Supporting Information

Etching of Transition Metal Dichalcogenide Monolayers into Nanoribbon Arrays

Zixing Wang, Xiang Zhang, Jordan A. Hachtel, Amey Apte, Chandra S. Tiwary, Robert Vajtai, Juan Carlos Idrobo, Ramazan Ozturk* and Pulickel Ajayan*



Figure S1. MoS_2 under the effect of different solvents. Solvents with lower polarity are not shown since there is no change in morphology. MoS_2 soaked in isopropanol (a, d) and ethanol (b, e) had minimal degradation. (c) MoS_2 soaked in water are lifted from the edges after 1 hr. (f) Almost all MoS_2 are lifted off after 24 hours. This result shows only water has significant detaching ability compared to other solvents.



Figure S2. (a) accumulation of ethanol on Si/SiO₂ around MoS₂ flakes. Ethanol was used to observe the accumulation before lifting and tearing occurs, since the tearing process is slower with ethanol than water. Ethanol accumulates at the edges of the flake, indicating the edges are more hydrophilic than MoS₂ and SiO₂ surface. (b) contact angle measurement of a water droplet on Si/SiO₂ covered with MoS₂ monolayer. A contact angle of 89.6° indicates the wafer is hydrophobic macroscopically. (c) The MoS₂ flakes after ethanol was dried off. The edges with ethanol started to be lifted off the Si/SiO₂ surface. Some lifted MoS₂ pieces folded over.



Figure S3. Full XPS spectra of the product after MoS₂/ascorbic acid reaction.



Figure S4: S 1s XPS spectra of (a) dehydroascorbic acid from the reaction with MoS₂, (b) pristine ascorbic acid and (c) pristine MoS₂ powder. Pristine MoS₂ powder have small amount of C contamination (~10 at%) at 284.8 eV and 287.0 eV.



Figure S5. MoS_2 etched with different potency of reducing agents with the same concentration (1.5 mM). (a) Etched with pure de-ionized water. Pure water only produces short and dense nanoribbons at the edges and large liftings in the center. 44% of MoS₂ was lifted off the SiO₂ surface. (b) MoS₂ etched with iron (II) sulfate (FeSO₄). By adding this weak reducing agent, longer nanoribbons start to form. However, the ribbons are thick and the conversion from the MoS₂ flake to the ribbons is 40%. (c) MoS₂ etched with ascorbic acid. 66% of MoS₂ was etched off. (d) MoS₂ etched with sodium thiosulfate (Na₂S₂O₃). Sodium thiosulfate yields a similar etching result as ascorbic acid (67%), due to similarity in reducing ability. (e) MoS₂ etched with formaldehyde. Low density of thin ribbons can be found after etching (5%). (f) MoS₂ etched with sodium borohydride. Sodium borohydride etched more than 94% of MoS₂ off the Si surface.



Figure S6. (i) AFM image of MoS_2 nanoribbons. The group of ribbons generated are parallel to each other. (ii) AFM image of $MoSe_2$ ribbon. (iii) depth profile of MoS_2 (top) and $MoSe_2$ (bottom) ribbons along the line indicated in (i) and (ii). The MoS_2 nanoribbons are thinner with width between 300 nm to 400 nm. $MoSe_2$ nanoribbons are wider (1.8 µm).



Figure S7. AFM of the roots of MoS_2 and $MoSe_2$ nanoribbons. (a) AFM of the roots of the MoS_2 nanoribbon bundles. Thin strings of ribbons are torn from the bulk, leaving ribbons on the Si/SiO₂ surface. MoS_2 also tears from the edges of triangular vacancies. (b) The tear of a

piece of MoS₂ nanoribbon from the flake. The edge of the tear is clean. (c) Height profile from the location indicated in (b). (d) The formation of MoSe₂ nanoribbons from AFM. Large pieces are lifted from the wafer, torn and folded onto the remaining flake, leaving ribbons. (e) Higher magnification of (d). (e) A height profile showing the remaining piece and the torn piece has the same thickness, indicating the big piece was mechanically torn from the bulk and not damaged.



Figure S8. MoS_2 nanoribbons from unidirectional etching. 1.5 mM ascorbic acid water solution was used to rinse the Si/SiO₂ wafer in the direction as indicated from the picture. However, nanoribbon formed in different directions independent of the direction of the solution flow. The ribbons formed are parallel to each other and around 60° from the edge, indication the tearing is independent of external force but depends on the crystal structure.



Figure S9. Before and after optical images of the MoS_2 etching on Si/SiO_2 . (a) MoS_2 before etching. Triangular and polygonal shapes are observed. No defects can be found from those flakes under optical microscope. (b) Result of etching with 0.5 mM ascorbic acid after 3 minutes. Some flakes are etched from the edges. The remaining area is 64% of the original area as measured by ImageJ. (c) Result of etching with 1.0 mM ascorbic acid after 3 minutes. The etching is more significant compared to 0.5 mM ascorbic acid. The remaining area is around 59% of the original area. (d). Result of etching with 2.5 mM ascorbic acid after 3 minutes. Most of the flakes are converted into nanoribbons. The remaining area is around 46% of the original area. (e) Percentage of MoS₂ etched from the original with different concentrations of ascorbic acid. The etched area increases with ascorbic acid concentration. (f) Box and whisker graph of the length and width of the nanoribbons produced by 0.5 mM, 1.0 mM, and 2.5 mM ascorbic acid. When etched with the lowest concentration of 0.5 mM, the first and third quartile of nanoribbon width falls at 1023 nm and 1626 nm, respectively. The median width is 1316 nm. The two quartiles lower to 768 nm and 1133 nm when the ascorbic acid concentration is doubled to 1.0 mM, with the median width of 950 nm. After etching with 2.5 mM ascorbic acid, 50% of the nanoribbons falls between 379 nm and 1405 nm. The median width is 684 nm. Length of nanoribbons produced by 0.5 mM ascorbic acid

has the first and third quartile at 7.5 and 21 μ m. Mean and median length are 17 μ m and 14 μ m. Length of nanoribbons produced by 1.0 mM ascorbic acid has the first and third quartile at 12 and 46 μ m. Mean and median length are 30 μ m and 29 μ m. Length of nanoribbons produced by 0.5 mM ascorbic acid has the first and third quartile at 15 and 51 μ m. Mean and median length are 37 μ m and 30 μ m.



Figure S10. TEM images of MoS_2 nanoribbons (scale bar: 100 nm). The ribbons are 120 nm and 40 nm wide respectively. They show good structural integrity.



Figure S11. A histogram of the angle between the direction of MoS_2 ribbons and the edge of the MoS_2 triangular flake. The angles are measured as shown in inset on the right. Most of the ribbon edges are 65° from the edge of original MoS_2 flake. Compared to the $MoS_2/MoSe_2$ atomic structure (yellow: S or Se, blue: Mo), the tears are along zigzag direction, which corresponds to the finding by STEM.



Figure S12. Optical image of the MoSe₂ nanoribbons etched by 1.5 mM ascorbic acid.