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Surface Topotactic Growth of Edge-Terminated MoS_2 Catalysts

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Molybdenum disulfide (MoS_2) is widely applied to catalyze industrial oil refining, hydrogen evolution and photo-oxidation reactions. The catalysis is typically attributed to the MoS_2 edge terminations whereas chemically inertness is considered predominant at the basal planes. Consequently, methods for preparing MoS_2 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 MoS_2 nanomaterials with a tunable degree of edge terminations, it would be beneficial with mechanistic insight into the growth of MoS_2 nanostructures.

While transmission electron microscopy (TEM) provides detailed information about MoS_2 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 MoO_2 nanocrystals *in situ* during exposure to H_2S/H_2 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 MoS_2 structures grew with two distinctly different orientations with respect to the surface of the MoO_2 nanoparticle (Figure 1) [9]. One structure (p-MoS_2) consists of MoS_2 layers that contour the MoO_2 nanoparticle surface and expose mainly basal plane sites. The second structure (e-MoS_2) consists of MoS_2 layers, which grew through the inward progression of the MoO2(20-2):MoS2(002) interfaces and result in upright and edge-exposing MoS_2 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 MoS_2 and our findings reveal that edge-exposed MoS_2 is particular favorable at the MoO_2(110) surface. The analysis thus demonstrates surface topotaxy as an innovative principle for bottom-up design of MoS_2 and, possibly other transition metal dichalcogenide, nanomaterials with superior edge-functionalities.

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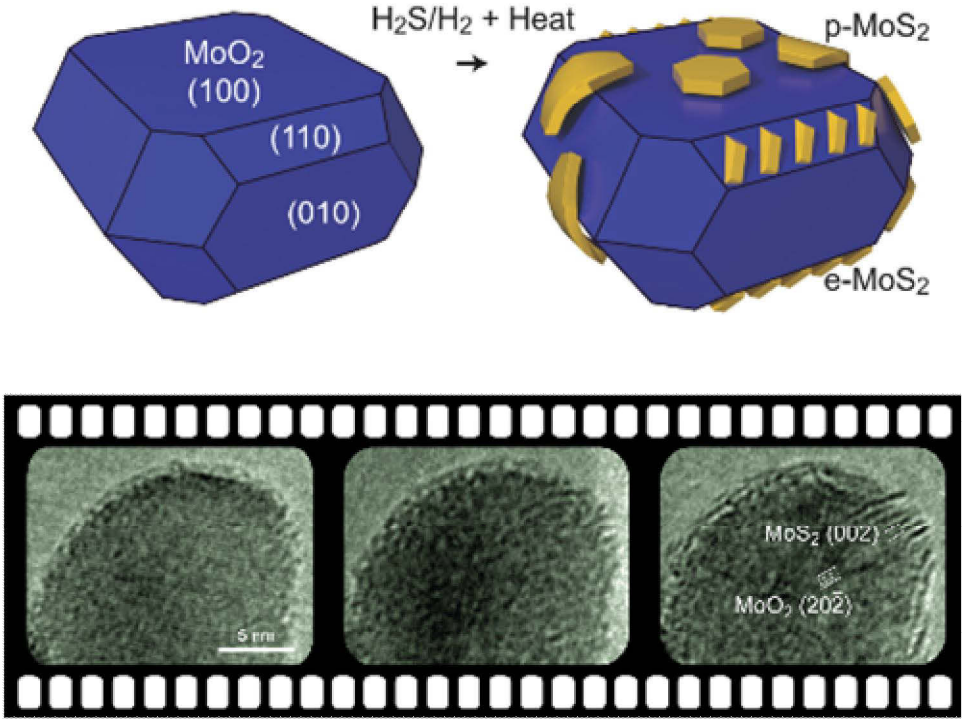

Figure 1. Growth of edge-terminated MoS_2. (a) Illustration of *p*-MoS_2 with predominantly exposed MoS_2 basal plane sites, and *e*-MoS_2 with edge-exposing MoS_2 layers. (b) Stills selected from a TEM image series of MoO_2 in H_2S:H_2 = 0.1:0.9 at 1 mbar and 250 °C at times 0, 40 and 235 min relative to the gas mixture inlet. Adapted from ref. [9].

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