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Atomic-Scale Structure of Single-Layer MoS$_2$ Nanoclusters

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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.

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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 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 $3.15 \pm 0.05$ 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 2.0 Å contains two S-Mo-S layers. Since the triangular-shaped structure observed (Fig. 1) may therefore be a unique feature of the single-layer MoS₂ 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 MoS₂ nanoclusters have a morphology different from that for bulk MoS₂ nanoclusters might be interesting, since previous studies have shown that single and multilayer MoS₂ 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 MoS₂ as depicted in Fig. 3(a). Recent density functional theory (DFT) calculations [13,14] have shown for the Mo terminated DFT 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 MoS₂, 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 MoS₂ basal plane is fairly inactive [15], and that the HDS reactivity occurs preferentially at the MoS₂ 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
atoms must be formed by sulfur removal before hydro-desulfurization 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.

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