centrifugation.

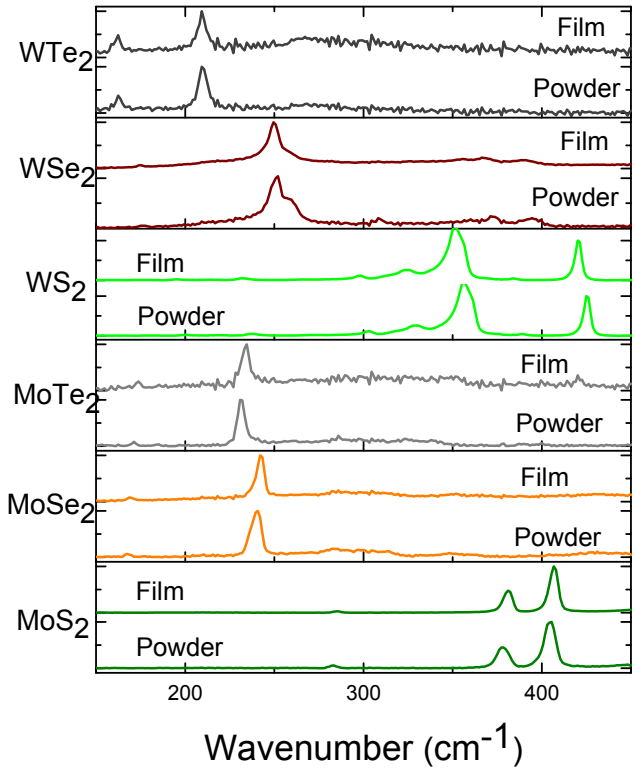

Figure S2: Raman spectra of both powder and films obtained with 532 nm excitation wavelength for all materials studied.

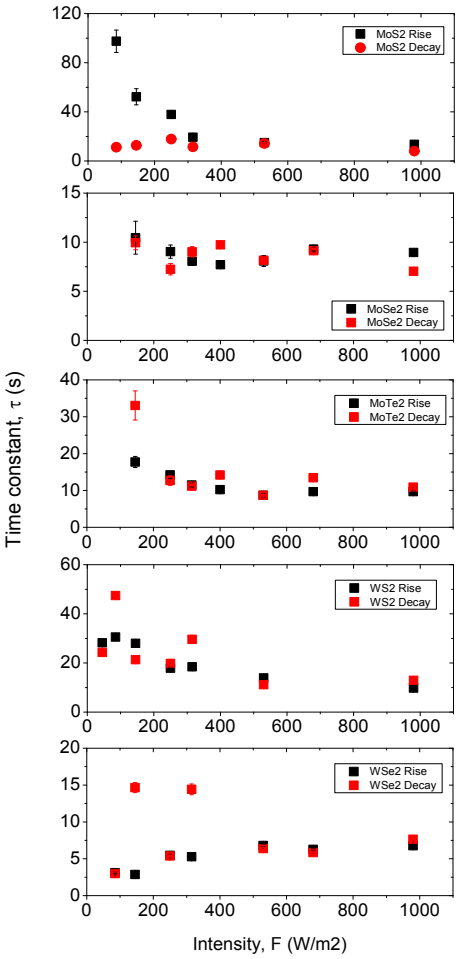

Figure S3: Measured time constants associated with both rise and decay of photocurrent with time for all materials, plotted versus incident intensity.

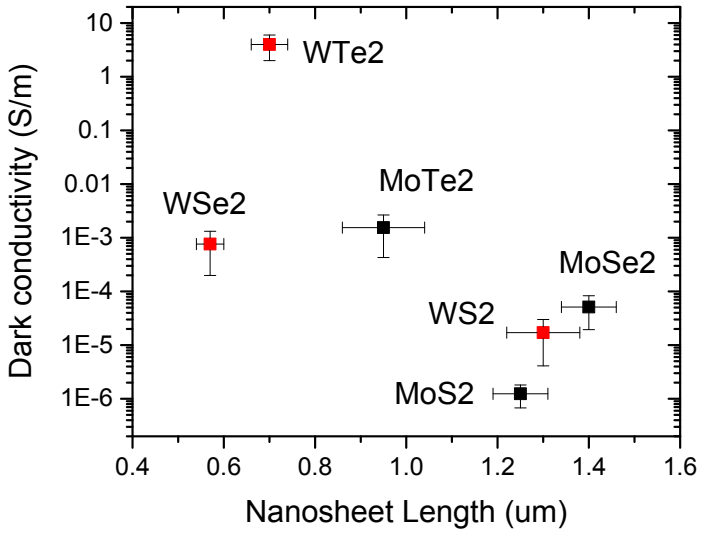

Figure S4: Dark conductivity plotted versus flake length. The apparent reduction in conductivity with increasing flake length is implausible from a physical perspective and is unlikely to be real.

Bulk Indirect Bandgaps of TMDs

The table below outlines the sources from which we take the bulk indirect bandgaps for the six TMDs studied.

Material	MoS_2	$MoSe_2$	$MoTe_2$	WS_2	WSe_2	WTe_2
Values (eV)	1.2 [1,2]	1.1 [1,3]	1.0 [4], 0.9 [5]	1.3 [1,2]	1.2 [1,3]	0.9 [5], 0.8 [6]
Value used	1.2	1.1	0.95	1.3	1.2	0.85

It is important to note that although layered and exfoliable, WTe_2 is not a typical Group VI TMD. This material is distinguished by its distorted octahedral co-ordination of the metal atom and is similar in structure to the high temperature β-phase of $MoTe_2$.[7-9] The associated reduction in M-M bond length induces a band overlap,[7,8] which is thought to cause WTe_2 to be somewhat metallic[10] or semi-metallic[10-12] and much more conductive than the other group VI TMDs.[10,12] This has been supported by measurements on its Seebeck co-efficient[13] and temperature dependence of resistivity[10] and is in stark contrast to the semiconducting 2H-polytype with trigonal prismatic co-ordination, commonly manifest in the other five regular group VI TMDs.

The little that is known about WTe_2 experimentally comes from older studies on bulk crystals.[7,8,10,13] Whilst its bandstructure has recently been studied computationally along with the other five members of the group VI TMD family, these studies render it hypothetically in the 2H-polytype as a semiconductor with a bulk indirect bandgap of roughly 0.8 eV for consistency.[5,6] This idealisation somewhat confuses matters as such a phase has not been found to exist in practice (at least so far).

However, for presentation purposes, we plot WTe_2 as if it has a bandgap of 0.85 eV as predicted for 2H WTe_2.

Schottky barrier analysis of dark current

For a metal semiconductor interface with a Schottky barrier, the current is given by

$$J = A^* T^2 e^{-q\Phi/kT}\left[e^{qV/kT} - 1\right]$$

where A* is the Richardson constant and Φ is the size of the Schottky barrier. In our case we have back to back M-S junctions and so are always in the reverse bias regime. To address this, we consider the slope of the J-V relationship at the origin as this is the same in both forward and reverse bias regimes.

For extremely small voltages, we can expand the exponential to give

$$J = A^* T^2 e^{-q\Phi/kT} qV / kT = \frac{A^* Tq}{k} e^{-q\Phi/kT} V$$

We write the barrier height as some fraction of the bandgap: $\Phi = E_g / c$ where c>1. We can then express this as an effective conductivity (i.e. as reported in figure 5A) via $\sigma = L(dJ / dV)_{V=0}$ where L is the inter-electrode spacing to give:

$$\sigma = \frac{LA^* Tq}{k} e^{-qE_g/ckT}$$

This equation can be used to analyse the data in figure 5A. For both types of material, the data is consistent with c=1.5. This would be consistent with the presence of large Schottky barriers, equal to about 66% of the bandgap are present e.g. ~800 meV for MoS_2. This is certainly not impossible.

However, this model is inconsistent with the data in certain respects. First, it is unclear why the Schottky barrier should be ~66% of the bandgap for all six materials, especially given they have widely varying conduction and valence band positions,[5] although it may of course be associated with Fermi Level pinning.

In addition, here, the combination $LA^* Tq / k$ =2×10^8 S/m. This is reasonably close to the value of the intercept in figure 5A for the MoX2 data (9×10^7 S/m). However, for the WX2 data, the intercept is considerably higher (1.6×10^{10} S/m). It is not clear how such a discrepancy should arise within the framework of Schottky barriers.

Thus, while we cannot rule out the presence of Schottky barriers, we believe that the data does not conclusively demonstrate their presence.

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