doi:10.1017/S1431927622009291

Potassium-Mediated Anisotropic Etching of Transition Metal Dichalcogenides Driven by Self-Running Oxide Droplets

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Two-dimensional (2D) transition metal dichalcogenides (TMDs) have superior electrical, optical, and catalytic properties, especially at their edge sites. Thus, various edge engineering methods of TMDs have been devised with the aim to improve their properties. Edge engineering of MoS_2, which is a representative TMDs materials, has been actively studied. By adjusting synthetic parameters (e.g., precursors, substrates, and catalysts), synthesis of edge-rich MoS_2 has been proposed. In addition, the triangular pits formation which are terminated with Mo ZZ edges by thermal oxidation at 400 °C were reported. At the same time, orthorhombic-phase MoO_3 (α-MoO_3) nanosheets are epitaxially formed on the underlying MoS_2 at the same time. [1] Moreover, new types of edges including metallic Mo_6S_6 nanowires and distorted 1T edges have been reported. [2] However, the anisotropic etching that does not follow Wulff construction has only rarely been studied in MoS_2.

Here, we suggest a novel anisotropic etching method of MoS_2 by modulating the oxides with the assistance of potassium. We discover that potassium-mediated oxidation of MoS_2 leads to the formation of K-intercalated hexagonal phase molybdenum oxides (h-K_xMoO_3) at 330 °C, whereas α-MoO_3 are formed in the absence of potassium ions. Because the formed h-K_xMoO_3 oxides are unstable, they are easily decomposed and agglomerated into oxide droplets at 400 °C. The oxide droplets move toward armchair direction of MoS_2 due to the surface-energy instability between generated oxide particles and underlying MoS_2 layer. Self-running of the oxide droplets leads to layer-by-layer anisotropic etching of MoS_2 along the armchair direction. Thermodynamically unstable AC edges appear to be converted to sawtooth-like edges with repeating Mo ZZ and S ZZ edges by following thermal etching. [3] This study provides fundamental insights into the interactions between nanodroplets and 2D materials for edge engineering. In addition, we believe that this novel etching mechanism can be effectively used to design and manufacture novel edge-rich 2D crystals that do not follow the equilibrium Wulff shape and also enables patterning of 2D TMDs without surface damage for electronic and energy applications [4].

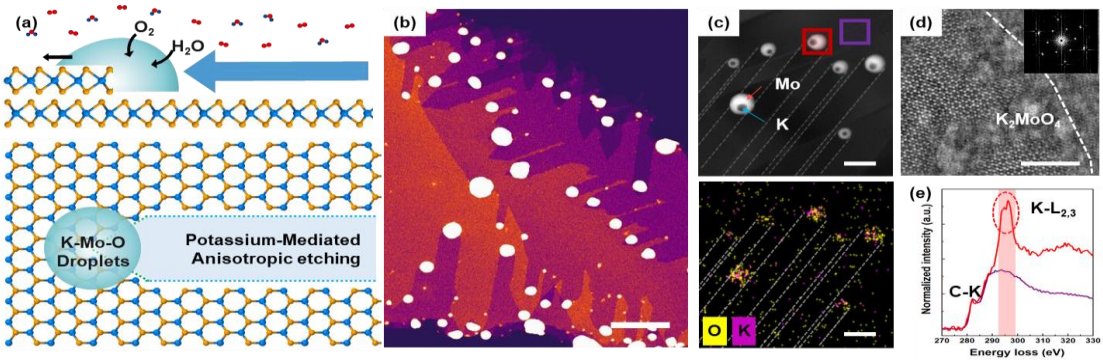

Figure 1. (a) Schematic diagram and (b) HAADF-STEM image of anisotropic etched MoS_2 driven by self-running oxide droplet. (c) HAADF-STEM image and the corresponding EDS mapping image, and (e) EEL spectrum (taken from the marked region in (c): The basal plane of MoS_2 (purple), and the particle (red)) shows that the particles contain potassium and oxygen. (d) Inverse-FFT HAADF-STEM image of the reconstructed K_2MoO_4 oxide particle. The MoS_2 specimen in (b-d) were oxidized at 400 °C for 5 min. The scale bars in (b-d) are 200, 100, and 3 nm, respectively. Reprinted from [3] with permission of American Chemical Society.

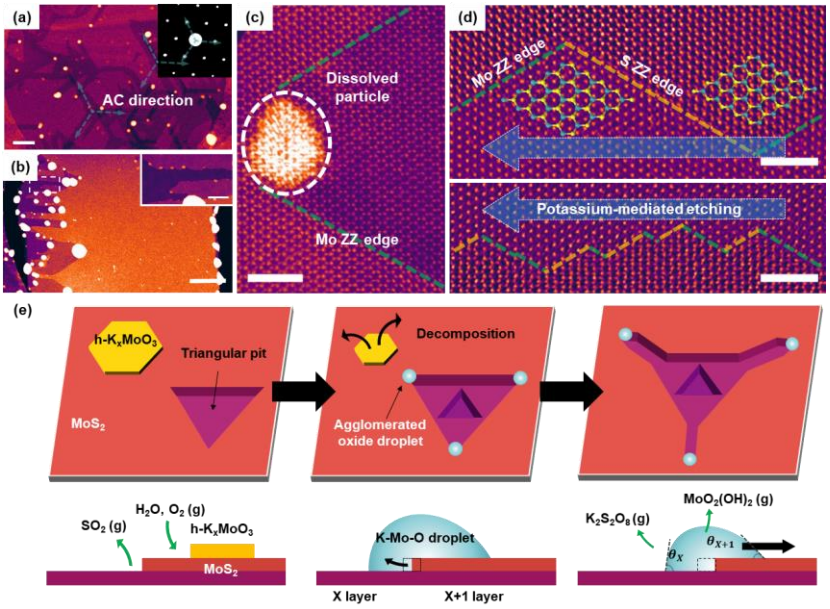

Figure 2. HAADF-STEM images of (a) basal planes and (b) edges of the 1D etched MoS_2. Atomic-resolution STEM images show (c) front end and (d) both edge sides formed by 1D etching. (e) Possible mechanism for the potassium-mediated anisotropic etching. The scale bars in (a, b) are 200 nm, and (c, d) are 2 nm. Reprinted from [3] with permission of American Chemical Society.

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[2] W Huang et al., Nano Research **11**(11) (2018), p. 5849.
[3] A Yoon et al., ACS Appl. Mater. Interfaces **13**(41) (2021), p. 49163.
[4] Work supported by IBS (IBS-R019-D1)

https://doi.org/10.1017/S1431927622009291 Published online by Cambridge University Press