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Published in:
Physical Review Letters

Link to article, DOI:
10.1103/PhysRevLett.84.951

Publication date:
2000

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Atomic-Scale Structure of Single-Layer MoS$_2$ Nanoclusters

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Received 11 October 1999

PACS numbers: 82.65.Jv, 61.16.Ch, 61.46.+w, 77.84.Bw

We have studied using scanning tunneling microscopy (STM) the atomic-scale realm of molybdenum disulfide (MoS$_2$) 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 MoS$_2$ 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.

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 nanostructures. 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 MoS$_2$ nanostructures, as a model system of an HDS catalyst. MoS$_2$ nanocrystals, single layer in height and $\sim$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 MoS$_2$. The catalytically important MoS$_2$ edges are found to be reconstructed relative to the perfect MoS$_2$ lattice. The first direct images are presented of the catalytically active sites in the form of S vacancies at the edges of MoS$_2$, 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 $\sim$30 Å wide Mo clusters are 73 and 140 Å, corresponding to the lattice parameters of the unit cell of the reconstructed Au(111) superlattice. Thus, the Au(111) surface acts as a template to disperse the Mo into small islands, which facilitates the subsequent sulfidation into MoS$_2$ nanocrystals.

We have explored a number of different sulfidation procedures. In the results discussed below, the Mo is evaporated in an H$_2$S atmosphere of $1 \times 10^{-6}$ mbar at 400 K, and subsequently, the crystal is annealed at 673 K for 15 min while maintaining the H$_2$S background pressure. In this case, the majority of the Mo islands are transformed into crystalline MoS$_2$ 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 $\sim$30 Å. The orientations of the triangles reflect the sixfold symmetry of the substrate. As will be discussed below, these clusters are interpreted as one layer thick MoS$_2$ nanocrystallites lying flat on the surface with the basal (0001) plane of the MoS$_2$ 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 MoS$_2$, 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 prismatically 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 MoS$_2$ 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...
islands (Fig. 2) have an apparent height of only
contains two S-Mo-S layers. Since the triangular-shaped
which is the common form found in nature, the unit cell
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surface and with the protrusions reflecting the hexagonally
basal plane being oriented parallel to the Au(111) substrate
2H-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
to the S edge, or vice versa, is at least a factor of 2 un-
der 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 associ-
ated 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 termina-
tions 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 struc-
tures 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 con-
stant relative to the S atoms in the basal plane, as in the
STM images. For the S terminated edges none of the
structures 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

![Image](https://example.com/image1.png)

**FIG. 1.** (a) An STM image (4035 Å \(\times\) 4090 Å) of Mo de-
posited onto Au(111) at 307 K under UHV conditions. The inset
is a close-up (397 Å \(\times\) 354 Å) showing the herringbone recon-
struction of the Au(111) [8]. The regular array of elbows on the
dislocation lines acts as nucleation sites for the Mo [9]. (b) An
STM image (744 Å \(\times\) 721 Å) of the sulfided Mo clusters on
Au(111). Mo is deposited in 1.0 \(\times\) 10^{-6} mbar H\(_2\)S while the
gold substrate was cooling down from 420 K to 357 K. Subse-
sequently, the surface is annealed to 673 K in the H\(_2\)S atmos-
phere. current, we interpret the triangular-shaped islands in the
STM images to be MoS\(_2\) nanocrystallites with their (0001)
basal plane being oriented parallel to the Au(111) substrate
surface and with the protrusions reflecting the hexagonally
arranged S atoms in the topmost S layer. In 2H-MoS\(_2\),
which is the common form found in nature, the unit cell
contains two S-Mo-S layers. Since the triangular-shaped
islands (Fig. 2) have an apparent height of only 2.0 \(\pm\) 0.3 Å, we conclude that the MoS\(_2\) nanoclusters are present
as single layers on the Au surface. Thus, only one of the
two building blocks of the unit cell is present.

With respect to the morphology of the MoS\(_2\) nanoclus-
ters, the STM images directly reveal that the clusters are of
triangular shape under the present sulfiding conditions. In
principle, the morphology of a MoS\(_2\) slab should be deter-
mined by two types of edge terminations, a (\(\bar{1}0\)0) S-edge
and a (10\(\bar{1}0\)) Mo-edge. In Fig. 3(a), the two edges are il-
lustrated for a hypothetical hexagonal MoS\(_2\) cluster, where
the edges are simple terminations of the bulk MoS\(_2\) struc-
ture. 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
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![Image](https://example.com/image2.png)
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 4 shows an STM image of the resulting structures, which clearly demonstrates that hydrogen has stripped off a few of the S atoms at the edges forming S vacancies. It is thus likely that we are directly imaging, on an atomic scale, the catalytically active sites for the HDS reaction. The energy involved in creating a vacancy is calculated within the DFT scheme to be 0.6 eV [13,18]. By exposing the sulfided structure to low doses of very reactive H atoms, this energy barrier is surmounted. Under ordinary HDS conditions the high pressures of H$_2$ and higher temperatures ensure a reasonable population of the active sites.

In the past, it has been speculated that the MoS$_2$ clusters could exist in different shapes (hexagonal, truncated hexagonal, rhombohedral, etc.), but direct experimental evidence of such structures has been lacking [5]. Similarly, the lack of suitable experimental techniques to reveal the atomic-scale structure of the edges has led researchers to assume that the Mo and S atoms at the edges are located at the bulk truncated atomic positions. The present STM results thus provide new insight into both the morphology (shape) and the edge structures of MoS$_2$ nanoclusters. We have shown that it is possible to synthesize MoS$_2$ nanostructures and to resolve their structure at the atomic scale. We have presented the first direct real space STM images of the shape and edge structure of single-layer high MoS$_2$...
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.

We acknowledge stimulating discussions with L. Pleth Nielsen and L. S. Byskov, and financial support from the VELUX and the Knud Højgaard Foundations. The Center for Atomic-scale Materials Physics (CAMP) is sponsored by The Danish National Research Foundation. S. H. acknowledges support from the Danish Research Academy and the Interdisciplinary Center for Catalysis (ICAT).

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[18] This is the energy for the reaction *S + H2 → * + H2S, where * denotes an S vacancy, or an active site.