

Surface Topotactic Growth of Edge-Terminated MoS₂ Catalysts

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Molybdenum disulfide (MoS₂) is widely applied to catalyze industrial oil refining, hydrogen evolution and photo-oxidation reactions. The catalysis is typically attributed to the MoS₂ edge terminations whereas chemically inertness is considered predominant at the basal planes. Consequently, methods for preparing MoS₂ materials with abundant edge-terminations are being explored [1,2], but the edge-formation is inherently impeded due to the higher surface energy of the edges compared to the basal plane. To offset the energetic drive in the design of bottom-up synthesis procedures of MoS₂ nanomaterials with a tunable degree of edge terminations, it would be beneficial with mechanistic insight into the growth of MoS₂ nanostructures.

While transmission electron microscopy (TEM) provides detailed information about MoS₂ structures, defects and edge terminations at the single-atom level [3-5], complementary dynamic insight into growth processes has been limited. Prominent synthesis procedures involve the transformation of molybdenum oxide precursors by exposure to gaseous sulfidation environments. While technology has become available for high spatial and temporal resolution TEM of nanomaterials under reactive gas environments [6], sulfur-containing gases are challenging by being highly corrosive to the microscope equipment. To overcome this challenge, we have upgraded a differentially pumped TEM instrument to dedicated *in situ* studies of chemical reactions involving sulfur [7,8]. This instrument was used to acquire time-resolved TEM image series of MoO₂ nanocrystals *in situ* during exposure to H₂S/H₂ gas mixtures at elevated temperatures [9]. The TEM images were recorded using a low electron dose-rate imaging protocol in order to suppress electron-beam induced alterations and to ensure chemical relevance of the observed dynamic processes [6,10].

Surprisingly, time-resolved TEM image series reveal that MoS₂ structures grew with two distinctly different orientations with respect to the surface of the MoO₂ nanoparticle (Figure 1) [9]. One structure (p-MoS₂) consists of MoS₂ layers that contour the MoO₂ nanoparticle surface and expose mainly basal plane sites. The second structure (e-MoS₂) consists of MoS₂ layers, which grew through the inward progression of the MoO₂(20-2):MoS₂(002) interfaces and result in upright and edge-exposing MoS₂ layers. This surface topotactic growth is rationalized in interplay with density functional theory calculations by successive O-S exchange and Mo sublattice restructuring reaction steps. These reaction steps describe the propensity of a surface to mediate growth of edge-terminated MoS₂ and our findings reveal that edge-exposed MoS₂ is particularly favorable at the MoO₂(110) surface. The analysis thus demonstrates surface topotaxy as an innovative principle for bottom-up design of MoS₂ and, possibly other transition metal dichalcogenide, nanomaterials with superior edge-functionalities.

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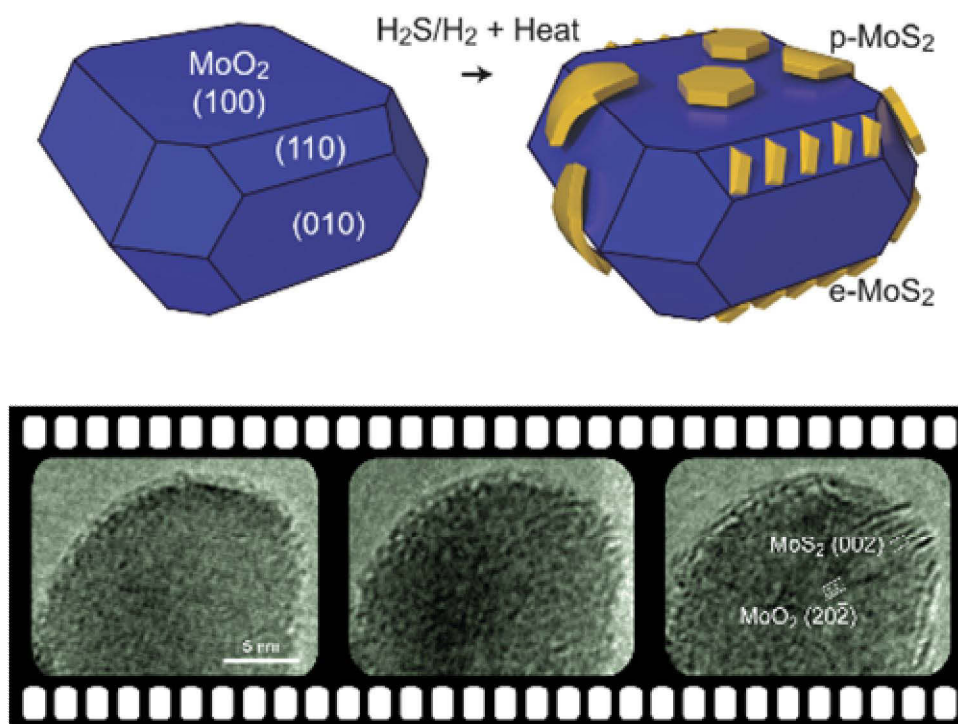


Figure 1. Growth of edge-terminated MoS₂. (a) Illustration of *p*-MoS₂ with predominantly exposed MoS₂ basal plane sites, and *e*-MoS₂ with edge-exposing MoS₂ layers. (b) Stills selected from a TEM image series of MoO₂ in H₂S:H₂ = 0.1:0.9 at 1 mbar and 250 °C at times 0, 40 and 235 min relative to the gas mixture inlet. Adapted from ref. [9].