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Long-Term Exposure of MoS₂ to Oxygen and Water Promoted Armchair-to-Zigzag-Directional Line Unzippings

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Abstract: Understanding the long-term stability of MoS₂ is important for various optoelectronic applications. Herein, we show that the long-term exposure to an oxygen atmosphere for up to a few months results in zigzag (zz)-directional line unzipping of the MoS₂ basal plane. In contrast to exposure to dry or humid N₂ atmospheres, dry O₂ treatment promotes the initial formation of line defects, mainly along the armchair (ac) direction, and humid O₂ treatment further promotes ac line unzipping near edges. Further incubation of MoS₂ for a few months in an O₂ atmosphere results in massive zz-directional line unzipping. The photoluminescence and the strain-doping plot based on two prominent bands in the Raman spectrum show that, in contrast to dry-N₂-treated MoS₂, the O₂-treated MoS₂ primarily exhibits hole doping, whereas humid-O₂-treated MoS₂ mainly exists in a neutral charge state with tension. This study provides a guideline for MoS₂ preservation and a further method for generating controlled defects.



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Keywords: molybdenum disulfide; line defect; unzipping; zigzag; oxygen

1. Introduction

Molybdenum disulfide (MoS₂) is a representative of the transition metal dichalcogenide (TMDC) MX₂ family which has sandwiched layer structures with the transition metal M (groups four, five, and six atoms) located between chalcogen atoms X (S, Se, and Te). Owing to the presence of a band gap associated with its few-atom-thick layers held together by van der Waals forces, MoS₂ possesses interesting optical [1–3], spin–valley polarization [4,5], and catalytic properties [6–8]. In the context of its optical properties, neutral MoS₂ displays two features known as A (~1.89 eV) and B (~2.08 eV) excitons [1,2,9], which are associated with direct transitions from the highest spin-split valence bands to the lowest conduction bands. Furthermore, the A exciton has subcomponents in the form of a charge-neutral exciton band A⁰ at 1.89 eV and a lower-lying charged exciton (trion) band A[−] at 1.86 eV, whose relative intensities and positions are dependent on the doping [10–12] and strain (ε) [11,13–16] of MoS₂. Applications of the optoelectronic properties of MoS₂ require an understanding of its long-term stability.

MoS₂ is amenable to both electron (*n*) or hole (*p*) doping [10,11] and it can possess strain (ε) [11,13–16]. The effects of environmentally abundant oxygen and water on the optoelectronic properties of MoS₂ have been studied [17–19], but how these species affect the doping and ε properties of MoS₂ under ambient conditions remains largely unknown, and this is an important issue. Treatments under harsh oxidative conditions such as with oxygen plasma [18], UV-ozone [20], and high-temperature annealing (>300 °C) [18,21,22] are known to induce oxidation of the basal plane of MoS₂. Following these treatments, the basal plane of MoS₂ exhibits reduced photoluminescence (PL), while edges and cracked regions display increased PL, suggesting that oxidation plays different roles in governing the properties of the basal plane and periphery. Moreover, O₂ incubation of up to one year

leads to random cracks and defects [19]. In contrast, physisorption of oxygen by MoS₂ activated at 450 °C under vacuum results in a large basal-plane PL enhancement [17] caused by MoS₂-to-O₂ charge transfer. Because chemisorbed oxygen modulates the optical properties of MoS₂ differently from physisorbed oxygen, it is important to gain an understanding of how chemical oxidation controls the doping and ϵ , which in turn govern the band-gap structure of MoS₂ [12].

Theoretical study [23] suggests that the basal plane of MoS₂ exhibits a large kinetic barrier (i.e., 1.6 eV) for O₂ chemisorption, whereas vacancies (i.e., sulfur vacancies) at the surface of MoS₂ reduce the barrier to 0.8 eV. The experimentally determined activation energy for bulk MoS₂ oxidation (0.54 eV and 0.79 eV) [22,24] is somewhat lower than the theoretically predicted value. However, recent scanning tunneling microscope measurements [25] show that point-like oxygen-substitution reactions producing oxygenated MoS₂ occur spontaneously, even under ambient conditions. Along with the fact that Mo-terminated edges of MoS₂ readily react with O₂ [26], these findings indicate that oxygenated MoS₂ possesses various point defects which are randomly distributed over the plane.

The investigation described below was designed to address this issue. For this purpose, chemical vapor deposition (CVD)-grown MoS₂ crystals were exposed to four different conditions for two weeks: N₂, N₂ with 75% relative humidity (N₂-75RH), O₂, and O₂ with 75% relative humidity (O₂-75RH). Using various methods, including Raman spectroscopy, photoluminescence (PL) spectroscopy, and atomic force microscopy (AFM), we observed that the basal plane of MoS₂ possessing tensile strain (ϵ_T) associated with its preparation using CVD, undergoes zigzag (zz)-directional unzipping upon long-term exposure to an oxygen atmosphere. Specifically, during the initial phases of exposure to O₂ and O₂-75RH, MoS₂ crystals display initial macroscopic armchair (ac)-directional micrometer-scale defects near triangular edges. Following increased exposure times of up to a few months, the initial ac-directional defects near the periphery change into zz-directional unzipping in the basal plane. This unique unzipping behavior is associated with the susceptibility of S defects in the basal plane to tension caused by oxidation. Moreover, Raman and PL spectroscopic studies show that changes occurring in the optoelectronic properties of MoS₂ upon chemical oxidation are a consequence of changes in ϵ_T and doping.

2. Materials and Methods

2.1. Materials and Instrumentation

MoO₃ (product no. 267856, ACS reagents, purity \geq 99.5%) and sulfur (product no. 13803, purity \geq 99.5%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sulfur was further recrystallized using vacuum sublimation at ca. 10^{-3} torr, as described previously [27]. Sodium cholate (SC), with a purity of over 98%, was purchased from TCI (Tokyo, Japan) and used as a surfactant and an adhesion promoter to a silicon substrate. Deionized water with a resistivity greater than 18 M Ω was used. All gases, including N₂, Ar, and O₂ with purities of over 99.99% were obtained from Donga Gas (Jinju, Korea). The 285-nm thick SiO₂/Si substrates (lot no. 7400397-601, Shin-Etsu, Tokyo, Japan) were spin-coated with MoO₃ and converted to MoS₂. The as-received wafer was cut into pieces of size 1.0×1.0 cm² and further rinsed with methanol, acetone, and isopropanol while undergoing bath sonication, then subjected to drying with a N₂ stream. Optical microscope (OM) images were obtained using an upright fluorescence microscope (BX-51, Olympus, Tokyo, Japan) with a CMOS camera (3.6 μ m/pixel, 1280 \times 1024 pixels, part no. DCC1645C, Thorlabs, Newton, NJ, USA) and a light-emitting diode light source (cold white color, part no. MCWHL2, Thorlabs) with an optional dichroic cube set (MWG, Olympus), which could image the 660 nm PL of MoS₂. SEM images were acquired using field-emission SEMs (SU8000, Hitachi or 7610f-plus, JEOL Ltd., Tokyo, Japan) operating at an acceleration voltage of 5 kV.

2.2. Precursor Preparation

MoS₂ growth involved the use of SC as adhesion promoter and surfactant for MoO₃ powder, according to the procedure described in the literature [28]. Aqueous MoO₃ dispersion was prepared by sonication using SC as a surfactant. Briefly, 20 mM MoO₃ was added to 1 wt. % SC in 100 mL of water. The suspension was subjected to bath sonication for 1 h (70 W, Branson1519, Brookfield, CT, USA) followed by tip sonication for 2 h (300 W amplitude, probe tip diameter: 13 mm, VCX 750, Sonics and Materials, Newtown, CT, USA). The dispersion was centrifuged using a table-top centrifuge (Wisepin CF-10, Daihan Scientific Co, Ltd., Wonju-si, Korea) to collect an 80% supernatant. 100 µL of the MoO₃ dispersion was spin-coated at 3000 rpm for 80 s by drop-casting on precleaned SiO₂ on a Si substrate. Sulfur was prepared by vacuum sublimation. Briefly, 1 g of sulfur was placed at the bottom of a sublimation kit with a cold finger. The sublimation temperature was set to 200 °C under vacuum (10^{−3} torr).

2.3. Growth of MoS₂ Crystal

MoS₂ was prepared by using a hot-wall CVD apparatus [29] operating at atmospheric pressure, with the aforementioned spin-coated MoO₃ and the sublimed sulfur powder as precursors, modified from the previous study [27]. Prior to the MoS₂ growth, a quartz tube in a tube furnace was pre-annealed for 30 min at 1000 °C with a 20 standard cubic centimeter per min (sccm) Ar flow to remove any physisorbed water, in a CVD chamber. After cooling, the MoO₃ spin-coated substrate was loaded into the hot zone of a tube furnace with the SiO₂ side face up, and an alumina boat containing 30 mg of sulfur was placed in an upstream position. Crystal growth was conducted at 750 °C for 20 min, at which time the alumina boat containing the sulfur reached ~220 °C. The substrate was then cooled to room temperature.

2.4. Environmental Control of MoS₂

Four different environments (i.e., N₂, N₂-75RH, O₂, and O₂-75RH) were prepared using a Schlenk line technique and a septum-capped vial, with precautions as follows. For the N₂-75RH or O₂-75RH environments, a vial containing saturated brine solution maintaining 75RH [30] was bubbled with the N₂ (or O₂) for 90 min using a syringe to remove any O₂ dissolved in the solution. For the N₂ or O₂ environments, a vial containing a moisture-absorbing silica gel was initially flame-dried thoroughly with a hand-held torch while a vacuum (10^{−3} torr) was pulled, and the sample was subsequently treated with a cycle of N₂ (or O₂) purging/vacuum, at least four times. Each sample was incubated for two weeks prior to any measurements. A further one month of incubation was conducted for observation of long-term changes.

2.5. Raman and PL Measurements

The samples were loaded into an environmental chamber (TS1000V-17/3 with T96-S, Linkam Scientific Instruments Ltd., Redhill, UK) which allowed observation of the sample through a coverslip while measurements were made. Raman and PL spectra were obtained using a micro-Raman spectroscopy setup with a backscattering geometry, as described in the literature [27,29,31]. Briefly, a spectrometer (Triax 320 with 1800 gr/mm) and coverslip-tolerant 40× objective (UPlanSApo, N.A.: 0.95, Olympus) were utilized to obtain the Raman and PL spectra. Calibration for Raman spectroscopy was conducted with multiple Hg/Ar lamp peaks using a light source (HG-1, Ocean Optics, Oxford, UK), according to the procedure described in the literature [29]. The Si peak at 520.89 cm^{−1} was used as an internal reference and an intensity-normalizing peak. Laser power was maintained below 0.06 mW to minimize any light-induced damage. The obtained Raman and PL spectra were further deconvoluted with Lorentzian fitting. Especially in the PL spectra, A⁺, A[−], and B excitons were fitted to an unrestricted position and area.

2.6. Construction of Coordination System for ε - n Plot

The Raman origin ($(E_{2g}^1, A_{1g}) = (385.3 \text{ cm}^{-1}, 404.8 \text{ cm}^{-1})$) for the ε and n plot was taken from the values derived from suspended MoS₂ in the literature [11]. Biaxial ε vs. n coordinates were introduced by modification of the ε - n diagram described previously [32–34], as in the case of graphene [35]. Since CVD-grown MoS₂ exhibits biaxial ε_T [36], biaxial ε_T and Raman responses were utilized [11]. The changes in in-plane vibration E_{2g}^1 ($\Delta\omega_E$) and out-of-plane vibration A_{1g} ($\Delta\omega_A$) and their variations were $\Delta\omega_E = -5.2 \text{ cm}^{-1}/\%$ and $\Delta\omega_A = -1.7 \text{ cm}^{-1}/\%$. Using the formula $\gamma = [\omega - \omega_0]/[2\varepsilon\omega_0]$, we determined the Grüneisen parameters γ for the Raman modes to be $\gamma_{E_{2g}^1} = 0.68$ and $\gamma_{A_{1g}} = 0.21$, with the slope per ε or $\Delta\omega_A/\Delta\omega_E = 0.35$ [11]. In the case of n , vibrational changes in E_{2g}^1 and A_{1g} and their extents were $\Delta\omega_E = 0.21 \text{ cm}^{-1}$ and $\Delta\omega_A = 1.97 \text{ cm}^{-1}$ per $1 \times 10^{12} \text{ cm}^{-2}$, with the slope of n with $\Delta\omega_A/\Delta\omega_E = 9.4$ [35].

2.7. AFM Measurements

AFM height and phase images were obtained by using a tapping mode with an NX-10 AFM (Park Systems, Suwon, Korea). Al-coated silicon cantilevers (force constant: 37 N/m, resonance frequency: 300 kHz, ACTA-20, App Nano, Mountain View, CA, USA) were used. Typically, 512×512 pixels for a $40 \mu\text{m}$ length were routinely acquired at a speed of 0.2 Hz. The XEI program (Park Systems, Korea) was used to flatten topographies along the fast axis of scan using a polynomial, by excluding speckles of size 5 nm.

3. Results

CVD-grown triangular MoS₂ crystals were single crystals terminated with zz edges [37] and were used to probe the effects of oxidation reactions on the morphological and optoelectronic properties. The MoS₂ crystals were grown by CVD, using the procedure developed in our previous investigation [27], starting with MoO₃ and sublimed sulfur (see Materials and Methods section). First, a well-dispersed aqueous MoO₃ dispersion containing 1 wt. % sodium cholate (SC) as a surfactant and adhesion promoter [28] was spin-coated onto a 285 nm thick SiO₂/Si substrate. After annealing at 1000 °C to eliminate adsorbates, a quartz tube was loaded with the MoO₃-coated substrate and a boat containing freshly sublimed sulfur. A 20 sccm Ar flow was used as a carrier gas and the temperature of the hot zone was raised to 750 °C for 20 min, to promote MoO₃ reduction with sulfur. The growth of the MoS₂ crystals was terminated by cooling the tube to room temperature for 40 min while maintaining the Ar flow.

The Initial characterization of the as-grown MoS₂ as a control was conducted using various methods, including optical microscopy (OM), atomic force microscopy (AFM), photoluminescence (PL) imaging/spectroscopy, and Raman spectroscopy (see Figure 1A–E). Inspection of the representative CVD-grown MoS₂ via the OM image (Figure 1A) shows the MoS₂ crystal as a ca. $46 \mu\text{m}$ long equilateral triangle with uniform contrast. The corresponding AFM height image (Figure 1B) shows that the crystal has a clean surface and a 0.70 nm edge height, indicating a monolayer of MoS₂ [37]. Notably, the PL image (Figure 1C) shows a gradient of PL brightening from the center to the peripheral regions. Other researchers [16,36] have found that such gradual PL intensity (I_{PL}) and peak position (λ) changes, as well as shifts in the Raman bands in CVD-grown MoS₂, occur when proceeding from the center to the peripheral regions owing to differences in tensile strain (ε_T) caused by thermal expansion coefficient differences between the Si substrate and the MoS₂. Since biaxial ε_T shifts the excitonic A band by $-99 \text{ meV}/\%$ [11], the observed λ of 675 nm in the PL spectrum at the center (Figure 1D) suggests the presence of substantial ε_T (i.e., 0.4%) compared to that at peripheral regions where the λ is ca. 660 nm. The positions of the two characteristic Raman bands of the in-plane vibration E_{2g}^1 and out-of-plane vibration A_{1g} are known to be sensitive to ε_T , and E_{2g}^1 undergoes larger downfield shifts compared to A_{1g} with increasing ε_T [11,13–16,38]. The Raman spectrum of the central MoS₂ region (Figure 1E) contains E_{2g}^1 at 383.1 cm^{-1} and A_{1g} at 406.2 cm^{-1} [39], whereas the spectra

at the peripheries contain upshifted 383.6 cm^{-1} and 406.8 cm^{-1} bands, which is in good agreement with reported spectra of MoS_2 under ε_T . The results suggest that ε_T is a major contributor to the anisotropy present in the PL and Raman spectra of the as-prepared MoS_2 crystal. Immediately after characterization, the MoS_2 crystals were incubated under the four different atmospheres N_2 , N_2 -75RH, O_2 , and O_2 -75RH for two weeks (see Figure S1A in the Supplementary Materials (SM) for schematics of the environmental incubation processes).

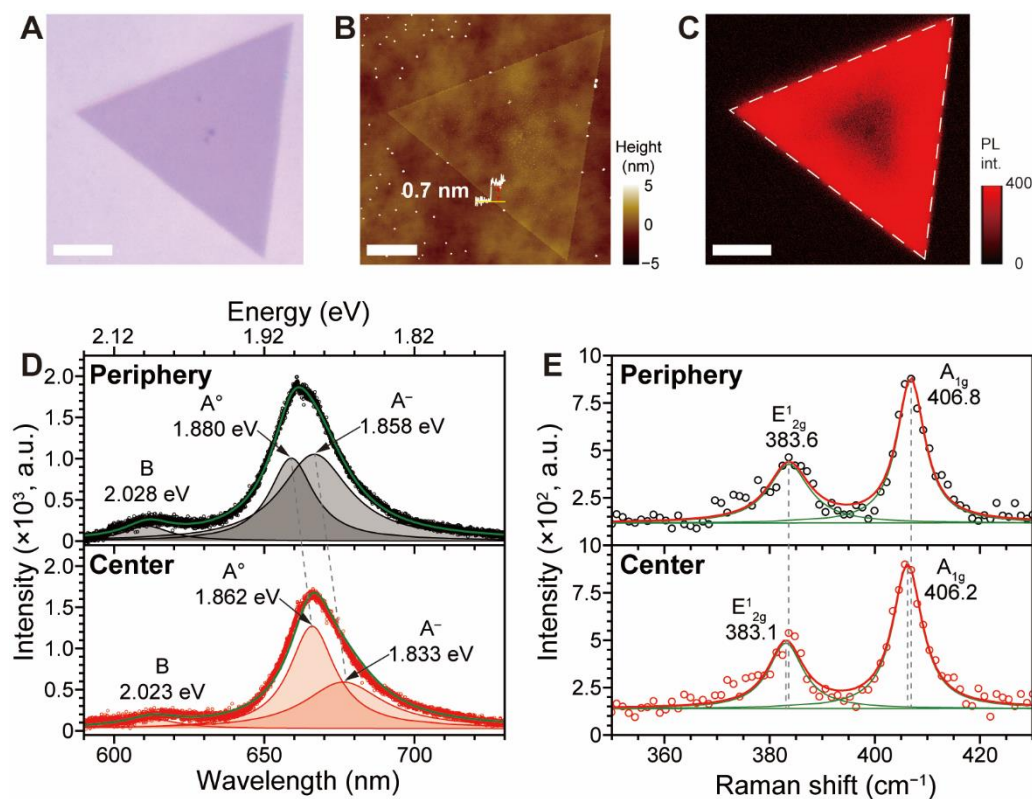


Figure 1. The characterizations of the as-grown MoS_2 grains by various methods: (A) OM image; (B) the corresponding AFM height topography; (C) PL image with emission filtered using a 660 nm bandpass filter. Scale bars: 10 μm . (D) PL spectra obtained from central and peripheral parts of MoS_2 and its Lorentzian deconvolutions to indicate A^+ , A^- , and B, respectively. Dashed lines are drawn for comparison of the position. (E) The corresponding Raman spectra (circles) and its Lorentzian deconvolutions (green).

The effects of various environments on the morphology of MoS_2 were first examined using AFM (Figure 2a–d). All crystals under the four conditions have triangular shapes and heights (white traces) varying from 0.6 to 0.85 nm, indicating monolayer MoS_2 . While the N_2 and N_2 -75RH samples (Figure 2a,b) have topographies similar to the as-grown material, surprisingly, the MoS_2 subjected to an O_2 atmosphere (Figure 2c) displays few micrometer-long directional line defects originating from the edges. These defects are more visible in the phase image (Figure S2C,D), compared to those from N_2 -treated samples. Notably, the angles of the line defects against zz edges were ca. 30, 90, and 150° (see inset of Figure 2c), suggesting ac-directional line defects. This result contrasts with the report in [19] that aging of CVD-grown MoS_2 and WS_2 under ambient environmental conditions leads to random cracks and defects. This result suggests that the conditions for CVD growth affect the oxidative defects. Furthermore, the O_2 -75RH-treated sample (Figure 2d) shows that unzipping occurs from the edges in the ac directions. The inset in Figure 2d shows that unzipping, instead of occurring at ac line defects, occurs at the edges, and that crack directions are at 120° from each other (see red arrows for the intersection). This result

suggests that dry and humid O_2 oxidations promote stepwise transformations in the MoS_2 crystal, from line defects to eventual unzipping.

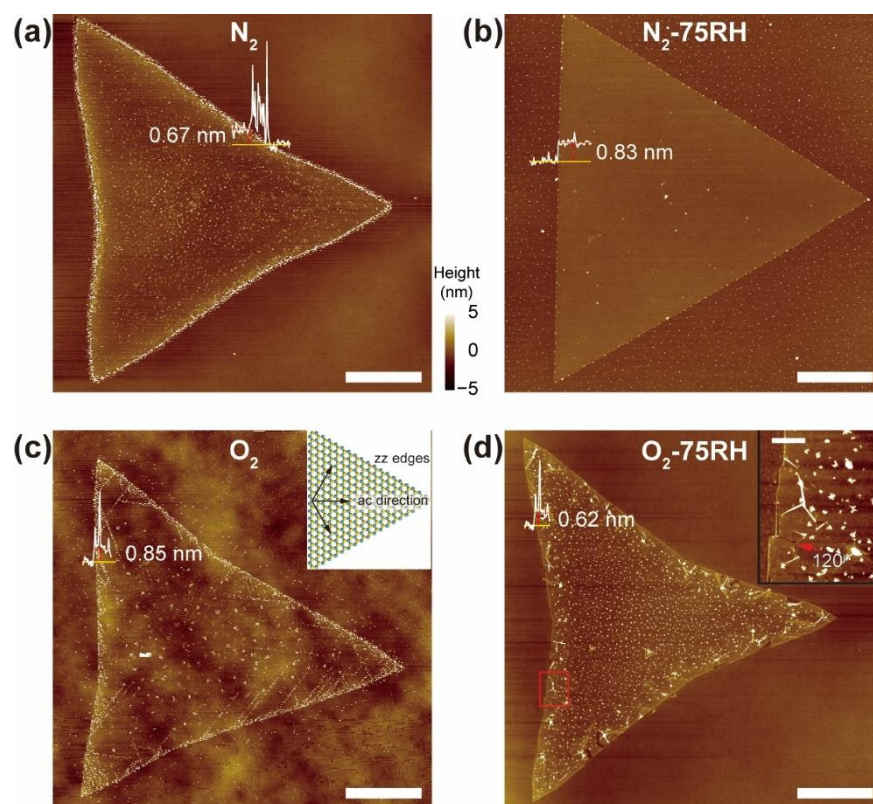


Figure 2. AFM height images of MoS_2 crystals treated with: (a) N_2 ; (b) N_2 -75RH; (c) O_2 ; (d) O_2 -75RH. White traces are height profiles of MoS_2 . Inset of (c): crystallographic orientation of line defects of O_2 -treated MoS_2 , with Mo and S color-coded in green and yellow, respectively. Inset of (d): AFM height image of directional unzipping from MoS_2 edges in red box in (d). Scale bar: 10 μm for (a–d); 1 μm for the inset of (d).

Because unzipping typically begins at the mechanically weakest points, the line defects and the subsequent unzipping are likely to be correlated with the ϵ_T of the MoS_2 , which in turn is associated with the optical properties of the MoS_2 crystal. Figure 3A–D show the corresponding PL images of the samples. The images show that the I_{PL} for the N_2 -treated crystal gradually increases from the center to the periphery, suggesting that the ϵ_T behavior is similar to that of as-prepared MoS_2 . Interestingly, the N_2 -75RH sample (Figure 3B) has a uniform I_{PL} at both the center and periphery. A humid environment is known to form entrapped water between graphene and the substrate [40–42] or MoS_2 and the substrate [43]. To confirm that such entrapped water is related to the uniform I_{PL} , AFM height measurements of the basal plane from the N_2 -75RH sample (Figure S3A) were made. Water was entrapped evenly over the sample, and water entrapped regions is 0.5 nm thick and a few micrometers wide (Figure S3B) were entrapped between the MoS_2 and the substrate. This was a phenomenon not seen in the N_2 -treated sample. These results are in agreement with the previous study, which demonstrated that a monolayer of water adhered under the MoS_2 surface to a thickness of ~ 0.5 nm [43], as seen in other two-dimensional materials such as graphene [40–42]. This result suggests that the increased height induced by water and the subsequent strain might increase ϵ_T and lead to the observed uniform I_{PL} over the MoS_2 crystal.

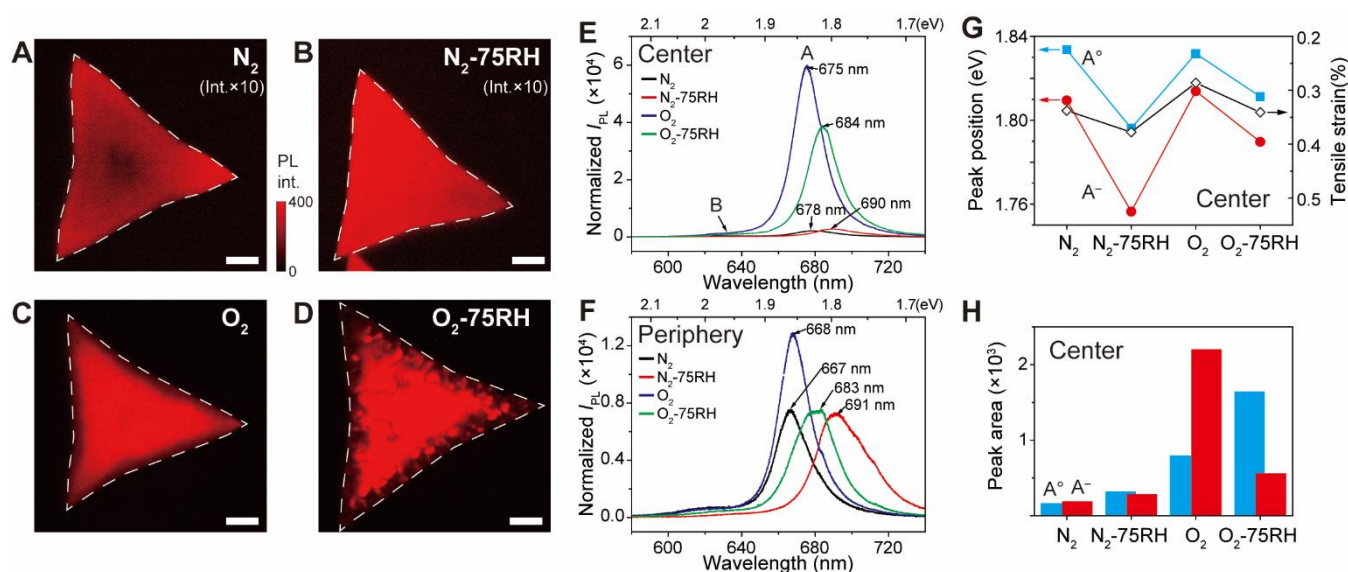


Figure 3. PL images, spectra, and analysis at central and peripheral positions of MoS₂ crystals after incubation for two weeks under each condition. PL images from: (A) N₂; (B) N₂-75RH; (C) O₂; (D) O₂-75RH samples. Scale bar: 10 μ m. PL intensities of (A,B) were multiplied for visual comparison. Normalized PL spectra from (E) central, and (F) peripheral regions with respect to the 520.89 cm⁻¹ Si peak. (G) PL peak position and (H) PL peak-area changes of A⁰ and A⁻ derived by each treatment from central regions.

The PL image from the O₂-treated sample (Figure 3C) shows that I_{PL} gradually increased from the periphery to the center, a trend that is opposite to that occurring in the N₂-treated sample. The low I_{PL} near the periphery overlaps with the AFM-observed line defects present in the O₂-treated MoS₂. These results suggest that, unlike for samples treated using harsh oxidations [18,20,22], physisorbed O₂ at the center of the crystal actually results in an enhancement of I_{PL} , which is in accordance with the previous report [17]. In contrast, chemically oxygenated species evidenced by line defects form near the periphery and result in the reduced I_{PL} . Similar to the O₂ sample, the crystal incubated under the O₂-75RH condition (Figure 3D) displays an I_{PL} that is brighter at the center and dimmer and more irregular at the periphery. Such spatial inhomogeneity originates from unzipping and folding of the MoS₂, as evidenced by comparing the PL and AFM images.

Qualitative information was gained about doping and ϵ_T by analyzing the PL spectra from the central (Figure 3E) and peripheral (Figure 3F) regions of the incubated MoS₂ crystals. Inspection of the spectra of the basal planes (Figure 3E) treated using humidified atmospheres (i.e., N₂-75RH and O₂-75RH) show that the λ values of the A bands display a bathochromic shift from 24 to 32 meV compared with those treated with N₂ and O₂ only. Moreover, the basal plane of the O₂-treated sample exhibits an I_{PL} about 11 times larger than that of the crystal exposed to N₂. The spectra from the peripheries (Figure 3F) show that while the peripheral I_{PL} s of the O₂ and O₂-75RH samples were lower than those associated with the basal plane, the peripheral I_{PL} of the N₂ sample was increased and that of N₂-75RH was unchanged. These results suggest that the center and periphery of the MoS₂ crystal experience different degrees of doping and ϵ_T .

The λ and I_{PL} of A⁰ and A⁻ peaks in the PL spectra of MoS₂ are dependent upon ϵ and n , and this serves as a foundation for deciphering the roles that O₂ and H₂O play in forming peripheral defects and unzipping [12,36]. To elucidate these values, the PL spectra at the central positions of the MoS₂ crystals were deconvoluted using Lorentzians (shaded area), as shown in Figure S4. As evidenced by the dashed lines, the λ values and peak areas of A⁰ and A⁻ underwent a systematic change for crystals treated using each condition. For example, among the four samples, the dry N₂- and O₂-treated samples exhibited the most blue-shifted λ values for the A⁰ and A⁻ peaks, suggesting that they are associated

with a smaller ε_T . In addition, the λ values of the A^0 and A^- (Figure 3G) bands of samples treated using humid atmospheres exhibited proportional red shifts. A comparison of the relative areas of the A^0 and A^- bands (Figure 3F), which provides information about the charge state of MoS_2 [10], shows that peak areas are much greater in the spectra of O_2 and O_2 -75RH samples. Moreover, the comparison shows that water induces an increase in the population of the charge-neutral A^0 state, and O_2 causes an increase in the area of the charged A^- state. This result is opposite to that of a previous study suggesting that water has a p -doping effect [43], and suggests that water promotes neutral exciton formation while physisorbed O_2 facilitates trion formation. Similar analysis of the PL spectra of peripheral regions (Figure S5A–C) shows that analogous but lesser shifts in λ occur (Figure S5B) and that the relative areas of A^0 and A^- bands are relatively smaller compared to those in the spectra of basal planes. These observations in peripheral regions are in line with doping created by line defects and unzipping [19].

Raman spectroscopy is a powerful tool for gaining an understanding of the quantitative ε and n - or p -doping density of MoS_2 , because these parameters are closely related to chemical bond strengthening or weakening, which alters the vibrational behavior. A previous study [35] showed that ε and n contributions in graphene are quantitatively associated with two Raman bands (i.e., G and 2D modes). A similar concept has been utilized to evaluate ε and n for monolayer MoS_2 [32–34]. To apply this treatment, we chose the frequencies from the spectra of suspended MoS_2 as an origin for the unperturbed, pristine state [44,45]. Utilizing the published values for ε and n of monolayer MoS_2 [11,46], an ε – n coordinate system in units of % and $1 \times 10^{12} \text{ cm}^{-2}$ (Figure 4c) was devised in a coordinate framework comprising two prominent Raman bands (E_{2g}^1 , A_{1g}). Specifically, Figure 4c is a plot of ε (black dashed line) and n (red dashed line), with an origin $O = (E_{2g}^1, A_{1g}) = (385.3, 404.8)$, corresponding to pristine MoS_2 . In addition, ε_C values are compressive strains, and n and p denote n and p doping, respectively. Representative crystal spectra acquired from the center and periphery are shown in Figure 4a,b. It is noteworthy that Raman bands near 275 cm^{-1} corresponding to MoO_3 are not present [21]. As shown in Figure 4c, the central (peripheral) position of the N_2 sample displays two bands at 381.8 (383.1) and 403.8 (403.8) cm^{-1} . In terms of strain doping, the central part has ε – n coordinates of $(0.34, -0.4)$, and the peripheral part has coordinates of $(0.2, 0.7)$. This result suggests that while ε_T decreases from the center to the periphery, in accordance with previous findings [27,36], a slight p - to n -doping transition occurs simultaneously. The doping of the N_2 -treated sample is likely to be related to the interaction of the basal MoS_2 with the SiO_2/Si substrate, which acts as a p dopant [29,35]. Compared to the N_2 -treated sample, the N_2 -75RH sample (orange) exhibited much higher ε_T values (from 0.37 to 0.42%) at both the central and peripheral positions and experienced only a negligible doping density change. This result further supports the idea of the presence of water-induced tensile strain. This result underscores the advantage of utilizing an ε – n plot for analyzing the spectroscopic data, because otherwise the p -doping and ε_T results are both included in a similar downshift in vibrational frequencies [11].

Inspection of the ε – n plot shows that the two prominent Raman bands (E_{2g}^1 and A_{1g}) associated with the central and peripheral regions of the O_2 - and N_2 -treated MoS_2 crystals exhibited nearly similar movement along the p -doping axis. This observation suggests that O_2 treatment results in p -doping, which is in agreement with the occurrence of charge transfer from MoS_2 to physisorbed O_2 [17]. Finally, the O_2 -75RH treated sample has ε – n coordinates of $(0.4, -1)$ and $(0.25, 1)$ for the central and peripheral positions, respectively. The different doping densities with different signs observed for the central and peripheral regions are closely connected to the existence of peripheral unzipping and folding, which decrease ε_T . The increase in ε_T and the charge neutralization taking place in changing from O_2 to O_2 -75RH, in conjunction with the PL results, indicate that treatments with O_2 and H_2O lead predominantly to p -doping and ε_T , respectively.

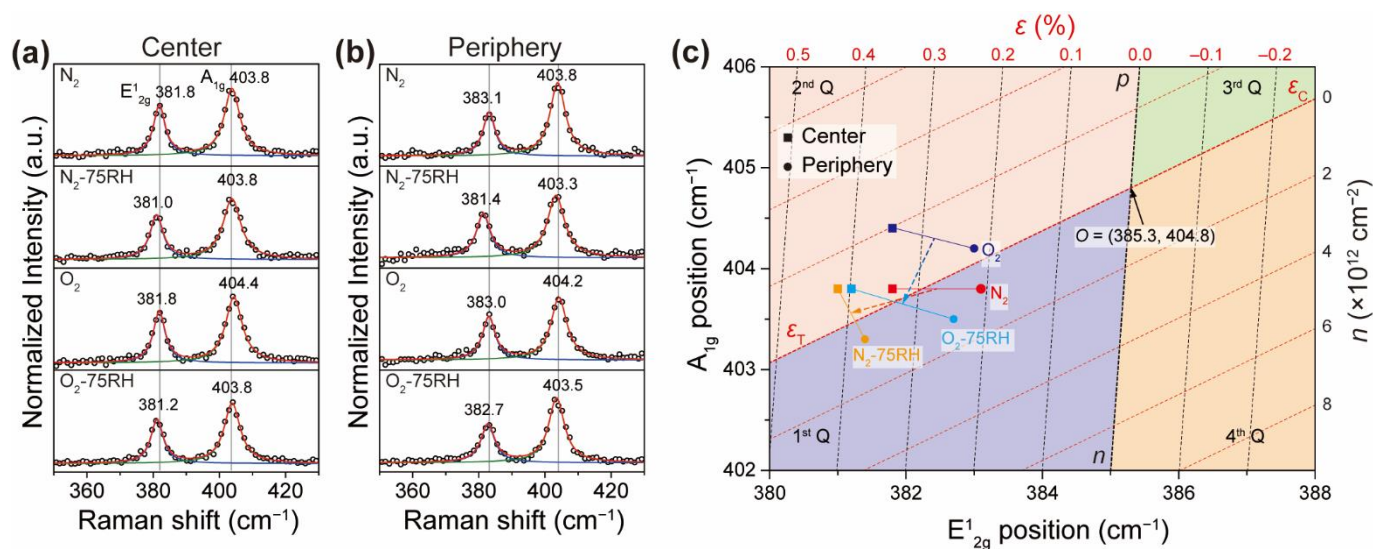


Figure 4. Raman spectra of (a) central and (b) peripheral regions from the incubated MoS₂ crystals. Excitation wavelength: 532 nm. Raman spectra were deconvoluted by Lorentzian shape analysis and normalized according to the Si peak at 520.84 cm⁻¹ nm. (c) Plot of ϵ (black dashed line) and n (red dashed line) with origin $O = (E_{2g}^1, A_{1g}) = (385.3, 404.8)$ extracted from Raman spectra of suspended MoS₂ sample. Here, ϵ_T and ϵ_C stand for tensile and compressive strains, respectively, and n and p denote n and p doping, respectively. Solid lines between Raman points are drawn for grouping the same samples.

The results suggest that regardless of the environmental conditions used, MoS₂ samples possess considerable ϵ_T , albeit with different doping densities. However, only O₂-treated crystals experienced line defects and unzipping. This observation prompted us to perform an experiment in which MoS₂ crystals were exposed to O₂ and O₂-75RH environments for three months. Figure 5A,D show the respective AFM phase images, facilitating the visualization of unzipping. Remarkably, both samples show zz-directional line unzipping with respect to zz-terminated edges. The O₂-treated sample had a wider unzipping width compared to the O₂-75RH-treated MoS₂. Unzippings occurred at 120° with respect to each other. Although unzipping near the periphery is ac-directional with respect to the edge, it changes to the zz direction in the basal plane. This finding stands in stark contrast to the etched triangular pit of exfoliated MoS₂ prepared by high-temperature annealing (i.e., 300 °C) [21,47] and the random cracks incubated at room temperature [19]. Inspection of the normalized PL spectra of the O₂-incubated crystal (Figure 5B) shows that both unzipping and basal positions occur at ~670 nm, which corresponds to the near-absence of tension. Similarly, both Raman spectra (Figure 5C) show similar interpeak separations (i.e., ~25 cm⁻¹). A similar unzipping behavior but associated with a larger difference in ϵ_T was observed for the O₂-75RH-treated sample. In this case, the PL peak position (Figure 5E) of the unzipped region (black circle in Figure 5D) displayed a large blue shift (20 nm) compared to that from the basal plane, showing that the ϵ_T was relieved. Raman spectra analysis (Figure 5F) further supported the fact that the basal plane has a larger ϵ_T (larger interpeak separation) compared to that for the O₂-treated crystal.

These defects are different from the defects that can exist in the as-grown state. Figure S6A,B show PL images of the as-prepared MoS₂ sample and the same sample after incubation. Bright PL originates from the crack or unzipping regions, showing an increase in line defects. However, the existing cracks in the as-prepared sample appear to be random, in contrast to the precise zz-directional unzipping after O₂-75RH treatment. The AFM phase image (Figure S6C) clearly shows that the O₂-75RH-treated sample had precise turns and angles of unzipping with respect to the edges. In addition, proceeding from the edges to the center slowly changed the unzipping direction from ac to zz lines. Figure S7 shows the AFM phase images from O₂- (Figure S7A–C) and O₂-75RH-treated

(Figure S7D–F) samples. Irrespective of the presence of H₂O, nearly all the ac unzipping at the edges changed into the zz direction in the basal plane within a few micrometers. Interestingly, the width of the ac unzipping is much less than that of the zz unzipping, presumably owing to the ϵ_T difference in the central and peripheral regions. Along with the PL and Raman studies, this finding strongly supports the fact that directional unzipping is dependent on ϵ .

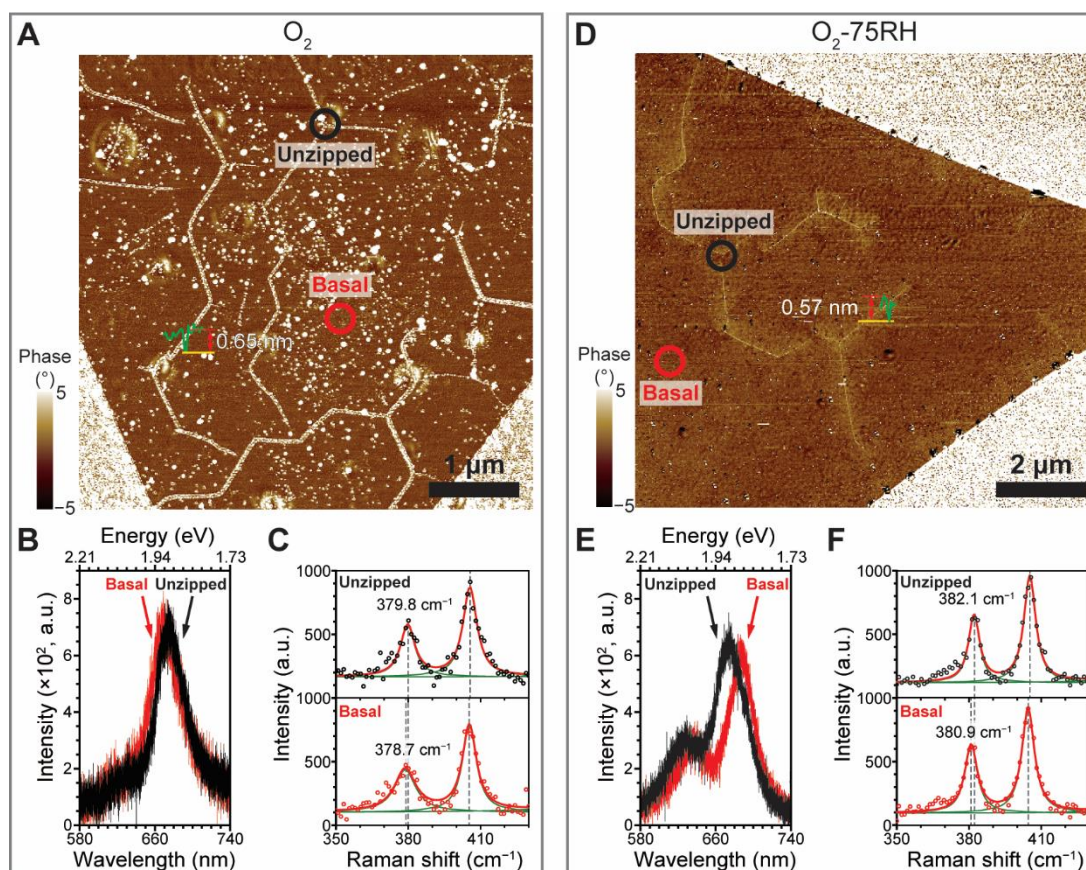


Figure 5. The zz-directional line unzipping of MoS₂ induced by a three-month exposure to O₂ and O₂-75RH environments. (A) AFM phase image of MoS₂ with O₂. (B) Corresponding normalized PL spectra and (C) Raman spectra obtained from marked positions in (A). Line profile was obtained from the corresponding height image. Raman bands were deconvoluted by Lorentzian shape analysis. (D) AFM phase image of MoS₂ after three-month incubations with O₂-75RH. (E) Corresponding PL spectra and (F) Raman spectra obtained from marked positions in (D).

The AFM image (Figure 6A) reveals details of the zz-directional line unzipping and origin. The O₂-treated sample shows 45 nm wide unzipping. The width is persistent along the unzipped segments. In addition, the 120° turns are very sharp. Since the observed typical ϵ_T is in the range of 0.2–0.4%, the width of the MoS₂ grain extends by 20–40 nm, which accounts for the few unzippings with a 45 nm width. Similarly, the AFM phase image of the O₂-75RH sample (Figure 6B), which has similar ϵ_T , displays somewhat similar line width (i.e., 30 nm). As evidenced by Figure S7, typical unzipping occurs in two or three lines along the 10 µm wide MoS₂ crystals, in good agreement with the observed line unzipping. Moreover, MoS₂ with a few layers also has similar unzipping. Figure S7A–C shows the AFM and corresponding OM images of MoS₂ with a few layers. The few-layered regions have less line unzipping compared to single-layered MoS₂. In addition, line unzipping is much more random, as indicated by the yellow arrows. We speculate that this effect of fewer and more random unzippings originates from the lesser ϵ_T exerted on few-layered MoS₂.

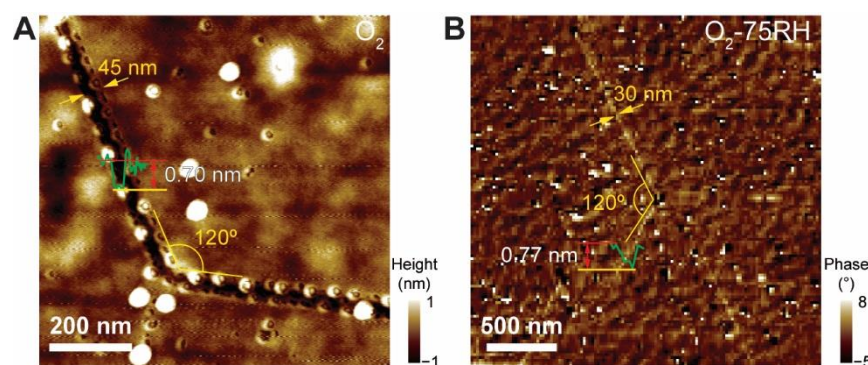


Figure 6. (A) AFM height image of line unzipping from O₂-treated MoS₂ sample. (B) AFM phase image of line unzipping from O₂-75RH-treated MoS₂ sample. It is noteworthy that the phase image was selected to display cracks. Line profile was obtained from the corresponding height image.

The remaining question to be addressed is that of how O₂ treatment causes MoS₂ to unzip along the *zz* directions. Raman spectroscopic analysis did not show the presence of detectable signals associated with MoO₃. In addition, the energy dispersive spectrum (EDS) using scanning electron microscopy (SEM) was also used to attempt to probe the nature of line defects, and this only showed strong Si and O signals from the substrate (Figure S8A–C). Mo-terminated edges readily produce oxygenated Mo. Because the Mo–O bond length (ca. 2.1 Å) [23] is shorter than that (ca. 2.4 Å) of Mo–S, additional ϵ_T should exist near the substitution defect sites, facilitating initial unzipping. Proceeding to *zz* unzipping seems to be associated with abundant S vacancies in CVD-grown MoS₂ [48], which are expected to be much higher than the S vacancies present in exfoliated MoS₂ (i.e., ranging from 5×10^{12} to 5×10^{13} cm^{−2}) [49]. The S vacancies accumulate and are transformed into O-substituted defects with high density up to 1×10^{15} cm^{−2} upon long-term exposure to ambient conditions [25]. Furthermore, the transmission electron microscopy study [50] showed that, at a high e-beam dose, S vacancies are formed owing to the excision of S atoms. Then, ac line defects up to a few tens of nanometers form as a result of the accumulation of S vacancies by adjacent S diffusion in the MoS₂ sheet before forming a *zz* unzipping. Therefore, the formation and accumulation of S vacancies represent a possible model for the formation of directional unzipping near the center. Directional unzipping change from ac to *zz* is likely to be associated with a larger ϵ_T in the basal plane than at the peripheries.

4. Conclusions

In summary, in the study described above, we found that initial armchair-directional line defects and subsequent zigzag-directional line unzipping occurred upon treatment with O₂. Moreover, we showed that these phenomena originate from tension in the chemical-vapor-deposition-grown monolayer MoS₂ crystals, caused by the thermal expansion coefficient difference with the substrate. The O₂-treated MoS₂ crystal exhibited armchair-directional line defects, and the inclusion of water in the incubation atmosphere resulted in further unzipping and folding of MoS₂. Raman and photoluminescence spectroscopic studies revealed that different prevailing tensions exist in MoS₂ grown by CVD under the four different conditions. Oxygenated defects, along with tension, further facilitated zigzag line unzipping in the MoS₂ basal plane upon long-term exposure to an O₂ atmosphere. The observations provide a potential strategy for directionally selective engineering of the MoS₂ basal plane as part of efforts to prepare novel building blocks such as MoS₂ nanoribbons [51]. In addition, the analysis developed for assessing the net contributions of O₂ and H₂O utilizing a strain-doping plot should be useful for the understanding of redox and catalytic effects.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano12101706/s1>. Figure S1: Schematics of environmental incubations for MoS₂-containing substrates; Figure S2: AFM phase images of the sample; Figure S3: AFM height images of entrapped water; Figure S4: A⁺ and A[−] contributions to PL spectra from central regions of MoS₂; Figure S5: PL spectrum analysis of the peripheral regions of MoS₂ treated by different environments; Figure S6: PL image and AFM phase image of MoS₂ before and after O₂-75RH treatment for three months; Figure S7: The ac-to-zz directional unzipping change, proceeding from edges to center; Figure S8: EDS of selected area from zz unzipped samples.

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Long-Term Exposure of MoS₂ to Oxygen and Water Promoted Armchair-to-Zigzag-Directional Line Unzippings

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Figure S1. Schematic of environmental incubations for MoS₂-containing substrates.

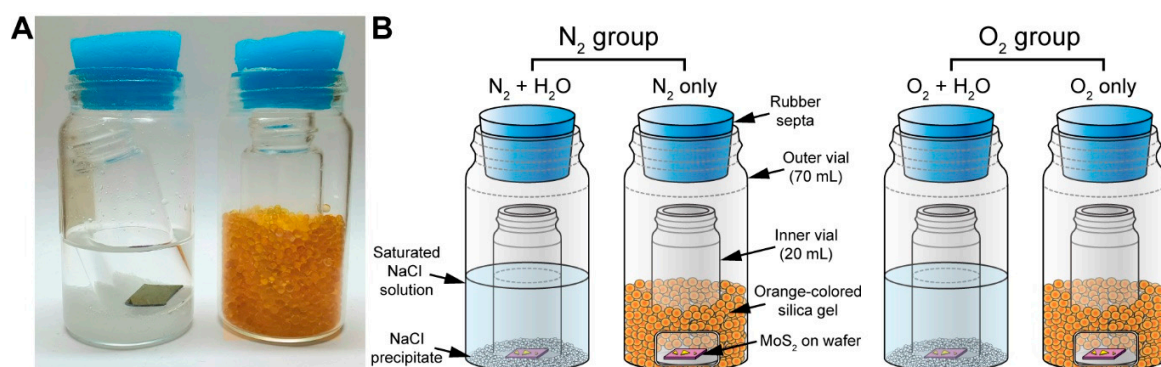


Figure S2. AFM phase images of the sample treated with (A) N₂, (B) N₂-75RH, (C) O₂, and (D) O₂-75RH. Scale bar: 10 μ m.

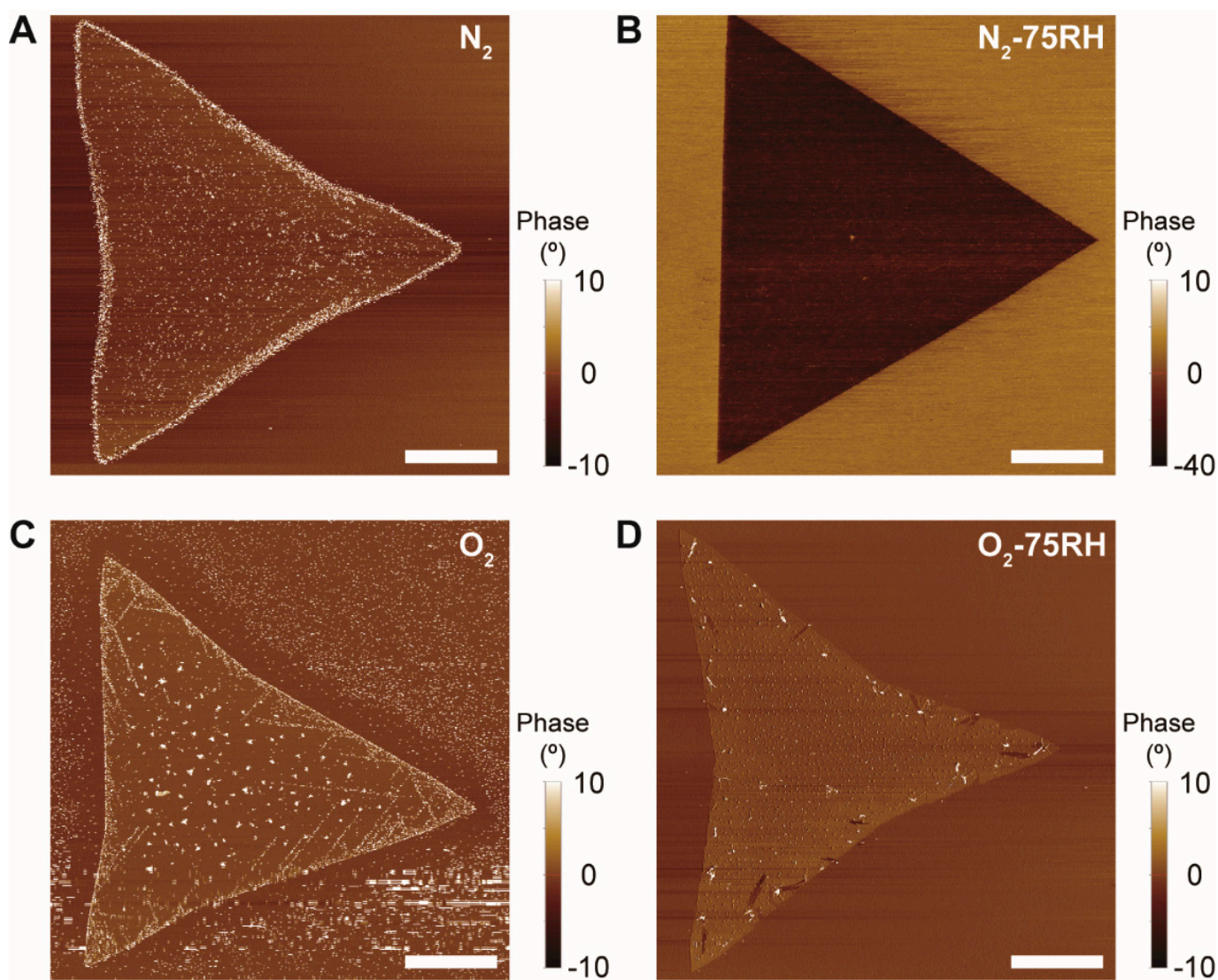


Figure S3. (A) AFM height images of entrapped water between MoS₂ and substrate from N₂-75RH sample, and (B) height profile along the red line in (A).

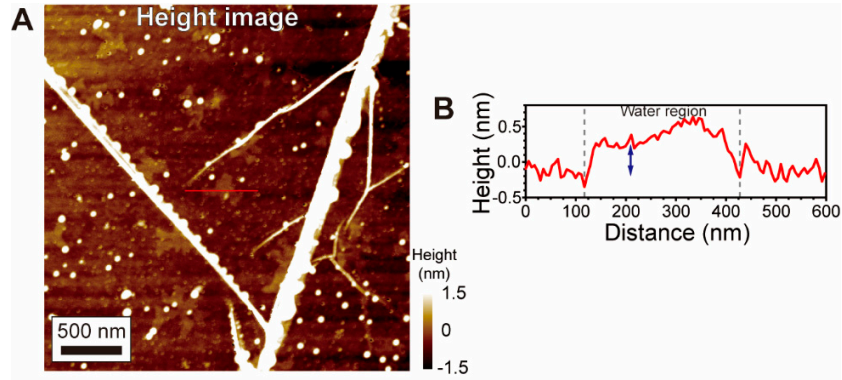


Figure S4. A° and A^{-} contributions of PL spectra from central regions of MoS₂ by each treatment obtained by deconvolution.

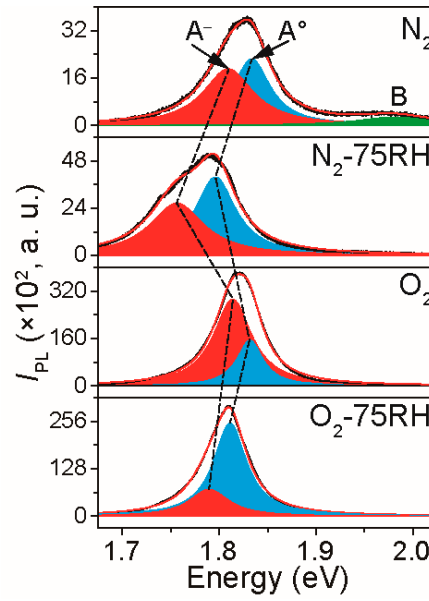


Figure S5. PL spectrum analysis of the peripheral regions of MoS₂ treated by different environment. (A)

A° and A^{-} contributions of MoS₂ by each treatment obtained by deconvolution. (B) Peak position and (C) Peak area changes of A° and A^{-} derived by each treatment.

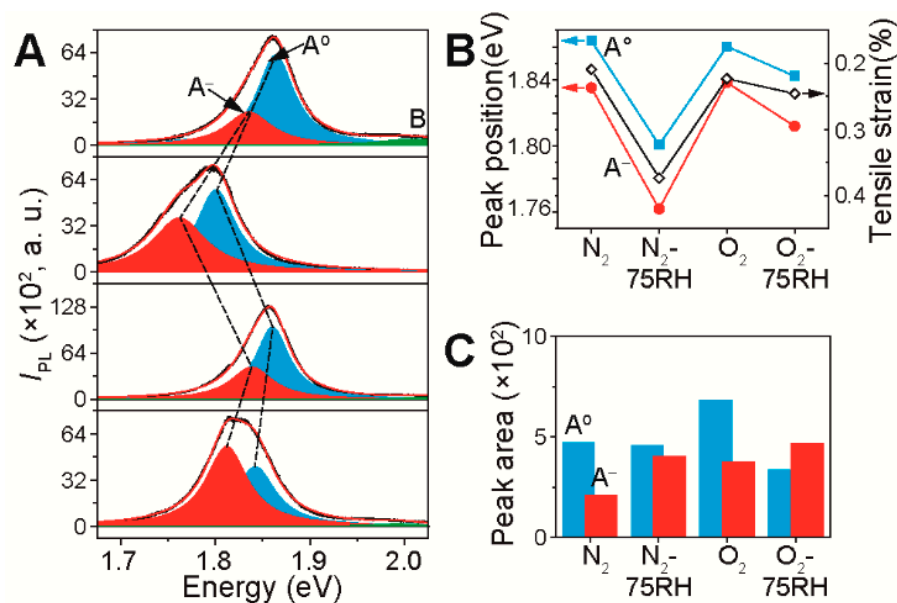


Figure S6. PL image and AFM phase of MoS₂ before and after O₂-75RH treatment for three months. PL images of (A) before and (B) after the treatment. (C) AFM phase image after the treatment.

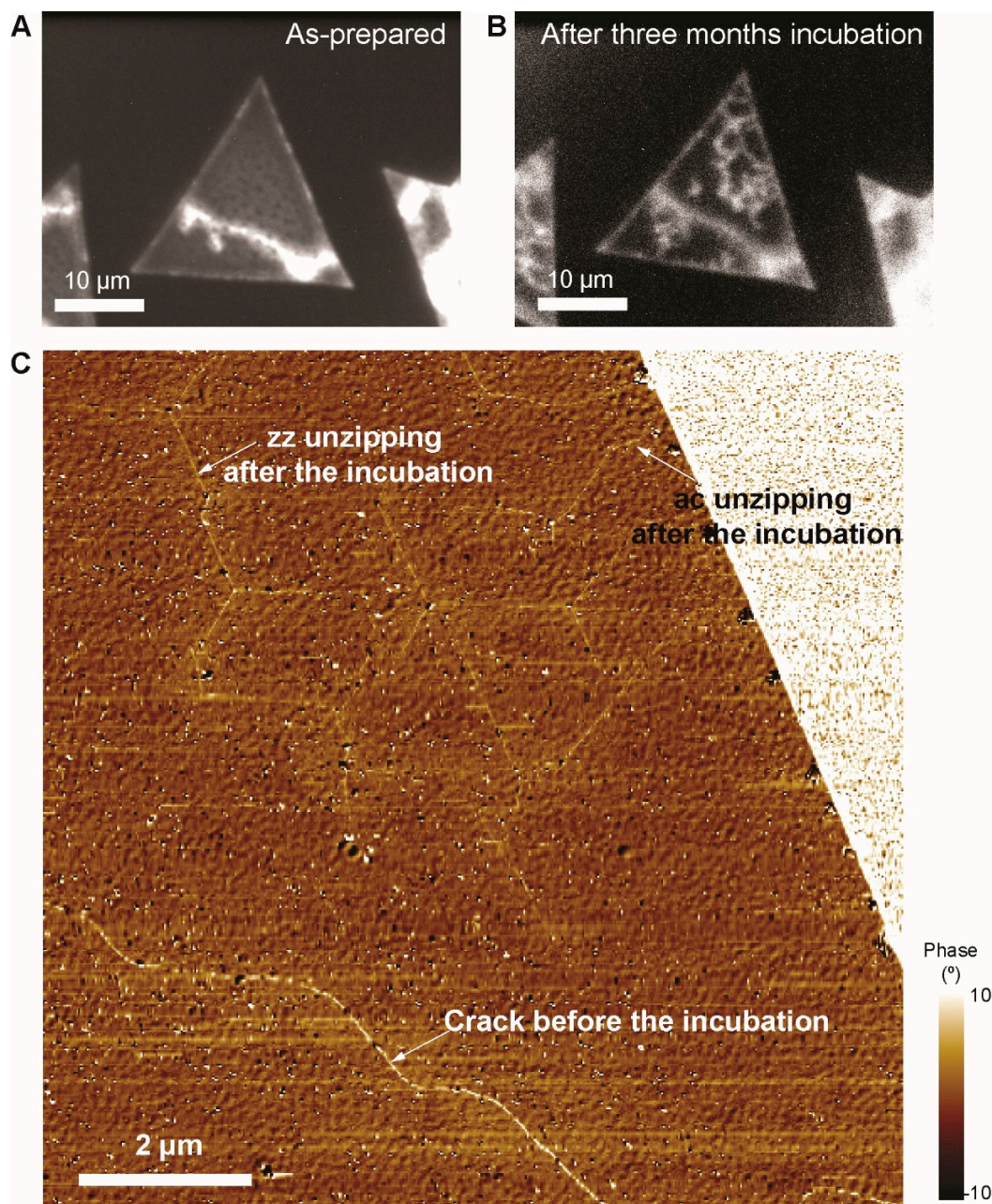
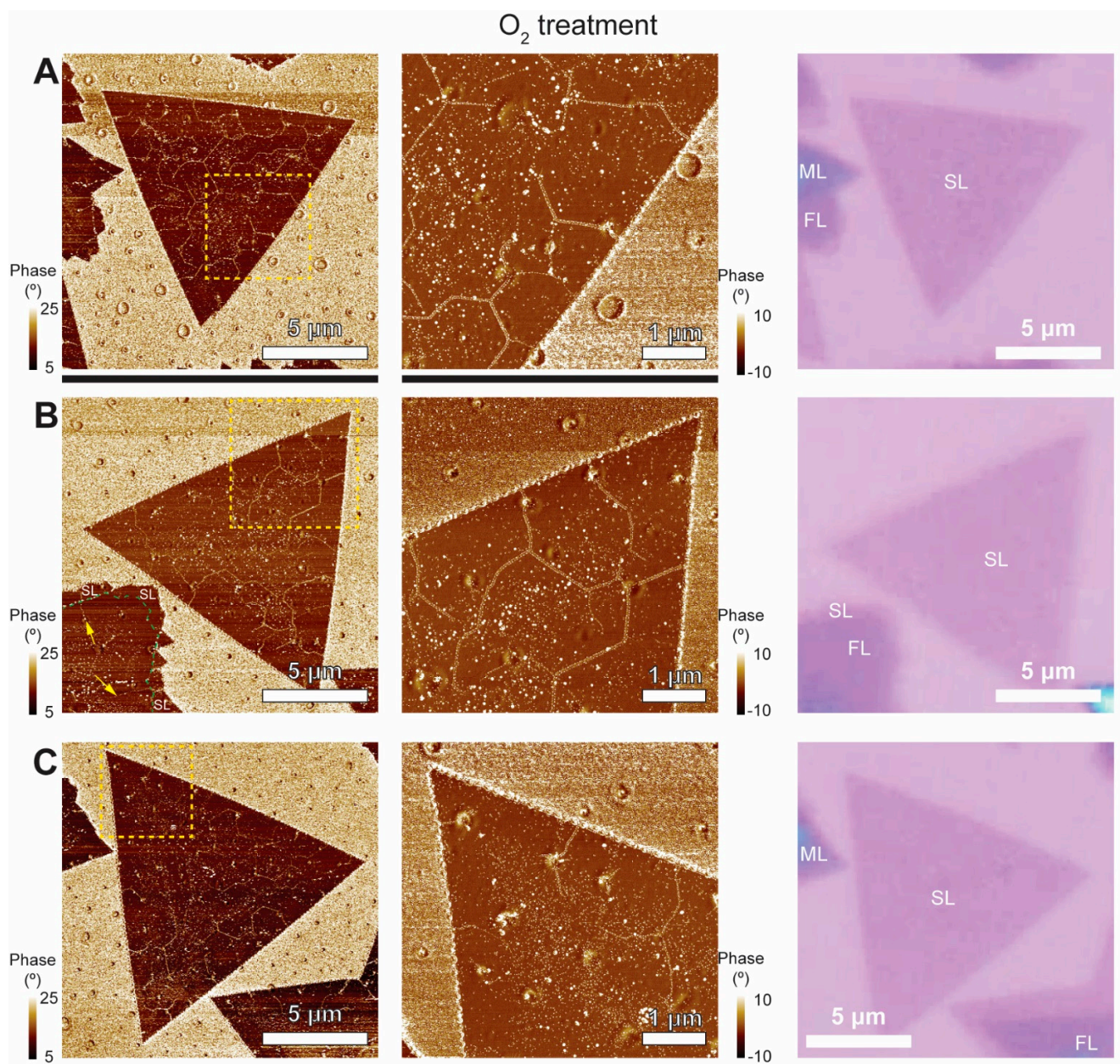


Figure S7. ac to zz directional unzipping change by proceeding from edges to center. AFM phase images of (A–C) O₂-treated and (D–E) O₂-75RH-treated samples. Left image is whole crystal and middle one is zoomed-in image of yellow enclosure in left one. Right is corresponding OM image with indication of number of layers (SL, FL and ML for single, few- and multi-layered MoS₂).



O₂-75RH is continued to the next page

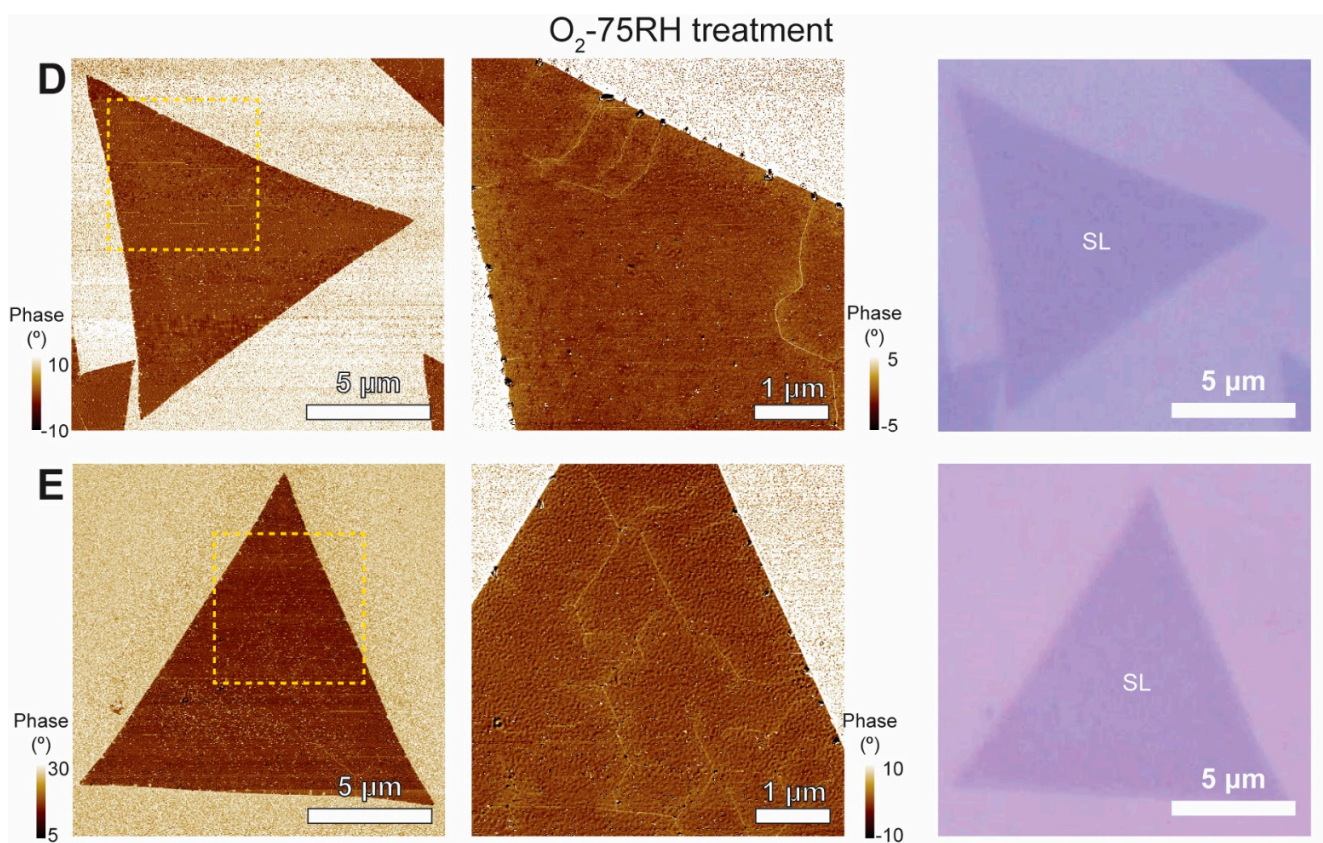


Figure S8.EDS of selected area from zz unzipped samples by using scanning electron microscopy (SEM).

(A,C) Basal area and (B) zz line defects area. Left one is SEM image, right one is EDS of selected area marked in left image. Inset of right figure lists atomic % present in the samples.

