Supplementary Information

Formation of MoO₃ and WO₃ Nanoscrolls from MoS₂ and WS₂ by Atmospheric Air Plasma

Ximo S. Chu,¹ Duo O. Li,¹ Alexander A. Green,² and Qing Hua Wang*¹

¹ Materials Science and Engineering, School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287, United States
² Biodesign Center for Molecular Design and Biomimetics, The Biodesign Institute, and the School of Molecular Sciences, Arizona State University, Tempe, AZ, USA, 85287

* Corresponding author:
qhwang@asu.edu

Figure S1: Nanoscroll formation after air plasma treatment of MoS₂ and WS₂. Atomic force microscopy (AFM) images of MoS₂ and WS₂ before and after air plasma treatment. (a) AFM image of monolayer MoS₂ as exfoliated, and (b) magnified in the area in the dashed box in (a). (c) AFM image in the same area as (a) after 2 s air plasma treatment, and (d) magnified in the area in the dashed box in (c). (e) Monolayer WS₂ as exfoliated and (f) magnified in the area in the dashed line box in (e). (g) The same area as (e) after 2 s air plasma treatment and (h) magnified in the area in the dashed box in (g).
Figure S2: Field emission scanning electron microscopy (FESEM) images of MoO$_3$ nanoscrolls. The FESEM was conducted using a Hitachi S4700 system. Panels (a) and (b) show nanoscrolls in different regions of a sample. The nanoscroll features are similar to those seen in AFM images.
Figure S3: MoS$_2$ and WS$_2$ optical microscope images before and after air plasma treatment. (a) Optical microscope image of as exfoliated MoS$_2$ and (b) the same region after air plasma treatment. (c) Optical microscope image of as exfoliated WS$_2$ and (d) the same region after air plasma treatment. After air plasma treatment of both materials, the monolayers are nearly invisible.
Figure S4: Raman and PL spectra for monolayer MoS$_2$ and WS$_2$. (a) Raman spectra for pristine mechanically exfoliated monolayer MoS$_2$ and in the same region after air plasma treatment. The distance between the characteristic E$_{2g}^1$ and A$_{1g}$ peaks in the pristine MoS$_2$ sample is 19 cm$^{-1}$. The peaks are no longer present after plasma treatment. (b) Photoluminescence (PL) spectra for pristine monolayer MoS$_2$ and the same region after air plasma treatment. After air plasma, the PL peaks are gone. (c) Raman spectra for pristine mechanically exfoliated monolayer WS$_2$ and in the same region after air plasma treatment. The characteristic E$_{2g}^1$ and A$_{1g}$ peaks are marked. (d) PL spectra for monolayer WS$_2$ and the same region after air plasma treatment.
Figure S5: Formation of nanoscrolls in single crystal CVD-grown MoS$_2$. (a)-(c) AFM images of single crystal MoS$_2$ after CVD growth. Images show increasing magnification of the same sample. (d)-(i) AFM images of MoS$_2$ after 2 s air plasma treatment showing formation of nanoscrolls. Images (d)-(f) show the same sample with increasing magnification, and images (g)-(i) show the same sample with increasing magnification. (j) Schematic illustration of experimental setup for CVD growth of single crystal MoS$_2$. 
Figure S6: Image analysis for nanoscroll orientations. (a) Single crystal MoS$_2$ after 2 s air plasma treatment. (b) Each nanoscroll has been marked as a line segment, along with the edge of the original MoS$_2$ crystal. The color of each line corresponds to its angle with respect to the MoS$_2$ edge.

Figure S7: Air plasma treatment of MoSe$_2$ and WSe$_2$. (a)-(b) AFM images of MoSe$_2$ as exfoliated ((b) shows the area marked by the dashed square in (a)), and (c)-(d) after 2 s air plasma treatment. Some nanoscrolls have formed in the monolayer region ((d) shows the area marked by the dashed square in (c)). (e)-(f) AFM images of WSe$_2$ as exfoliated ((f) shows the area marked by the dashed square in (e)), and (g)-(h) after 2 s air plasma treatment ((h) shows the area marked by the dashed square in (g)). No nanoscrolls have formed, but there are some cracks.
Figure S8: Nanoscroll formation in large-area CVD-grown MoS$_2$ after air plasma treatment. A large-area continuous film of monolayer MoS$_2$ was grown by chemical vapor deposition (CVD). After the same air plasma treatment that was applied to other samples, nanoscrolls are also formed, as shown in the AFM image here.

Figure S9: MoS$_2$ after Ar plasma and Ar/O$_2$ gas mixture plasma. (a) AFM image of MoS$_2$ as exfoliated and (b) after 2 s Ar plasma treatment. (c) AFM image of MoS$_2$ as exfoliated and (d) after Ar/O$_2$ gas mixture plasma treatment. In both cases, nanoscrolls do not form.
Figure S10: MoS$_2$ after N$_2$ plasma treatment and after O$_2$ plasma treatment. (a), (d) AFM images of different MoS$_2$ samples as exfoliated, (b)-(c) after 2 s N$_2$ plasma treatment, and (e)-(f) after 2 s O$_2$ plasma treatment. In both cases, nanoscrolls do not form, but there is an increase in roughness with N$_2$ plasma, and cracks and increasing height with O$_2$ plasma.

Figure S11: X-ray photoelectron spectroscopy (XPS) of pristine MoS$_2$ and treated by O$_2$ plasma. Lower spectrum: pristine MoS$_2$. Upper spectrum: after O$_2$ plasma treatment. (a) Peaks in Mo 3d region. (b) Peaks in S 2p region.
Figure S12: MoS$_2$ and WS$_2$ samples after plasma treatment with an N$_2$/O$_2$ gas mixture. (a)-(b) AFM images of MoS$_2$ as exfoliated ((b) shows the area marked by dashed square in (a)), and (c)-(d) after 2 s N$_2$/O$_2$ gas mixture plasma treatment ((d) shows the area marked by dashed square in (c)). (e)-(f) AFM images of WS$_2$ as exfoliated ((f) shows the area marked by dashed square in (e)), and (g)-(h) after 2 s N$_2$/O$_2$ gas mixture plasma treatment. No nanoscrolls have formed in either material.
Figure S13: Formation of nanoscrolls on multilayered MoS$_2$. (a) AFM image showing formation of nanoscrolls after air plasma treatment of MoS$_2$ flake with different initial layer numbers. The lines A, B, and C correspond to regions where the initial thicknesses were 1L, 3L and 5L, respectively. (b) Height profiles along lines A, B, and C. Profiles are vertically offset for clarity. The thickness changes due to air plasma treatment suggest that only the top layer of the multilayer MoS$_2$ rolls up. (c) Raman spectra for the multilayer (5L) region after air plasma treatment. The characteristic peaks for MoS$_2$ are still clearly visible because only the top layer is oxidized. (d) Schematic illustration showing air plasma treatment only causes the top layer to oxidize and roll into MoO$_3$ nanoscroll, while the remaining material remains as MoS$_2$.
Figure S14: Nanoscroll formation of monolayer, bilayer, and multilayered MoS$_2$. (a) AFM images of MoS$_2$ as exfoliated with monolayer (1L) and bilayer (2L) regions marked, and (b) after 2 s air plasma treatment. The 2L labels indicate the same position on a bilayer region in panels (a) and (b). In the monolayer (1L) region, nanoscrolls have formed. There are no cracks or nanoscrolls in the bilayer (2L) region. There are cracks and nanoscrolls in the multilayer (>3L) region.

Figure S15: Raman and PL spectra for bilayer MoS$_2$. (a) Raman spectra for pristine bilayer MoS$_2$ and in the same region after air plasma treatment. The characteristic E$_{2g}^1$ and A$_{1g}$ peaks are still visible after plasma treatment, and new peaks from MoO$_3$ appear. (b) PL spectra for pristine bilayer MoS$_2$ and the same region after air plasma treatment. After air plasma, the PL peaks are significantly lower in intensity.