In situ edge engineering of two-dimensional transition metal dichalcogenides

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The edge structures of two-dimensional (2D) materials greatly affect the electronic,[1] magnetic,[2,3] nonlinear optical,[4] photoluminescence,[5] and catalytic properties.[6] It is therefore critical to understand stable edge structures and edge evolution within different chemical environments to develop controlled edge engineering methods to achieve desired functionality. Here, using atomic-scale *in situ* scanning transmission electron microscopy (STEM), we directly observe the formation of fresh edges following the formation of faceted pores in $MoWSe_2$ monolayer flakes at elevated temperature from combined electron beam irradiation and thermal effects. Figure 1 shows the structural evolution of the monolayer $MoWSe_2$ at 500 °C captured with time-resolved atomic-resolution high angle annular dark field (HAAD)-STEM images. Various edge structures were observed during the experiments, with the most common edge structures being zigzag edges terminated with Se atoms or MoSe nanowires (NW). The edge reconstruction from zigzag edges to NW-terminated edges was directly observed experimentally, as shown in Fig. 1d - 1e. Density functional theory (DFT) calculations on 59 different hypothetical edges confirms that the observed edges have the lowest formation energy at metal-rich environments. Different edges exhibit very different electronic properties. While Se-terminated edges are generally semiconducting, NW-terminated edges are conductive. Ferromagnetism arises due to atomic rearrangement on NW-terminated zigzag Se edges. *Ab initio* molecular dynamics (AIMD) simulations confirm the observed edge structural evolution, which is attributed to changes in Mo chemical potential during *in situ* heating. As the local Mo chemical potential increases, the edge structure evolves from Se-terminated zigzag edges to NW-terminated zigzag edges. This work demonstrates edge engineering of 2D materials via the electron beam in STEM for targeted functional applications.

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References

1. K. A. Ritter, J. W. Lyding, The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons. *Nature Materials* **8**, 235 (2009).
2. G. Z. Magda *et al.*, Room-temperature magnetic order on zigzag edges of narrow graphene nanoribbons. *Nature* **514**, 608-611 (2014).
3. M. Saab, P. Raybaud, Tuning the Magnetic Properties of MoS2 Single Nanolayers by 3d Metals Edge Doping. *J. Phys. Chem. C* **120**, 10691-10697 (2016).
4. X. Yin *et al.*, Edge Nonlinear Optics on a MoS_2 Atomic Monolayer. *Science* **344**, 488-490 (2014).
5. H. R. Gutiérrez *et al.*, Extraordinary Room-Temperature Photoluminescence in Triangular WS2 Monolayers. *Nano Lett.* **13**, 3447-3454 (2013).
6. T. F. Jaramillo *et al.*, Identification of Active Edge Sites for Electrochemical H_2 Evolution from MoS_2 Nanocatalysts. *Science* **317**, 100-102 (2007).

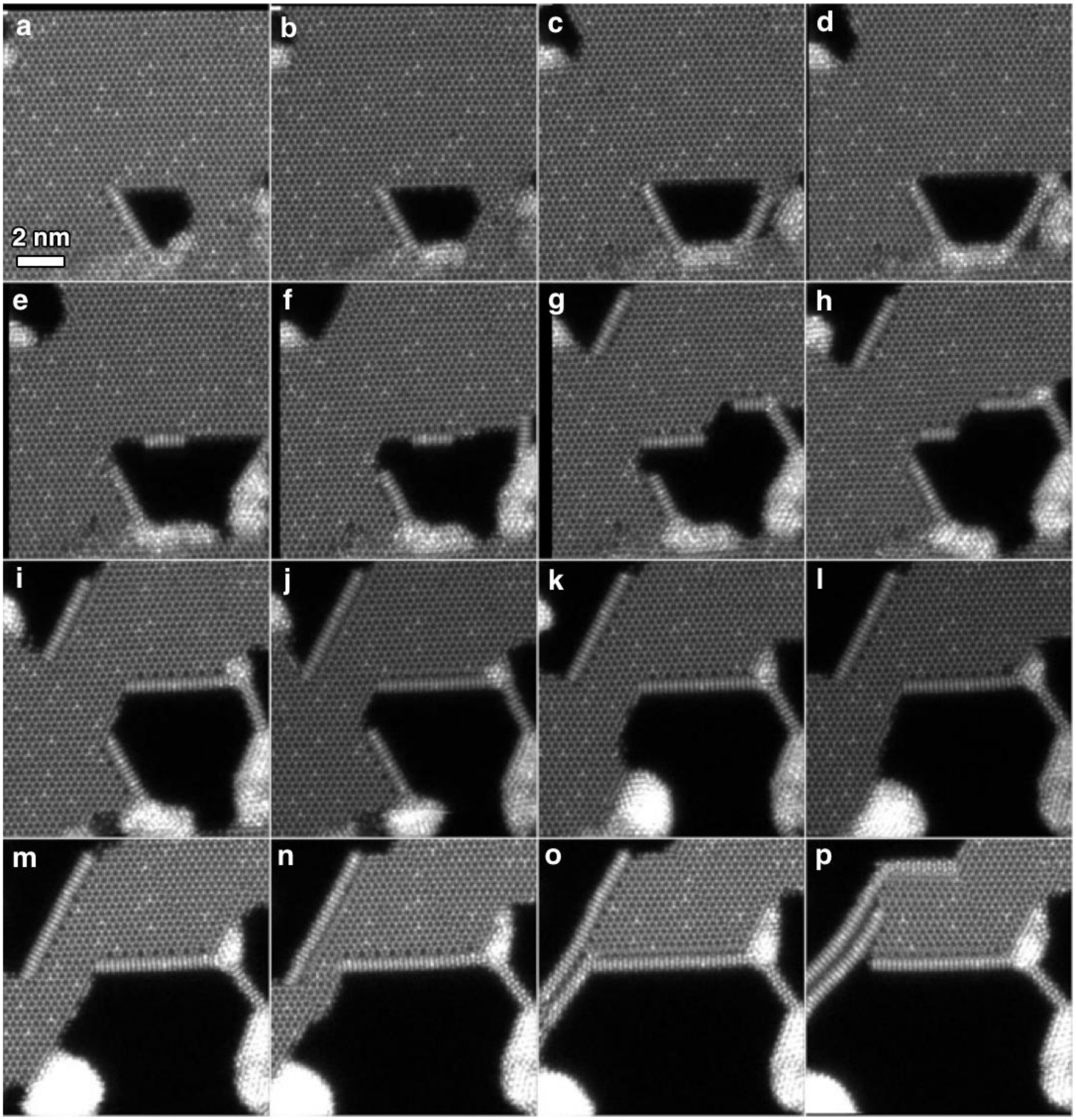

Figure 1. Dynamic shape evolution and edge reconstruction of etched pores at 500 °C in a $MoWSe_2$ monolayer flake. The time interval between acquisition of each HAADF-STEM image in a-p is 35 s.