Supporting Information

Low Energy Implantation into Transition Metal Dichalcogenide Monolayers to Form Janus Structures

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Notes

Note 1. - Ion Probe Measurements, ICCD Imaging, and Spectroscopic Diagnostics

The ion probe current gives a convenient representation of the ionized component of the plume, especially in background gases, as it is proportional to the ion flux (Nv) arriving at the probe position versus time, and can be recorded with a digital oscilloscope for each laser shot.¹ As shown in Fig. S1, the progression and attenuation of this ionized component of the plasma can be easily recorded by moving the probe to different positions from the target. Plotting the leading edge or peak of the probe current vs. distance (as in Fig. 1c) allows the slowing of the plasma plume to be understood. This diagnostic alone permits the tuning the maximum kinetic energy of the species in the plasma plume, as illustrated in Fig. 1c. The neutrals and clusters are more difficult to characterize but can be revealed through techniques such as laser induced fluorescence, as shown in Fig. S3 and Fig. S4. Laser ablation plasma propagation has been studied extensively in the past, as well as the interactions of this distribution with a background gas. Briefly, the velocities of the ionized and neutral atoms and molecules can normally be fit using shifted center-of-mass Maxwell-Boltzmann distributions. This velocity distribution originates in the dense collisional (Knudsen) layer near the target as the thin slab of plasma expands normal to the target surface following laser ablation, typically resulting in different species (for multicomponent targets) tending to have similar velocities despite their different masses. The ions at typical 1-3 J/cm² laser energy fluences utilized for KrF-laser ablation of solid targets tend to be singly charged and propagating at the leading edge of the neutrals. Laser ablation can create ions directly producing a plasma plume or by consequent laser interaction with the plume. The excited state emission that is typically imaged using the ICCD photography is typically originates from excited neutrals, and persists since it is continually fed by recombination of the ions as the plume expands, as well as electron impact excitation of neutrals. Ejected clusters tend to come later in the thermal component of the plume. The most striking example clearly illustrating these 3 components can be seen in the carbon plasma used for amorphous diamond deposition.² In the Se plasma plume described in this manuscript, the very weak plasma emission seen during propagation in vacuum is due to Se clusters and products of their dissociation.

The slowing of the plasma plume due to background gas collisions has been modeled several ways, starting with phenomenological drag models that are sufficient to capture the key features of the plasma in these and other studies (with deceleration proportional either to velocity (v) or more accurately, v-squared (as used here for the fits in Fig. 1c)). A comprehensive scattering model was developed to describe the entire shape of the ion probe waveform.^{3–5}

In this manuscript we are concerned with the maximum kinetic energy of the species in the plume. From Laser Desorption/Ionization (LDI) experiments we determined the plume to be mostly clusters Se₂....Se₉, which account for the difficulty in slowing the plume by a background gas and its highly forward-directed angular distribution compared to plasma plumes containing principally atoms, dimers, and trimers. The heaviest Se₉ clusters should be the most difficult to slow and their distribution might be skewed to arrive before the lighter clusters. However, fragmentation of the heavier clusters due to collisions with the background gas appears to be responsible for the luminous ball of Se₂* emission observed in the ICCD images, so it appears that both heavier clusters and their lighter fragments arrive together at the substrate with a common velocity in the weak shock front that we observed in low-pressure background argon used in these studies. This maximum velocity was used to adjust the limiting kinetic energy of the Se₂ and Se₉ impacts in the modeling.

Note 2. – Defect Energetics Considerations Between MD Simulations and DFT Calculations

The threshold displacement energy (T_d) of a S atom in a WS₂ ML was used to compare the MD simulations used in the studies with DFT and DFT-MD calculations in the literature. Utilizing the potentials developed by Mobaraki *et al.*⁶ for a WS₂ ML, MD simulations with different incoming single-Se-atom kinetic energies were run to determine $E_{min} = 7.8$ eV, the minimum incident energy for a single Se atom needed to produce a S vacancy in WS₂. From this value, the threshold displacement energy, T_d , was calculated by:

$$T_d = \frac{4E_{min}m_1m_2}{(m_1 + m_2)^2}$$

and determined to be 6.4 eV, where m_1 the mass of the incident Se atom, and m_2 the mass of the targeted S atom on the top of a WS₂ ML. This is consistent with the values of T_d reported from both DFT calculations and DFT-MD simulations in the literature for S atoms residing far from the edge of a WS₂ ML, which were found to be 6.8-7.0 eV.^{7,8}

To assess defect energetics in WS₂ monolayers using the potentials in Ref. 11, the approach used for MoS₂ ML by Ghorbani-Asl *et al.* was used.⁹ Formation energies were calculated for three kinds of defects: S vacancy, W vacancy, and WS₃ vacancy structure in a WS₂ monolayer, noted as V_s, V_w, and V_{WS3}, respectively, with the vacancy formation energy defined as the energy difference between the initial structure and the defected structure. Using the effective potentials used in the MD simulations, V_s, V_w, and V_{WS3} were found to be 5.9, 6.5, and 20.4 eV, respectively. DFT calculations yielded V_s, V_w, and V_{WS3} to be 7.5, 19.5, and 37.1 eV, respectively. The interatomic potential reproduces well the V_s, but underestimates V_w, and V_{WS3}. Nevertheless, the same trend, $V_s < V_w < V_{WS3}$, is observed in both methods, which is also consistent with the trend observed for the defects in MoS₂.⁹

The similarity between the T_d and V_s energies in the MD simulations and DFT calculations lends support to the remarkable agreement between the kinetic energy window for selective implantation suggested by the MD simulations and the experimentally-derived thresholds for top- and bottom-layer selenization of WS₂ ML. While more accurate interatomic potentials need to be derived and benchmarked for ternary systems, the most accurate treatment of the energy landscape in such an evolving ternary system should ultimately involve *ab initio* MD simulations. Such simulations of Se cluster irradiation on WS₂ ML are possible using the supercomputers such as SUMMIT at Oak Ridge National Laboratory, and will be presented in a future work.

Note 3. - Selenization of MoS₂ to form Janus MoSSe - Raman and PL Measurements

In order to test the generality of the selenization approach, the same < 4.5 eV/atom plume conditions that were successful for the formation of Janus WSSe from WS₂ ML were applied to MoS₂ ML crystals under the same conditions. Raman and PL micro-spectroscopy characterization was again performed for comparison with theoretically-calculated Raman modes and band gaps (see below). After selenization, the experimental E_{2g} (384 cm⁻¹) and A_{1g1} (404 cm⁻¹) Raman modes measured for MoS₂ ML in Fig. S11b were transformed to reveal A_1 (290 cm⁻¹, 443 cm⁻¹) and E (355 cm⁻¹) modes that correspond within 5 cm⁻¹ to the predicted out-of-plane and in-plane modes of Janus MoSSe ML in Fig. S11d and the literature.^{10,11} Also, the measured photoluminescence peaks at 1.72 eV for the selenized MoS₂ ML match the theoretical values for the direct optical bandgap of Janus MoSSe MLs, as shown in Fig. S11f.^{12,13}

Note 4. - Theory for the Raman spectra of Janus WSSe and MoSSe monolayers

First-principles DFT calculations were performed to understand the experimentally observed Raman peaks in monolayer TMDs and the Janus systems. Note that pristine monolayer TMDs, such as MoS_2 , $MoSe_2$, WS_2 and WSe_2 , belong to space group *P6m2* (No. 187), and they have six optical phonon modes at the Γ point: 2E", 2E', A'_1, A"_2, where E" and E' modes are doubly degenerated.^{14,15} The A"_2 mode is Raman inactive and thus cannot be observed in Raman scattering; the doubly degenerated E" mode is Raman active, but cannot be detected in the typical experimental back-scattering geometry; the

doubly degenerated E' mode and the A'₁ mode are Raman active and observable in the back-scattering geometry.^{16,17} Indeed, monolayer TMDs generally exhibit two characteristic Raman peaks corresponding to E' and A'₁, respectively (in the bulk counterpart, E_{2g}^{1} and A_{1g})^{14,18}.

For the Janus MLs (MoSSe and WSSe), however, the non-equivalence of the top and bottom chalcogenide layer reduces the structural symmetry so that the Janus MLs belong to P3m1 (No. 156) with the point group C_{3v}. As a result of such symmetry reduction, all six optical phonon modes are Raman active in the Janus MLs: E" and E' are changed to E symmetry, while A'₁ and A"₂ are changed to A₁ symmetry (see Fig. S14 for the changes of symmetry assignments and vibrational patterns)¹³. They are in principle observable in the experimental back-scattering geometry, and thus four first-order Raman peaks (two peaks with E symmetry, doubly degenerated, and the other two with A₁ symmetry) can appear in the calculated and experimental Raman spectra of the Janus WSSe and MoSSe shown in Fig. S13, although some of these peaks are rather weak. In the following discussions, we will focus on the characteristic E' and A'₁ Raman peaks of pristine TMDs ML and their counterparts in the Janus MLs. According to our calculations (Table S1), WS2 and WSe2 MLs have the E' peak located around 360 and 250 cm⁻¹, respectively, and the corresponding E peak in WSSe ML is around 335 cm⁻¹, sitting between the E' peaks of WS₂ and WSe₂. Similarly, WS₂ and WSe₂ MLs have the A'₁ peak located around 420 and 251 cm⁻¹, respectively, and the corresponding A₁ peak in WSSe ML is around 284 cm⁻¹, sitting between the A'₁ peaks of WS₂ and WSe₂ as well. These trends are expected since the Janus WSSe is the mixture of WS₂ and WSe₂. Another indicator is that the optimized lattice constant of WSSe is between the values of WS₂ and WSe₂. The calculated Raman spectra of first-order Raman modes for WS₂ and WSSe ML are consistent with the experimental ones, in both frequencies and intensities, as shown in Figs. S13, S14, confirming that Janus WSSe ML has been successfully synthesized. Similar analysis can be carried out for monolayer Janus MoSSe when compared with MoS₂ and MoSe₂ MLs (Table S1 and Fig. S13). Finally, we note that for WS₂ and WSSe ML (Figs. 4, S13), resonant Raman effect can be strong under the 532 nm laser excitation, and therefore additional Raman peaks appear besides the aforementioned four peaks corresponding to phonon modes at the Γ point.^{14,19} For instance, the LA(M) phonon mode (Fig. S15) and its second order, 2LA(M), are known to show up in the resonant Raman scattering for CVD TMDs samples.^{14,19}

Tables

Phonon modes	Mode # 1		Mode # 2		Mode # 3		Mode # 4	
	frequency	symmetry	frequency	svmmetrv	frequency	symmetry	frequency	symmetry
	(cm ⁻¹)		(cm ⁻¹)		(cm ⁻¹)		(cm^{-1})	
WS_2	298.63	E″	359.91	E'	420.35	A' 1	441.03	A''_2
WSe ₂	175.61	E″	250.00	E'	251.30	A'_1	311.68	A″2
WSSe	204.87	Е	335.29	Ε	283.88	A ₁	422.73	A_1
MoS_2	288.74	E″	391.23	E'	410.83	A' ₁	475.65	A″2
MoSe ₂	170.10	E''	291.22	E'	245.02	A' 1	359.25	A″2
MoSSe	209.26	Е	359.34	Ε	294.58	A_1	446.20	A_1

Table S1. Calculated frequencies and symmetry assignments of pristine TMDs and the Janus MLs. For pristine TMDs, they have six optical phonon modes at the Γ point: 2E", 2E', A'₁, A"₂, where E" and E' modes are doubly degenerated. The A"₂ mode is Raman inactive and thus cannot be observed in Raman scattering; the doubly degenerated E" mode is Raman active, but cannot be detected in the typical experimental back-scattering geometry; the doubly degenerated E' mode and the A'₁ mode are Raman active and observable in the back-scattering geometry. For the Janus monolayers, however, the non-equivalence of the top and bottom chalcogenide layer reduces the structural symmetry so that all six phonon modes are Raman active (E" and E' are changed to E symmetry, while A'₁ and A"₂ are changed to A₁ symmetry), and they are observable in the experimental back-scattering geometry. The two characteristic Raman peaks (E' and A'₁) in the pristine TMDs and their counterparts in the Janus MLs are highlighted in bold font and red color. The vibrational patterns of these phonon modes are also shown in **Fig. S12**.

Figures



Fig. S1. Propagation of Se plasma plumes captured by an ion probe. Measured currents from a floating, biased (-40 V) ion probe record the time-resolved ion flux at different positions in vacuum and different background gas conditions: 10^{-6} Torr, 5 mTorr, and 10 mTorr argon. The plume is weakly ionized, so a 5 k Ω input resistance was used on a digitizing oscilloscope. Each R-t curve has been offset by 30 μ A to clearly present the propagation of the plume leading edge, which is defined in **Fig. 1c** inset, and represents the fastest moving observable material. The propagation for each pressure is fit by the $a = -\alpha v^2$ drag model, where $R = \alpha^{-1} \ln(1 + \alpha v_0 t)$ and $v = v_0(1 + \alpha v_0 t)^{-1}$. For all plots, $v_0 = 1.02 \text{ cm/}\mu$ s. $\alpha = 0.09, 0.104, 0.115, 0.125, 0.139, 0.165 \text{ cm}^{-1}$ for Ar pressures of 5, 10, 20, 30, 40, 50 mTorr, respectively.



Fig. S2. Mass spectrum of laser-evaporated Se clusters. Laser desorption/ionization mass spectrum of a 1 micron-thick Se film pulsed laser deposited on gold film in vacuum from the Se target used in the experiments under the same 1.0 J cm⁻² KrF-laser ablation conditions. A commercial Bruker MALDI-TOF Autoflex LRF instrument utilizing the third harmonic (355 nm) of a Nd:YAG laser operated at 1 kHz was used to laser vaporize the Se film (without matrix) to analyze the cluster distribution, accumulating 300 separated individual laser shots, confirming that the products are primarily small clusters.



Fig. S3. Emission spectroscopy of Se plumes. (a) Digital camera image of a Se plume in vacuum and (b) in 50 mTorr Ar gas. The vacuum plume is weakly visible in transit in (a), and visible at the substrate position 10 cm away, where incoming Se species collide with Se species that did not stick to the substrate. When background Ar gas is added in (b), collisionally-induced luminescence in transit becomes visible, in addition to the collisions in the near substrate region. Gated-ICCD photography images of the total visible emission shows these two components in (c) and (d). In (c), starting at $\Delta t = 4 \mu s$ after the laser pulse (with a 4 μs gate), the highly forward-directed plume shape in vacuum is visible. In 50 mTorr Ar at $\Delta t = 3 \mu s$ (with a 1 μs gate) in (d), the fast 'dark' component has undergone collisions to produce luminescence visible to the eye on the leading edge of the 'vacuum' plume shape of (c), with the propagation detailed in **Fig. 1**. Upon collision with the substrate, additional collisionally-induced luminescence is observed that is brighter than the plume luminescence in transit, shown in (e) and (f). In each image, dashed white lines indicate positions at the given times where emission spectroscopy was performed using a gated, intensified CCD-array detector coupled to a spectrograph. (g)-(j) show the emission spectra at the positions indicated by dashed lines in (c)-(f), respectively, with the labeled delays and acquisition gates, all showing similar broad bands displaying vibronic features. (g) In vacuum, the emission can barely be resolved with 1mm spectrometer slits, and 1 us exposure. (h) Upon rebound with the substrate in vacuum, the spectra shows both a broad band as well as three groups of atomic emission lines which can be assigned to Se* at (473.1, 473.9, 474.2) nm, (536.6, 537, 537.4) nm, and 632.6 nm. (i) In transit through 50 mTorr Ar, the leading edge of the plume shows similar broad band emission. (j) Upon rebound with the substrate at 50 mTorr Ar, the brightest emission is obtained showing broad band emission with vibronic features, as well as the Se* atomic lines. In summary, the weakly-emitting, highly-forward directed plume and broad band emission indicates clusters and molecules comprise the bulk of the plume, and these become excited via gas-phase collisions in the weak plasma or via background gas collisions to emit light from excited molecular bands, with partial dissociation into excited atoms in the collisional zone near the substrate.



Fig. S4. Laser induced fluorescence (LIF) experiments. LIF experiments were conducted in vacuum to understand the origin of the plasma emission in different pressures of background gases. These experiments revealed strong emission from Se dimers (Se₂) originated mainly from the LIF-laser dissociation of the large Se clusters comprising the laser ablation plume (see Figs. S1, S2). (b) Schematic of the LIF experiment showing an ICCD image of the laser induced emission generated in vacuum. A third harmonic of a Nd:YAG laser (355 nm, 8 ns pulse width, 1Hz repetition rate) was employed to excite and image the emission using 8 and 15 μ s delays between the excimer laser ablation pulse (248 nm, 25 ns FWHM, ~1 J/cm²) and the LIF-laser pulse with 0.8 and 1.5 µs ICCD gates, respectively. (c) LIF spectrum recorded using a second ICCD (PI-MAX 3, Princeton Instruments) coupled with a spectrometer (Acton Spectra Pro 2300i, f = 0.3 m, 1200 grooves/mm grating). The ICCD images in (b) were used to set up the timing and the plume location to acquire the spectra. The observed narrow spectral lines were assigned to the vibronic transitions from the vibrational levels, v', of the excited electronic state $(B0_u^+)$ of Se₂ to the vibrational levels, v'', of its ground electronic state $(X0_a^+)$. The 355 nm excitation wavelength is resonant with the $v' = 11 \leftarrow v'' = 1$ transition shown in (c) that induces a series of the corresponding emission lines assigned in (b) by dots based on the work described by Barrow et al.²⁰. The dissociation energy, D, of the ground electronic state is ~3.2 eV.²⁰ In summary, comparison the spectra shown in (a) and (c) allows one to conclude that Se₂ contributes a significant fraction to the observed plasma emission in Ar probably, due to efficient dissociation of higher clusters in a shock front region of the laser ablation plume.



Fig. S5. Comparison of photoluminescence obtained after selenization at different pressures and temperatures. (a) At low 250 °C temperatures, 800 pulses (at 5 Hz) Se implantation at d = 10 cm in 20 mTorr Ar conditions (Se KE/atom < 4.5 eV) produces bright PL, corresponding to no W-displacement in the WS_{2-x}Se_x crystals, while higher KE (5 mTorr, or < 8 eV/Se atom) produces W-defects and quenched PL. (b) However, the same 5 mTorr (< 8 eV/Se atom) implantation conditions at 600 °C produces bright PL, indicating that lattice defects can be significantly healed at this temperature compared to 250°C. (c) Similarly, even at the maximum KE in these experiments (~ 42 eV leading edge, 20 eV peak), despite displacement and sputtering of W atoms by collisions, 600 °C is sufficient to heal the surrounding lattice to recover PL compared to 250 °C conditions. PL spectra in each image were acquired under the same conditions in a commercial micro-spectroscopy system (Renishaw) utilizing a 100 X objective, 532 nm laser for excitation, and 3 acquisitions of 5 s.



Fig. S6. DFT calculation of Se adatom diffusion through WS₂. We modeled the atomistic process of a Se adatom diffusing from top to the bottom layer of WS₂ along the z-direction perpendicular to the WS₂ plane. First, we fully optimize the initial and final position where Se adatom forms a chemical bound to Se atom on the top and bottom surface. Then the diffusion pathway was constructed by equally dividing the atomic coordination of the adatom by 5 steps from the initial position to the final position in z direction. Each structures were then fully relaxed for a constrained z position. The pathway from the constrained optimization results in the diffusion partices where the adatom progress in z, while in-plane degrees of freedom are fully relaxed. The migration barrier of the pathway shown is estimated at ~8.8 eV per Se adatom, an upper bound barrier for the diffusion process.



Fig. S7. MD simulations of Se₂ cluster impacts with WS₂ ML with increasing kinetic energies. A series snapshots of MD simulations showing key moments during Se₂ cluster impacts on suspended 1L WS₂ for KEs ranging between 1.6 - 42 eV/atom. The simulations show that Se₂ softly lands on WS₂ surface at 1.6 eV/atom, start to implant the top S layer at 2.9 eV/atom, and implants selectively in the top S layer between 2.9 and 8 eV/atom. At 20 eV/atom the Se atoms can penetrate to the bottom S layer and can induce loss of W atoms. At even higher energy, e.g. 42 eV/atom, the Se atoms can penetrate through the WS₂ layer and sputter the layer. Note that the 1.6, 2.9, 3.6, 4.5, 5.4, 8, 20, 42 eV/atom correspond to the maximum KEs measured for ions at 50, 40, 30, 20, 10, 5, and 10^{-3} mTorr. (Yellow: S, Red: Se, and Black: W)



Fig. S8. MD simulations of Se₉ cluster impacts with WS₂ ML with increasing kinetic energies. A series of snapshots of MD simulations showing key moments during Se₉ cluster impacts on suspended WS₂ ML for KEs ranging between 1.6 - 42 eV/atom. The Se₉ cluster deforms and flattens, but essentially soft-lands without displacing S atoms at \leq 2.9 eV/atom. The Se atoms implant only within the top S layer at 4.5 eV/atom. At 5.4 eV, the cluster appears to penetrate the WS₂. At \geq 8 eV/atom, Se₉ clusters appear to sputter off the W atoms and even larger area with increasing KEs. Note that the 1.6, 2.9, 3.6, 4.5, 5.4, 8, 20, 42 eV/atom correspond to the maximum KEs measured for ions at 50, 40, 30, 20, 10, 5, and 10⁻³ mTorr. (Yellow: S, Red: Se, and Black: W)



Fig. S9. MD simulations of the structural reorganization processes occurring following implantation of Se₉ into WS₂. Snapshots of MD simulations that were performed at 1000 and 1100 K for 2 ns simulation time to understand possible recrystallization processes of structurally-modified WS₂ ML that occur following implantation by a Se₉ cluster at 8 eV/atom. Only the top layer of S and the Se atoms are shown, in yellow and red, respectively, to provide clear view of the top S layer. The atoms of bottom layer of S were kept stationary during simulations. (a-c) Snapshots of WS₂ ML impacted by a Se₉ cluster with 8 eV/atom at 1000 K (700 °C) consecutively taken between 1.73 - 2 ns show Se atoms diffused (a-b), incorporate into the lattice, and replace some S constituents (c). (d-f) Snapshots of the same impacted WS₂ ML at 1100 K (800 °C) consecutively taken between 1.07 - 2 ns show Se atoms diffused into the lattice of WS₂ ML faster compared to 1000 K.



Fig. S10. HAADF Z-STEM images of Se-irradiated WS₂ at 200°C. (a) Se atoms and clusters remaining on or within the surface of WS₂ ML after Se irradiation in 5 mTorr was conducted for just 30 pulses at 200 °C. The images reveal different types of defects that are highlighted by green circles and survived annealing at this temperature. (b) Another area contaminated with the residual Se atoms that enhance local brightness. Electron intensity line profiles, Line 1 and Line 2, and orange arrows indicate atomic Se residue can locate on top of the W atoms as an absorbent and also locate between the W and chalcogenide atoms as interstitials.



Fig. S11. Simulated HAADF-Z-STEM tilted images for (a) WS_2 (b) Janus WSSe (c) WSe_2 monolayers tilted at $x = +15^{\circ}$ and $y = +15^{\circ}$. For reference, the locations of representative S and Se atoms are indicated just above the atom positions in the images.



Fig. S12. Tilted HAADF-Z-STEM images of ML Janus WSSe (a) Experimental image tilted at $x = +15^{\circ}$ along with overlaid ball-and-stick model with W atoms (gray), Se atoms (red) and S atoms (yellow). (b) The line intensity profile across the atomic chain highlighted by the green box in (a) shows the relative intensity of detected electrons compared to the W peak, with definable shoulders of Se, then S, in a repeating pattern. (c) The corresponding simulated STEM image for Janus WSSe tilted at $x = +15^{\circ}$, confirms the relative intensity ratio measured experimentally.



Fig. S13. Summary for Raman and PL spectra of Janus WSSe and MoSSe ML. (a) Raman spectral signatures of Janus WSSe and the CVD WS₂ ML from which Janus monolayers were converted under a laser excitation at 532 nm. From WS₂ to WSSe, the characteristic E' peak at 355 cm⁻¹ is changed to an E symmetry peak at 334 cm⁻¹, and the characteristic A'_1 peak at 418 cm⁻¹ is changed to an A_1 symmetry peak at 286 cm⁻¹. (c) Theoretically predicted first-order Raman peaks of Janus WSSe and WS2 MLs under 532 nm laser excitation are consistent with experimental data, indicating successful synthesis of an ideal Janus structure. (e) PL spectrum of Janus WSSe and the CVD WS₂ ML that it was converted from were accumulated with different laser power and accumulating time to obtain similar PL intensities. A CVD WSe2 ML on the same substrate (300 nm SiO2) was included for comparison. (b) Raman spectral signatures of Janus MoSSe and the CVD MoS₂ ML from which Janus ML were converted under a laser excitation at 532 nm. From MoS_2 to MoSSe, the characteristic E' peak at 384 cm⁻¹ is changed to an E symmetry peak at 355 cm⁻¹, and the characteristic A'₁ peak at 404 cm⁻¹ is changed to an A₁ symmetry peak at 290 cm⁻¹. (d) Theoretically predicted first-order Raman peaks of Janus MoSSe and MoS₂ MLs under a 532 nm laser excitation are consistent with the experimental results. (f) PL spectrum of a Janus MoSSe and the CVD MoS₂ ML that it was converted from were accumulated with the same laser power and accumulating time. Photon energies of the experimental Janus WSSe and MoSSe MLs in (e-f) match the theoretical predictions for a direct-bandgap, Janus WSSe ML (1.83 eV)¹³ and Janus MoSSe ML (1.72 eV)¹². Another work that calculated the electronic bandgap and binding energy of 2D Janus structures separately provides a direct bandgap for both of Janus WSSe and MoSSe ML at 1.8 eV²¹.



Fig. S14. Schematic illustrations of the atomic displacements of the optical phonon modes in WS₂ and Janus WSSe ML. The symmetry assignments are also shown. The two characteristic Raman peaks (E' and A'₁) in WS₂ and their counterparts in the Janus WSSe are highlighted in red color, where the experimental and theoretical frequencies are shown to nicely agree with each other. The non-equivalence of the Se and S atoms in WSSe alters the symmetry assignment and the vibrational pattern of each phonon mode. Other TMD MLs, including MoS_2 , $MoSe_2$ and WSe₂, share the similar results with WS₂, and the Janus MoSSe shares the similar results with WSSe.



Fig. S15. Calculated phonon dispersion of WSSe ML. The LA phonon branch at the M point, referred as LA(M), is indicated by the blue dash circle. The LA(M) phonon mode and its second order, 2LA(M), can be involved in the Raman scattering when defects are present in the system.



Fig. S16. Images of converted Janus WSSe ML. (a) optical micrograph and (b) scanning electron microscope image of Janus WSSe ML converted in 20 mTorr argon at 300 °C showing a continuous and crack-free surface.



Fig. S17. First-principles modeling of $WS_{2(1-x)}Se_{2x}$ structures with different structures and Se content **x**. DFT calculations were performed with supercells (indicated by the dark solid lines in each plots) to determine ΔE (eV/nm²), the energy differences per unit area with respect to WS₂ and the gas phase forms of S_2 and Se_2 as reference energy structures for sulfur and selenium. (a) Side and top views of pristine WS_2 . (b) A WSSe Janus structure containing Se atoms that fully occupy the top layer and S atoms that fully occupy the lower layer of the monolayer, with energy 7.24 eV/nm² greater than WS₂. (c) A fully selenized structure, WSe₂, with total energy 13.39 eV/nm² greater than WS₂. (d) An intermediate alloy structure with 4% Se-doped WS₂ (Se atoms on both top and bottom layers) has total energy 0.32 eV/nm^2 greater than WS₂. (e) Structure resulting from a Se₉ cluster implanted into WS₂ with 4.5 eV kinetic energy, taken from the MD simulations (see Fig. 3c inset). After full relaxation, the structure shown has a total energy 9.0 eV/nm^2 greater than WS₂ and contains defective regions with four Se atoms incorporated in the host, while the remaining five Se atoms (and one S atom) have segregated above the surface. For this energy calculation, the 9.0 eV/nm² total energy was projected on the supercell of WS₂ in (a), while the structure was relaxed using the rectangular lattice as a supercell (the black solid line in (e)). (f) For comparison, a 15% Se-doped alloy configuration in which four S atoms are replaced by Se atoms in the WS_2 supercell area has 1.0 eV/nm^2 greater than WS₂. These first-principles calculations demonstrate that a continuous increase in total energy is necessary to construct more selenized WS_{2-x}Se_x structures. The hyperthermal implantation of Se clusters can directly result in structures with high local energies (e.g., 9.0 eV/nm^2 in (e)) sufficient to supply this selenization energy.

References for Supporting Information Notes and Figures

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