Manipulation and structural modifications of 2D materials for nano-electronic and nanofluidic applications remain obstacles to their industrial-scale implementation. Here, it is demonstrated that a 30 kV focused ion beam can be utilized to engineer defects and tailor the atomic, optoelectronic, and structural properties of monolayer transition metal dichalcogenides (TMDs). Aberration-corrected scanning transmission electron microscopy is used to reveal the presence of defects with sizes from the single atom to 50 nm in molybdenum sulphide (MoS2) and tungsten disulfide (WS2) caused by irradiation doses from $10^{13}$ to $10^{16}$ ions cm$^{-2}$. Irradiated regions across millimeter-length scales of multiple devices are sampled and analyzed at the atomic scale in order to obtain a quantitative picture of defect sizes and densities. Precise dose value calculations are also presented, which accurately capture the spatial distribution of defects in irradiated 2D materials. Changes in phononic and optoelectronic material properties are probed via Raman and photoluminescence spectroscopy. The dependence of defect properties on sample parameters such as underlying substrate and TMD material is also investigated. The results shown here lend the way to the fabrication and processing of TMD nanodevices.

1. Introduction

Among the expanding catalogue of 2D materials, transition metal dichalcogenides (TMDs) have generated significant interest due to their exceptional electronic, optical, and structural properties.[1–3] In particular, TMDs have been noted for transistors, solar cells, photodetectors, and gas sensors due to their unique electronic, optical, and mechanical properties.[11,12] For example, defects in atom thick materials can be used to manipulate electronic, magnetic, and catalytic properties.[13,14] For defects in wide-bandgap h-BN exhibit spin effects and potential quantum functionality.[15] The widespread realization of these applications is contingent upon the development of scalable processes for the fabrication of atomic-level defects with precisely controlled sizes, spatial densities, and locations within the lattice.

Focused ion beams (FIBs) are widely utilized for doping, device fabrication, and micromachining in semiconductors such as SiC, GaAs, and Ge.[15,16] More recently, FIB irradiation has been extended as a means of structural modification and nanomaterial fabrication in 2D materials such as graphene.[17] Theoretical studies[18–21] on the role of ion incidence angle and substrate effects in the defect creation process in 2D materials like TMDs and graphene, and similar experimental studies,[8,22,23] are starting to emerge. A wide range of techniques for defect creation have been reported in literature including plasma etching,[24] thermal decomposition,[25] acid etching,[26,27] electron irradiation,[28] and ion irradiation.[8,21] The latter two irradiation methods directly allow for accurate and spatially selective defect sites.

While electron irradiation is exercised for defect creation, it predominately leads to monosulfur and disulfur vacancies in TMDs.[28–30] In this study, exploiting the higher mass of energetic ions, we are able to generate single-atom vacancies in monolayer TMDs using ion irradiation. Previously, we have also demonstrated ion irradiation as a method of fabricating sub-nanometer pores in MoS2 for ionic transport through nanoporous membranes.[8]

As of now, there is a relatively poor correspondence between ion irradiation experiments and theory in 2D materials.[8,9,18,19,31] One likely reason for these discrepancies is the inadequate understanding of experimental parameters. For example, material contamination has been ubiquitously reported after ion irradiation and while it plays a significant role in analytical and structural characterization, such “substrates” are rarely accounted for in theoretical simulations.[8,17,31–34] Similarly, Surwade et al. demonstrated that water transport properties in nanoporous graphene with defects produced from electron and ion irradiation result in negligible water flux while defects from oxygen plasma etching exhibit rapid water transport, despite identical Raman spectra from the two defect creation techniques.[24] We speculate that this difference in filtration performance may result from the lack of thorough information of FIB operation on 2D materials. FIBs were developed with a primary focus for material fabrication and ablation to produce microstructures, and therefore their usage on 2D materials is still unconventional and underdeveloped. For example, traditional stopping range/transport of ions in matter...
(SRIM/TRIM) software\cite{35} is widely used to replicate FIB-based micromanufacturing/doping in bulk materials, but its approach of binary-collision approximation treats 2D materials as an amorphous material with no regard to atomic crystallinity and produces inaccurate results.\cite{18,22,23,36}

In this report, we investigate the effects of FIB irradiation on the structural, optoelectronic, and phononic properties of monolayer TMDs. Aberration-corrected scanning transmission electron microscopy (AC-STEM) along with scanning electron microscopy (SEM) provide information into a tenable irradiation mechanism and feature properties of fabricated defects with sizes over three orders of magnitude from 0.1 nm (atomic vacancies) to 50 nm large holes. Irradiated TMD materials appear less contaminated than graphene systems due to less reactive defect sites, which allows for consistent defect creation and analysis over comparatively large, millimeter-length scales across different samples. Characteristics of the irradiated membranes such as defect density percentage and average defect size are also quantified and reported as a function of TMD material, supporting substrate, and irradiation dose. Raman and photoluminescence (PL) spectroscopy results demonstrate macroscale changes in material properties due to FIB irradiation.

2. Results and Discussion

Figure 1a shows a schematic of the process used to irradiate monolayer TMDs. A TMD flake grown by chemical vapor deposition (CVD) is transferred through a chemical wet etch process (see the Experimental Section), suspended on a holey carbon substrate, and exposed to a 30 kV Ga$^+$ focused ion beam that is incident normal to the sample. In our study, we use a combination of Raman spectroscopy (see Figure S2 in the Supporting Information), PL spectroscopy (see Figure 3), and atomic resolution AC-STEM imaging (see Figures 1, 3, and 4, and Figure S1 in the Supporting Information) to confirm the monolayer nature of our materials. These data are consistent with previous reports of monolayer TMDs.\cite{4,12,28,37}

Exposure parameters and dose calculations are discussed later. Irradiated samples are first characterized through high-angle annular dark-field (HAADF) imaging, an AC-STEM technique by which mass contrast information of individual atomic positions is obtained, particularly well-suited to atomically thin 2D materials.\cite{8,34,37} Figure 1b,c shows HAADF lattice image of WS$_2$ and MoS$_2$, respectively, that have been exposed to FIB irradiation with doses of $1.5 \times 10^{14}$ and $5.1 \times 10^{13}$ ions cm$^{-2}$, respectively. Within the hexagonal lattice structure, single-atom defects (i.e., vacancies) are identified by the absence of contrast at regularly spaced lattice positions. We focus here on transition metal sites due to the weak HAADF contrast of S atoms compared to heavier Mo/W atoms\cite{38} and observe that defects with tunable densities and sizes down to a single atom can be engineered over millimeter-scale areas in TMDs (limited by the FIB exposure area). STEM imaging was performed at an acceleration voltage of 80 kV while focusing time and probe current were minimized (see the Experimental Section) such that transition metal defect fabrication from electron beam knock-on damage is expected to be negligible.\cite{28,29}

We first demonstrate the underlying mechanisms involved in the irradiation process and highlight certain features that are unique in the context of 2D materials. Ion beam exposure dose $D$ for bulk materials is typically given as

$$D = \frac{I t}{q A}$$

(1)

where $I$ is the ion beam current, $t$ is the total exposure time, $q$ is the ion charge, and $A$ is the exposure area.\cite{39} In bulk materials, dose—i.e., the number of ions hitting the sample surface per cm$^2$—is used as a measure of doping or implanting ions into a substrate.\cite{40,41} However, this concept has been loosely borrowed for 2D materials where ions are used for defect creation\cite{8,23,42} and as shown later, fails to accurately account for the irradiated area since beam raster can cause nonuniform irradiation on materials at the nanoscale.

We suggest the following empirical formula that more accurately describes the direct-ion impact which can cause the

-Note: The image referenced as Figure 1 contains graphs and images illustrating the irradiation process and its effects on TMD flakes, including FIB irradiation mechanisms, HAADF imaging, and defect analysis.
spatial distribution of defects formed in 2D materials. This is given as

\[ D = \frac{t \times N_s}{q \times A_{\text{beam}}} \]  

(2)

where \( t \) is the dwell time per pixel, \( N_s \) is the number of scans, and \( A_{\text{beam}} \) is the area of the ion beam spot. Compared to the bulk formula, total exposure time here is determined by the number of repetitive scans, \( N_s \), on each pixel. As in this study, \( N_s \) is applicable in techniques where imaging/rastering mode (or “grab frame”) capture is involved. We utilize an ion probe current of 10 pA and spot-size of 100 nm diameter (Figure 1a). Previous dose calculations\(^{[10,41]} \) typically use Equation (1) where area \( A \) corresponds to the total area of all pixels in the imaging area. However, only a small region of each pixel is exposed to the ion beam. Therefore, our dose calculation (Equation (2)) only accounts for the area of the ion beam spot size \( (A_{\text{beam}}) \) that is irradiated within each pixel (see Figures 1a and 2b). To calculate the dose, we multiply the irradiated area by the number of times the beam scans over the surface of the sample. Using the total scan area (Equation (1)) gives a less accurate dose estimate because defects caused by ion irradiation in 2D materials are only created in irradiated regions and not across the whole sample surface that is scanned under the ion beam. Differences in dose calculations between Equations (1) and (2) can be found in Table S9 in the Supporting Information. In this study, scans are controlled with a resolution \( (n_p) \) of 416 × 416 pixels, pixel width of 600 × 600 nm, and dwell time \( (t_d) \) of ~16 \( \mu \)s per pixel to irradiate a selected region of the suspended flake, unless otherwise specified.

Observation of these values and the corresponding dose calculation reveal the resolution at which the irradiation was conducted and the possible nonuniform spacing between defects. Figure 2a shows one such scenario where the raster pattern on a monolayer WS2 flake is noticed as dark, irradiated (pink line) and bright, unirradiated (blue line) bands in a scanning electron micrograph. This is intuitive as the ion beam spot can be described as a Gaussian function whose maximum is incident at the center of each pixel.\(^{[16,43]} \) With a set resolution, the FIB software divides the imaging area into a number of pixels over which the beam will scan in a raster pattern. The pixel width, spot size, and overlap % of the ion beam play a significant role in decoding and mapping the pattern and spacing of defects on an irradiated sample. This is clearly demonstrated in the low-magnification HAADF image of FIB-irradiated monolayer WS2 suspended over a 2.5 \( \mu \)m diameter hole in Figure 2b. Here, we observe linear bands of defective areas spaced ~500 nm apart. This nonhomogeneous pattern corresponds to the raster mechanism of the FIB where the spacing between bands or stripes is controlled by the specified resolution (i.e., pixel width).

High-magnification images reveal that the individual holes or tears in the material are shaped as equilateral triangles with side lengths of ~50 nm (area ~1200 \( \text{nm}^2 \)) (Figure 2c). Single triangles coalesce into larger defects near band centers, where the middle of the Gaussian ion beam hits the sample (Figure 2d). Quantitative analysis of the defects (see the Experimental Section) yields average and median defect areas of ~1420 and 1140 \( \text{nm}^2 \), respectively (Figure 2e).

We also probe the effects of varying irradiation dose \( D \), achieved by retaining a constant dwell time per pixel, \( t_d \), and changing the total number of FIB raster scans, \( N_s \). In addition to pristine material (Figure S1, Supporting Information), irradiation doses ranging over three orders of magnitude from \( 5.1 \times 10^{13} \) to \( 3.1 \times 10^{16} \) ions \( \text{cm}^{-2} \) are studied. Figure 3 shows a series of low-magnification (top row) and high-magnification (bottom row) HAADF AC-STEM images of variably irradiated suspended monolayer WS2 membranes. A low degree \( (5.1 \times 10^{13} \text{ions cm}^{-2}) \) of irradiation results in the appearance of single transition metal atom defects (Figure 3c,d). Larger levels of FIB irradiation \( (6.4 \times 10^{14} \text{1.9} \times 10^{15} \text{ions cm}^{-2}) \) show a denser distribution of single atom to sub-nanometer defects (Figure 3e–h). The atomic
configuration of these defects is described later in Figure 5b. We note observable defect areas of \( \approx 0.10 \), \( \approx 0.14 \), and \( \approx 0.27 \) nm\(^2\) for \( V(1_{W} + 6_{S}) \), \( V(2_{W} + 2_{S}) \), and \( V(3_{W} + 12_{S}) \), respectively.

Quantitative analysis for all doses is provided in Figure 4 and Figure S3 in the Supporting Information. Under an order of magnitude higher dose \( 3.1 \times 10^{16} \) ions cm\(^{-2}\), the membrane begins to display larger, nanometer-scale defects (Figure 3i,j). We note that unlike irradiated graphene, which becomes heavily contaminated due to the pinning of atmospheric impurities at defect sites\(^{31,33}\), the exposed TMDs did...
not exhibit a noticeable increase in contamination until doses above $10^{16}$ ions cm$^{-2}$ due to the presence of ablated material on the membrane. This suggests that defects in TMDs are less chemically reactive than defects in graphene, which can facilitate consistent structural characterization across samples and over large length scales. Above $3.1 \times 10^{16}$ ions cm$^{-2}$, irradiated membranes were observed to be mechanically unstable and prone to collapse.\textsuperscript{[44]}

Moving from atomic- to bulk-scale properties, we utilize PL and Raman spectroscopy to characterize the effects of FIB irradiation on the optoelectronic and phononic structure of TMDs, respectively. Figure 3k shows the PL spectra (excitation wavelength = 532 nm) obtained from suspended monolayer WS$_2$ membranes exposed to FIB irradiation from 0 (pristine) to $3.2 \times 10^{16}$ ions cm$^{-2}$. Spectra were fit to three characteristic WS$_2$ excitations: defect ($X_D$, 1.88 eV), trion ($X_T$, 1.96 eV), and exciton ($X_0$, 2.02 eV).\textsuperscript{[44]} The spectral weight percentage for each excitation as a function of irradiation dose is shown in the inset of Figure 3k. In particular, $X_D$ exhibits a direct dependence on dose and monotonically increases from 0.7% in the irradiation on the optoelectronic and phononic structure of TMDs, respectively.

Figure 4. a) Schematic of the irradiation mechanism for monolayer TMDs supported on a Si/SiO$_2$ substrate using a focused Ga$^+$ ion beam (yellow). b) After irradiation, samples are transferred onto holey carbon films and imaged using AC-STEM (electron beam, green). HAADF AC-STEM images of c) substrate-supported MoS$_2$, d) substrate-supported WS$_2$, e) suspended MoS$_2$, and d) suspended WS$_2$ after exposure to FIB irradiation with a dose of $5.1 \times 10^{13}$ ions cm$^{-2}$. Summarized g) defect density and h) average defect area values of (square) pristine, (diamond) substrate-supported, and (circle) suspended monolayer TMDs for irradiation dose values of 0, $5.1 \times 10^{13}$, $6.4 \times 10^{14}$, $1.9 \times 10^{15}$, and $3.1 \times 10^{16}$ ions cm$^{-2}$. Results for MoS$_2$ and WS$_2$ are shown in blue and red, respectively. Further statistics and histograms of individual defects are provided in Figures S3, S5, and S6 in the Supporting Information.
pristine case to 3% for $3.2 \times 10^{16}$ ions cm$^{-2}$. This is similar to the case of plasma-irradiated WS$_2$, in which $X_D$ increases up to 40% as a function of plasma exposure.$^{[45]}$ However, unlike plasma-etched WS$_2$, where $X_T$ steadily decreases with exposure time, FIB-irradiated WS$_2$ experiences a peak (57%) in $X_T$ at $6.4 \times 10^{14}$ ions cm$^{-2}$, which results in redshift of the PL signal. Similarly, $X_0$ is lowest (41%) at this dose. This suggests that $X_T$ and $X_0$ are not sensitive to atomic defects (i.e., sub-nanometer defects do not induce doping). We attribute this peak in $X_T$ at $6.4 \times 10^{14}$ ions cm$^{-2}$ to the presence of substitutional dopants in suspended WS$_2$ at this dose (see Figure S7 in the Supporting Information). The origin and effect of these substitutional dopants that appear in AC-STEM images in place of W atoms are being studied extensively as a part of a separate work. We are currently not able to confidently attribute their origin to a specific step during sample growth or subsequent handling. We also note that with increasing FIB irradiation, PL peak intensity decreases monotonically by roughly two orders of magnitude for both monolayer WS$_2$ and MoS$_2$.$^{[8]}$ Although further analytical TEM studies are needed, the PL intensity decrease observed here suggests that FIB irradiation likely produces mainly transition metal defects rather than chalcogen vacancies, because chalcogen vacancies were previously found to cause an increase in PL intensity, opposite from what we measure.$^{[37,46]}$

In addition to PL, Raman spectroscopy is widely implemented to characterize vibrational modes within 2D materials and has previously been used to analyze He$^+$-, Ne$^+$-, Mn$^{2+}$-, and Ga$^{+}$-irradiated MoS$_2$.$^{[8,23]}$ Figure 3l exhibits the Raman spectra for FIB-irradiated WS$_2$ for the corresponding doses in Figure 3k. Spectra were normalized and fit to characteristic WS$_2$ vibrational modes, in particular the second-order longitudinal acoustic 2LA(M), in-plane $E_{12g}(\Gamma)$, and out-of-plane $A_{1g}(\Gamma)$ modes (Figure S2, Supporting Information).$^{[47,48]}$ Over the irradiation dose range measured here, we do not observe any changes or significant shifts in the Raman spectra. This has also been reported in plasma-irradiated WS$_2$ under the same excitation (532 nm) by Chow et al. and implies that the primary phonon modes in WS$_2$ are not sensitive to defects at this wavelength.$^{[45]}$

While several low-frequency peaks do appear, we similarly did not see changes in the $E_{12g}(\Gamma)$ and $A_{1g}(\Gamma)$ modes of FIB-irradiated MoS$_2$. This is consistent with previous reports, which only observe peak shifts in highly defective MoS$_2$.$^{[21,49]}$ and suggests that sub-nanometer defects with low densities (<1%) do not affect the Raman spectra of monolayer MoS$_2$.

Due to the versatility of FIB instrumentation, irradiation can be performed on a wide range of substrates and materials under a variety of conditions. Here, we investigate the role of the underlying substrate on the resulting structural and defect characteristics of different monolayer TMD materials. Figure 4a,b shows
schematically the substrate-supported irradiation and characterization process. CVD-grown TMD flakes were exposed to 5.1 × 10^{13} ions cm^{-2} FIB irradiation while sitting on a Si/SiO$_2$ substrate, transferred to a holey carbon film using a wet etch process, and imaged using HAADF AC-STEM (see the Experimental Section for more details). Figure 4c,d exhibits the obtained AC-STEM images for MoS$_2$ (blue) and WS$_2$ (red) flakes, respectively. Figure 4e,f shows corresponding images for flakes that were exposed to the same irradiation dose (5.1 × 10^{13} ions cm^{-2}) while suspended on a holey carbon film (Figure 1a).

By sampling over multiple atomic resolution images (see the Experimental Section), we obtain values for average defect area and defect density, defined as the percentage of transition metal sites containing vacancies. The total image area analyzed for each sample configuration (total =10$^5$ nm$^2$) is listed in Table S4 in the Supporting Information while histograms of defect sizes for MoS$_2$ and WS$_2$ are given in Figures S5 and S6 in the Supporting Information, respectively. The results for different FIB exposure conditions including irradiation dose (see Figure 3), underlying substrate, and TMD material are summarized in Figure 4g,h. A direct dependence of defect density (Figure 4g), average defect area (Figure 4h), and median defect area (Figure S3, Supporting Information) on irradiation dose is observed (Figure 5). For example, suspended WS$_2$ (red circles, Figure 4g,h) has defect densities of ~0.01%, 0.08%, 0.2%, 0.9%, and 8% for increasing irradiation doses of 0, 5.1 × 10^{13}, 6.4 × 10^{14}, 1.9 × 10^{15}, and 3.1 × 10^{16} ions cm$^{-2}$, respectively. Such increases in defect area and density are expected due to the creation of new defects as well as the enlargement of existing defects as the number of raster scans (N$_r$) across the sample increases.

The application of different TMD materials and substrates offers additional methods of tuning defect properties. For example, under an irradiation dose of 5.1 × 10^{13} ions cm$^{-2}$, suspended monolayer MoS$_2$ (blue circles, Figure 4g,h) has a defect density and average area of 1.2% and 0.28 nm$^2$, respectively. These are significantly larger than the corresponding values of 0.08% and 0.12 nm$^2$ obtained for suspended WS$_2$. Similar trends are observed in supported materials and suggest that defects are more readily produced in MoS$_2$ compared to WS$_2$ possibly due to its lower displacement threshold energy. The relationship between average defect area and defect density (%) is presented for substrate-supported and suspended monolayer TMDs exposed to FIB irradiation in Figure 5a. We measure that the average defect area increases to ~1 nm$^2$, as the defect density increases to ~10%.

Figure 4g,h also demonstrates that the presence of a substrate causes lower defect densities and average defect areas. For instance, suspended MoS$_2$ displays an average defect area of 0.28 nm$^2$ while supported MoS$_2$ (blue diamonds, Figure 4g,h) has a lower value of 0.14 nm$^2$ under 5.1 × 10^{13} ions cm$^{-2}$ irradiation. Likewise, the defect density of 0.007% for supported WS$_2$ (red diamonds, Figure 4g,h) at this dose is an order of magnitude smaller than 0.08% for suspended WS$_2$.

We note that while supported WS$_2$ demonstrates a low defect density due to the occurrence of FIB-induced substitutional dopants (see Figure S7 in the Supporting Information), it displays an average defect area (0.08 nm$^2$) that is consistent with the size of a single transition metal vacancy (0.07 nm$^2$). In other words, for the same irradiation dose of 5.1 × 10^{13} ions cm$^{-2}$, we obtain single-atom defects in case of WS$_2$ and larger defects ranging from 0.05 to 0.4 nm$^2$ in the case of MoS$_2$ (see Figures S5 and S6 in the Supporting Information). This effect of larger defects in MoS$_2$ compared to WS$_2$, for a given dose is consistent for both suspended and supported material.

Recent simulations with kilovolt-range Ne$^+$ and Ar$^+$ ion irradiation of MoS$_2$ suggest that in addition to direct sputtering, further defects in supported MoS$_2$ are created due to backscattered ions and atoms sputtered from the substrate.$^{[18,23]}$ However, this is not expected for heavier ions such as Ga$^+$. This is consistent with the fact that we do not see larger/denser defects in supported materials and also shows that direct ion sputtering is more dominant than substrate-induced defects in Ga$^+$-irradiated TMDs. While FIB irradiation enables defect engineering with tunable densities and sizes down to a single atom, further experimental and theoretical studies are needed in order to clarify the different mechanisms that result in defects as a function of ion composition, TMD material, and different sample architectures.

3. Conclusion

In conclusion, we studied the effects of ion beam irradiation on the atomic structure and properties of monolayer TMDs and demonstrated how an industry-prevalent tool can be used to fabricate single-atom defects over millimeter-scale areas. In addition to ion beam current and exposure time, we have highlighted the importance of other overlooked parameters such as magnification/resolution, dwell time, and exposure technique under which the FIB irradiation is performed since this directly dictates the spatial distribution of defects, especially in 2D materials. It is important for future studies to recite the specifications of their ion irradiation parameters as presented in this study for any potential reproducibility and comparison. Using a precise set of parameters, we created defects with tunable sizes and densities over several orders of magnitude in MoS$_2$ and WS$_2$ for different sample configurations (i.e., suspended vs substrate-supported) across irradiation doses from 10^{13}–10^{16} ions cm$^{-2}$. SEM and AC-STEM revealed that average defect areas and densities were larger in suspended materials and in MoS$_2$ compared to WS$_2$. Raman spectroscopy under a 532 nm excitation revealed little to no variations in the phononic structure of FIB-irradiated TMDs while PL showed changes in the optoelectronic structure arising from increased defect states. The observations presented here promote future studies on utilizing defects for a thriving variety of potential applications in TMDs ranging from nanoporous membranes for gas and fluid transport to newly emerging ideas of quantum information processing.

4. Experimental Section

CVD Growth: Monolayer MoS$_2$ and WS$_2$ flakes were grown using CVD processes similar to previously reported methods.$^{[14,50]}$ Solutions of 0.2 (2%) sodium chlorate growth promoter and 18 (15) × 10^{-3} m ammonium heptamolybdate (metatungstate) were spun onto piranha-cleaned Si
substrates coated with 300 (150) nm of SiO₂, which were then loaded into the center of a 1 in. tube furnace (Thermo Scientific Lindberg/Blue M). For the MoS₂ growth, samples were heated under N₂ gas flow (700 scmc) at a rate of 70 °C min⁻¹ and held at 750 °C for 15 min. For WS₂ samples, were heated in Ar (100 scmc) at a rate of 65 °C min⁻¹ and held at 800 °C for 10 min, during which time 15 scmc of H₂ was also added. Additionally, 100 mg of sulfur precursor placed 22 mm from the substrates was kept at 180 °C during the growth procedures. Both substrates were rapidly cooled to room temperature by cracking open the furnace.

Device Fabrication: WS₂ and MoS₂ crystals were transferred from Si/ SiO₂ substrates to holey carbon TEM grids using a wet etch technique. Crystals were first coated with C4 PMMA while aqueous 1 M KOH solution was used to etch away the underlying substrate. After being washed in deionized (DI) H₂O, crystals were scooped onto TEM grids and dried for 30 min. Polymer liftoff and sample cleaning were performed using acetone and rapid thermal annealing in Ar:H₂ gas, respectively.

Gallium Ion Irradiation: Monolayer TMDs flakes were irradiated with a Ga⁺ sored ion beam JEOL Strata-Dual Beam instrument. The acceleration voltage of the ion beam was set to 30 kV and incident normal to the surface. The beam spot size was observed to be 100 nm for a flash second at 10 pA current. In order to produce atomic defects, an area of 250 × 250 µm was irradiated with the dwell time (16 µs), current (10 pA), and pixel resolution (1024 × 884) kept constant. The exposure was carried out in an imaging mode which followed a raster pattern where the beam sequentially exposed each pixel in a row. FIB FEI Strata DB 235 has an option to "grab frame" which takes a single scan at a set resolution; this option was employed for all the scans. The dose was varied by changing the number of scans. Suspended and substrate-supported samples were exposed to FIB irradiation while sitting on holey carbon TEM grids and Si/SiO₂ substrates, respectively.

AC-STEM Imaging: MoS₂ and WS₂ samples were imaged using a Cs-corrected JEOL ARM 200CFC STEM operating at 80 kV. Images were obtained using a HAADF detector with a collection angle of 6.0 < 2 s, and electron dose (≈ 10⁶ e⁻ cm⁻² s⁻¹) was applied to etch away the underlying substrate. After being washed in deionized (DI) H₂O, crystals were scooped onto TEM grids and dried for 30 min. Polymer liftoff and sample cleaning were performed using acetone and rapid thermal annealing in Ar:H₂ gas, respectively.

AC-STEM Image Analysis: All images from various doses were analyzed using Fiji or ImageJ software. Custom macros were built for studying large number of files. Since images for doses of 1.9 × 10¹⁵ and 3.1 × 10¹⁶ ions cm⁻² consisted of large/nanoporous defects, a repeatable macro was used to calculate the number of defects (see the Supporting Information of ref. [8] for more details). In order to reduce noise and increase visibility of the atoms, ImageJ was used, and a Gaussian blur filter with 0.03 nm of blurring radius was applied. Prior to defect counting from AC-STEM images, further noise reduction was applied using the "remove outliers" process. At this point, AC-STEM signal from sulfur atoms was spread. Cleaned images were then subjected to the "local threshold" process with the Sauvola method to obtain binary images which consisted of black-colored defect regions and white-colored TMD regions. Statistical analysis of the defect area and the number of defects were carried out using these binary images.

Images for doses of 0, 5.1 × 10¹⁵, and 6.4 × 10¹⁶ ions cm⁻² primarily consisted of smaller/single-atom defects such that filters and noise reduction tools were utilized as required by each image. The core procedure for image analysis remained the same as above. Overall, a Gaussian blur filter (radius = 0.03–2 nm) was applied to increase the signal of the transition metal atom. The sulfur site vacancy and sulfur defects were ignored due to lack of contrast caused by polymer contamination. Additional noise reduction tools such as "background subtraction" were employed if the resultant image yielded better contrast. The goal was to count the individual defect sizes (<0.06 nm², single W defect) from each image using "analyze particle" in ImageJ.

Raman and PL Spectroscopy: Raman and PL spectra from multiple pristine and FIB-irradiated samples were obtained in an NTEGRA Spectra system with 532 nm excitation and CCD detector. Raman and PL spectra were fit to three vibrational Lorentzian modes: 2LA(M) at 350 cm⁻¹, E₂g(Γ) at 356 cm⁻¹, and A₁g(Γ) at 418 cm⁻¹. PL data (intensity vs energy) were fit to three excitations: defect (X₀) at 1.88 eV, trion (X₁) at 1.96 eV, and exciton (X₂) at 2.02 eV.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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2D materials, defects, ion beam irradiation, nanopores, transition metal dichalcogenides

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