Preparation and Structural Characterization of RuS$_2$ Nanoislands on Au(111)

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Ruthenium sulfide (RuS$_2$) exhibits the highest catalytic activity for hydrodesulfurization (HDS) processes among all the transition metal sulfides,[1−3] making it a promising candidate to replace the current MoS$_2$-based catalyst to meet new and more stringent refinery requirements. Theoretical calculations of the (111) and (100) surfaces of RuS$_2$ suggest that the (111) plane is responsible for its catalytic activity.[4−7] To our knowledge this hypothesis has not been tested experimentally. The ruthenium sulfide particles prepared for reactivity evaluation are not suitable for surface studies that can probe the nature of the active sites directly. In this contribution we present a novel method for synthesizing ruthenium sulfide on a reconstructed Au(111) substrate under ultrahigh vacuum conditions. Scanning tunneling microscopy (STM) demonstrates the formation of RuS$_2$ nanocrystals and reveals the structural details of the RuS$_2$(111) surface.

Figure 1a is an STM image from an Au(111) terrace with Ru clusters covering 6% of the total area. Ruthenium was grown by chemical vapor deposition of Ru$_3$(CO)$_{12}$ as described in our previous study.[8] It is evident that ruthenium forms individual nanoclusters of uniform size, about 2 nm in diameter. At this low coverage, the Ru nanoclusters are located at the elbow sites of the herringbone of the Au(111) reconstruction. Only a few cases of cluster aggregation are observed.

To sulfide the Au-supported Ru nanoclusters, the Ru/Au sample was saturated with sulfur at room temperature followed by heating. Sulfur deposition was carried out using a solid-state electrochemical cell, Pt/Ag/AgI/AgS$_2$/Pt. After heating to 800 K, X-ray photoemission spectroscopy (XPS) data show a Ru 3d doublet with the 3d$_{5/2}$ peak at a binding energy of 279.8 eV (cf. 279.7 eV prior to sulfidation) and a broad S 2p signal centered near 162.0 eV, both within the range of the binding energy for Ru^{2+} and (S$_2$)$^{2-}$, respectively.[9−11] As sulfur has been shown to completely desorb from Au by 800 K,[12] the sulfur that remains after heating must be stabilized on the surface by strong interaction with Ru. The S/Ru atomic ratio based on XPS data indicates a stoichiometry of RuS$_{1.8}$. Since RuS$_2$ is the only existing compound in the Ru−S phase diagram,[13] we conclude that the interaction between sulfur and Ru nanoclusters on Au(111) leads to the formation of ruthenium sulfide. Notice that formation of sulfide on extended Ru (0001) surfaces under similar conditions has not been observed and reported.[14] Such a size-dependent activity has often been observed for small clusters.[15]

Sulfur interaction with Ru/Au changes the sample morphology significantly, as can be seen from a comparison of Figure 1, a and b. The majority of the ruthenium sulfide is in the form of small clusters each with a diameter about 1.3 nm, smaller than that of the original Ru nanoclusters. Rather than uniformly anchored at the elbow sites, the sulfide clusters aggregate and form clustered islands confined in the fcc region on the Au surface.

There is also a small number of visibly different features in Figure 1b in the form of flat islands. Our attempt to prepare selectively only one phase was not successful. Sulfidation of Ru
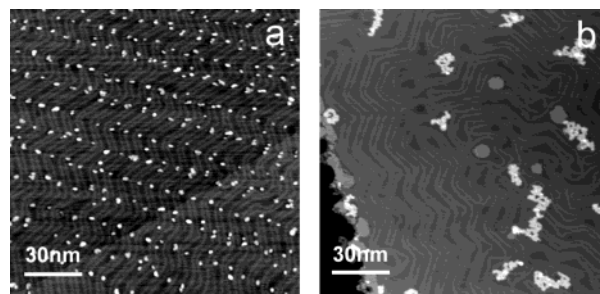

Figure 1. STM image of (a) Ru/Au with Ru nanoclusters covering 6% of Au(111).[8] (b) RuS$_2$ islands on Au(111) formed by exposing Ru/Au to sulfur at 300 K and then heated at 700−800 K.
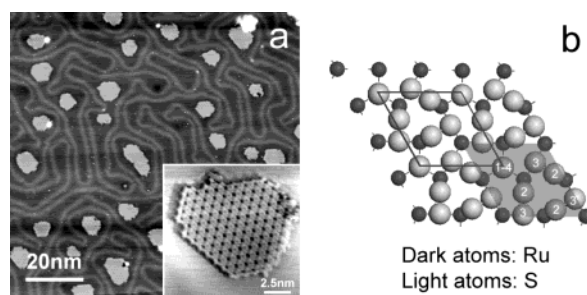

Figure 2. (a) STM image of flat RuS$_2$ nanoislands on S-modified Au-(111). Insert: structure I of flat RuS$_2$ islands. (b) Model of the bulk-terminated RuS$_2$(111) surface, (2 × 2) unit cell indicated.

nanoclusters with sulfur leads to formation of ruthenium sulfide mainly in the form of clustered islands with only a small fraction of flat islands regardless of Ru coverage, the sulfur exposure, and the substrate temperature. Initially, there is place exchange[16] in the Ru/Au system, and Ru atoms are embedded in the gold substrate.[17] During sulfur adsorption, Ru segregates at the surface[17] and reacts with S, producing mainly clustered RuS$_2$ islands.

As confirmed by XPS, ruthenium sulfide is formed also after Ru$_3$(CO)$_{12}$ adsorption on a S-modified Au(111) substrate and heating at 800 K. Since carbonyl does not adhere to sulfur-saturated gold surfaces, the sulfur coverage was lowered by desorption at 500 K. The STM image (Figure 2a) shows the results of this preparation: the flat RuS$_2$ islands are formed selectively. The flat islands have a narrow size distribution centered at 30 nm^2 in terms of island area. Their apparent heights are measured about 0.1 nm with respect to the fcc region of the Au(111) surface. The atomic resolution image (insert of Figure 2a) reveals the hexagonal symmetry of the flat islands together with the atomically resolved substrate. The most noticeable feature of the island is the dark depressions with a periodicity of ∼0.8 nm aligned along the Au lattice. Similar images have been acquired with different STM tips and under different tunneling conditions (bias polarity, tunneling voltage).

Ruthenium sulfide has a pyrite-type cubic structure, similar to a distorted NaCl structure where sulfur exists in S$_2$ discrete units with
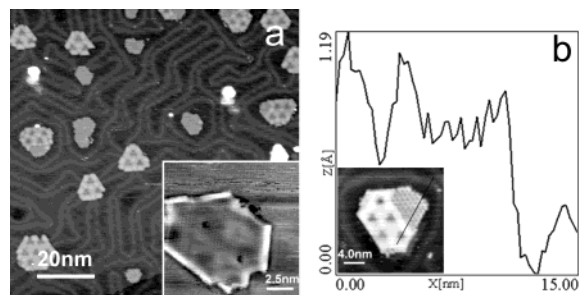
Figure 3. (a) STM image from the sample in Figure 2a after S$_2$ exposure and the anneal to 600 K. Insert: structure II of flat RuS$_2$ island. (b) Line profile across an island shown in the insert.

S−S distances close to an S−S single bond. The Ru atoms occupy Na positions, and the S pairs are centered at the Cl positions. The RuS$_2$ single crystal cleaves easily along (100) plane in an ideal bulk-terminated surface that is unreconstructed and very stable.[4,18] In contrast, the hexagonal (111) plane is the polar and less stable surface that may exist in several different stoichiometries.[4,5]

As schematically shown in Figure 2b, the unstable sulfur-saturated bulk-terminated (111) surface has a hexagonal (2 × 2) unit cell (shown as a shaded rhombus) in the size of (0.79 nm × 0.79 nm) with four Ru atoms per layer and four S$_2$ pairs above the Ru plane: three S2−S3 pairs tilted and rotated with respect to the surface normal, one S1−S4 pair perpendicular to the (111) plane with the S1 atom not directly bonded to Ru. Comparing the stability of several RuS$_2$(111) surface terminations with different stoichiometry, theoretical calculations has shown that the most stable configuration corresponds to a surface that has lost the topmost S1 atom, one in each unit cell.[4,5] This results in a surface with a periodic lattice of sulfur vacancies (rhombus in solid line, Figure 2b). Well matched both in symmetry and lateral scale, the dark depressions in the STM images of the flat islands (Figure 2a, insert) correspond to the locations of these sulfur vacancies. A simple calculation[19] rules out a Moiré pattern as a cause for the observed structure. We therefore suggest that the flat sulfide islands grown on Au(111) are RuS$_2$ with the (111) surface termination and one S vacancy per unit cell (structure I).

Interestingly, after the sample is exposed to additional S$_2$ and heated to a lower temperature of only 500−600 K, a different structure (structure II) appears on the flat islands (Figure 3a). The high-resolution image (Figure 3a, insert) reveals that structure II is composed of close-packed atoms with nearest-neighbor spacing of ∼0.3 nm, showing a triangular dislocation pattern. Our experiment shows that subsequent heating to temperatures above 700 K leads to the transformation of structure II back to structure I. Several islands in Figure 3a show coexistence of structure I and structure II on the same island, probably due to the incomplete transformation during the heat treatment. The line profile across such an island is plotted in Figure 3b, indicating that structure II is at a level about 0.3−0.4 Å higher than structure I.

On the basis of these observations, we propose that the difference between the structure I and structure II is caused by a variation in the sulfur concentration on the surface, which is controlled by the annealing temperature. Stable at relatively low temperature, the structure II is intuitively assigned to the sulfur-covered surface. Since the sulfur adsorption might induce relaxation and reconstruction on the RuS$_2$(111) surface, it is difficult to propose a reasonable model on which we can map structure II atom by atom. The structure II dislocation patterns observed in Figure 3a indicate a lattice mismatch between the RuS$_2$(111) surface and a close packed layer of adsorbed sulfur. Theoretical calculations are under way in our group seeking to understand the behavior of the RuS$_2$(111) surface in the presence of S$_2$.

According to the general accepted view, anion vacancies or coordinately unsaturated sites in sulfide catalysts are the active sites for HDS processes.[20] Such active sites are found at the edges in MoS$_2$ nanoclusters supported on the Au(111) surface.[21] Our studies suggest that a higher density of sulfur vacancies is present on the flat surface of RuS$_2$ nanoislands and could be one of the facts that lead to the higher activity observed for RuS$_2$ than for MoS$_2$ catalysts. The reversible adsorption and desorption of excess sulfur, as discussed above, on the surface of RuS$_2$ nanoislands indicates its potential activity toward sulfur-containing molecules.

In conclusion, we have described the formation of Au supported RuS$_2$ nanoislands using Ru$_3$(CO)$_{12}$ as a precursor and S$_2$ as a reactant. Depending on the preparation procedure, either mostly clustered or flat RuS$_2$ islands have been formed. The latter has been shown as RuS$_2$ nanocrystals with the (111) plane parallel to the Au(111) substrate. The atomically resolved STM images have revealed the presence of sulfur vacancies on the RuS$_2$ (111). Excess sulfur is stabilized on the sulfide surface at low temperature and leads to surface reconstruction, but desorbs at high temperature. The RuS$_2$(111)/Au provides a well-defined model system for studies of chemical and catalytic activity. We believe that future studies of RuS$_2$ as a catalyst for HDS processes will benefit from the present results.

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