Atomic-Scale Structure of Single-Layer MoS₂ Nanoclusters

S. Helveg,¹ J. V. Lauritsen,¹ E. Lægsgaard,¹ I. Stensgaard,¹ J. K. Nørskov,² B. S. Clausen,³ H. Topsøe,³ and F. Besenbacher¹,*

¹CAMP and Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark
²CAMP and Physics Department, Technical University of Denmark, DK-2800 Lyngby, Denmark
³Haldor Topsøe Research Laboratories, Nymøllevej 55, DK-2800 Lyngby, Denmark

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We have studied using scanning tunneling microscopy (STM) the atomic-scale realm of molybdenum disulfide (MoS₂) nanoclusters, which are of interest as a model system in hydrodesulfurization catalysis. The STM gives the first real space images of the shape and edge structure of single-layer MoS₂ nanoparticles synthesized on Au(111), and establishes a new picture of the active edge sites of the nanoclusters. The results demonstrate a way to get detailed atomic-scale information on catalysts in general.

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With the advent of the scanning tunneling microscope (STM) scientists now have a tool to directly image nanoscale structures on surfaces. This has opened up the field of nanotechnology where the aim is to make nanostructures with interesting functional properties. Up to now, the interest has been focused mainly on metal and semiconductor nanostructures [1]. In this Letter, we show how to synthesize and characterize transition metal sulfide nanoclusters. These are of interest as lubricants [2], as models of the active part of some enzymes [3], and as hydrodesulfurization (HDS) catalysts [4,5], which currently receive special attention due to the worldwide demand for cleaner transport fuels. Here we focus on MoS₂ nanostructures, as a model system of an HDS catalyst. MoS₂ nanocrystals, single layer in height and ~30 Å wide, are synthesized using the Au(111) surface as a template.

 Atom-resolved STM images reveal that the small clusters exhibit triangular morphology, contrary to the expectation from bulk MoS₂. The catalytically important MoS₂ edges are found to be reconstructed relative to the perfect MoS₂ lattice. The first direct images are presented of the catalytically active sites in the form of S vacancies at the edges of MoS₂, created by in situ treatment of the nanoclusters to atomic hydrogen.

The experiments were performed in a standard ultrahigh vacuum (UHV) chamber equipped with a homebuilt, high-resolution STM capable of resolving the individual atoms of close-packed surfaces and clusters on a routine basis [6]. The Au(111) substrate surface was sputter-cleaned by 1.5 keV Ar ion bombardment followed by annealing at 900 K. The Au(111) surface was chosen as a model substrate, since gold is noble and chemically inert [7], and since the characteristic herringbone reconstruction, which exists for this surface [8], is ideal for providing nucleation sites for epitaxial growth of highly dispersed metal islands [9]. Indeed, when molybdenum was deposited on the Au(111) surface using an e-beam evaporator, a self-assembled regular array of one or two layer high Mo islands is formed [Fig. 1(a)] extending over a mesoscopic length scale. The average lateral spacings between the ~30 Å wide Mo clusters are 73 and 140 Å, corresponding to the lattice parameters of the unit cell of the reconstructed Au(111) superlattice. Thus, the Au(111) surface acts as a template to disperse the Mo into small islands, which facilitates the subsequent sulfidation into MoS₂ nanocrystals.

We have explored a number of different sulfidation procedures. In the results discussed below, the Mo is evaporated in an H₂S atmosphere of 1 × 10⁻⁶ mbar at 400 K, and subsequently, the crystal is annealed at 673 K for 15 min while maintaining the H₂S background pressure. In this case, the majority of the Mo islands are transformed into crystalline MoS₂ nanoclusters. It is noteworthy that with respect to morphology, the majority of the nanoclusters are seen to be triangular in shape [Fig. 1(b)] with a side length of ~30 Å. The orientations of the triangles reflect the sixfold symmetry of the substrate. As will be discussed below, these clusters are interpreted as one layer thick MoS₂ nanocrystallites lying flat on the surface with the basal (0001) plane of the MoS₂ particles being oriented parallel to the Au(111) substrate.

Figure 2 depicts an atomically resolved STM image of one of the triangular clusters from Fig. 1(b). The protrusions are arranged with hexagonal symmetry with an average interatomic spacing of 3.15 ± 0.05 Å. This is exactly the interatomic spacing of S atoms in the (0001) basal plane of MoS₂, which is a layered compound, consisting of stacks of S-Mo-S sandwiches held together by van der Waals interactions. Each sandwich is composed of two hexagonal planes of S atoms and an intermediate hexagonal plane of Mo atoms, trigonal prismaticall coordinated to the S atoms. Before we proceed, it is important to point out that low bias, constant current STM images reflect the local density of states at the Fermi level projected to the position of the tip apex [10]. In general, the images thus reflect a convolution of the geometric and electronic structure of the surface. However, STM calculations on layered MoS₂ slabs show that for typical tunneling distances, only the S atoms in the topmost layer are imaged [11]. Since our STM images did not change by varying the tunnel...
and a (10T0) Mo-edge. In Fig. 3(a), the two edges are illustrated for a hypothetical hexagonal MoS$_2$ cluster, where the edges are simple terminations of the bulk MoS$_2$ structure. In the 2H bulk stacking sequence, alternate MoS$_2$ layers will expose Mo and S edges, respectively. One would thus expect that bulk crystals or multilayer clusters preferentially grow in a hexagonal morphology, since the difference in edge energies tends to cancel. The observed triangular shape (Fig. 1) may therefore be a unique feature of the single-layer MoS$_2$ clusters, and the triangular shape implies that one of the edge terminations is considerably more stable. Based on a simple Wulff type construction argument [12] (see inset of Fig. 2), we can indeed conclude that the ratio of the specific surface free energy of the Mo edge to the S edge, or vice versa, is at least a factor of 2 under the present sulfiding conditions. The fact that the single-layer MoS$_2$ nanoclusters have a morphology different from that for bulk MoS$_2$ nanoclusters might be interesting, since previous studies have shown that single and multilayer MoS$_2$ slabs have different catalytic properties [5].

To resolve which of the two edge structures is the more stable, we zoom in on the edge structure of the triangles. If we assume that also the edge protrusions are associated with S atoms, we can, from the grid superimposed in Fig. 2, conclude that the S atoms at the edges are out of registry with the S atoms in the hexagonal lattice of the basal plane. In fact, the S atoms are observed to be shifted by half a lattice constant along the edge.

The question of which edge termination is the more stable is complicated by the fact that under the present sulfiding conditions, the edges may not be simple terminations of the stoichiometric MoS$_2$ as depicted in Fig. 3(a). Recent density functional theory (DFT) calculations [13,14] have shown for the Mo terminated edge structures typically either one [Fig. 3(d)] or two [Fig. 3(e)] S atoms per Mo edge atoms are present. In both cases, the Mo atoms are coordinated to six S atoms, i.e., saturated with S as for the Mo atoms in bulk MoS$_2$, and thus the two structures have almost the same stability. However, the DFT calculations [13] show that only the structure with one S atom per Mo edge atom [Fig. 3(d)] results in S atoms at the edge, which are shifted by half a lattice constant relative to the S atoms in the basal plane, as in the STM images. For the S terminated edges none of the calculated structures appear to be reconstructed and thus consistent with the STM findings [13]. We therefore conclude that the model illustrated in Fig. 3(e) is the structure observed.

Previous studies have shown that the MoS$_2$ basal plane is fairly inactive [15], and that the HDS reactivity occurs preferentially at the MoS$_2$ edges [5,15,16]. The nanostructures shown in Fig. 1(b) are formed under sulfiding conditions, where all Mo atoms, even at the edges, appear to have a S coordination number of six. However, it is generally believed that such structures are not the most active ones in HDS catalysis, i.e., undercoordinated Mo...
Figure 2 (color). An atom-resolved STM image (41 Å × 42 Å, \( I_t = 1.28 \, \text{nA} \) and \( V_t = 5.2 \, \text{mV} \)) of a MoS\(_2\) nanocluster. The grid shows the registry of the edge atoms relative to those in the basal plane of the MoS\(_2\) triangle. The inset shows a Wulff construction of the MoS\(_2\) crystal. \( E_{Mo} \) and \( E_S \) denote the free energy for the Mo and S edges, respectively.

atoms must be formed by sulfur removal before hydrodesulfurization can take place [5,17]. We have performed the first preliminary experiments to create such S vacancies and thus produce the active sites for the HDS catalytic reaction by exposing the MoS\(_2\) nanoclusters to atomic hydrogen produced by dissociating H\(_2\) on a hot W filament.

Figure 3 (color). (a) A ball-model (top view) of a bulk truncated MoS\(_2\) hexagon with Mo and S edges being exposed. The Mo (blue) atoms at the Mo edges are coordinated to only four S atoms (yellow), whereas the Mo atoms in the bulk are coordinated to six S atoms. (b)–(d) Side view of Mo edges. (b) The naked Mo edge in (a). (c) The Mo edges are terminated with S atoms resulting in S dimers at the edges; i.e., we have 2 S per Mo atom at the edges. In (d) there is only one S atom per Mo atom at the edges. In this case, the S edge is reconstructed with respect to the S dimer model in (c). The S atoms move vertically to the Mo plane and shift laterally with half a lattice constant. (e) A top view of (d). Models (d) and (e) depict the triangular structure observed in the STM images with the S edge atoms being out of registry with the S atoms in the basal plane of MoS\(_2\).

Figure 4 (color). An atom-resolved STM image (\( I_t = 1.12 \, \text{nA} \) and \( V_t = -8.5 \, \text{mV} \)) of a MoS\(_2\) nanocluster exposed to atomic hydrogen at 600 K which resulted in the formation of S vacancies at the edges indicated by the white circles. A model (a side and a top view) is shown in which a S vacancy has been formed in the structure (d) in Fig. 3.
nanoparticles, and have experimentally established a new picture of active sites. The approach presented here should be applicable to inorganic clusters deposited on conducting substrates in general. Such detailed atomic-scale information may aid in the development of, e.g., better catalysts.

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*Corresponding author.
Email address: fbe@ifa.au.dk


