Chemical Reactivity of Ni-Rh Nanowires

J. Schoiswohl,1 F. Mittendorfer,2 S. Surnev,1 M. G. Ramsey,1 J. N. Andersen,3 and F. P. Netzer1
1Institute of Physics, Surface and Interface Physics, Karl-Franzens University Graz A-8010 GRAZ, Austria
2Institute for Materials Physics, University of Vienna A-1090 VIENNA, Austria
3Department of Synchrotron Radiation Research, Institute of Physics, Lund University S-22362 LUND, Sweden
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The properties of bimetallic Ni-Rh nanowires, fabricated by decorating the steps of vicinal Rh(111) surfaces by stripes of self-assembled Ni adatoms, have been probed by STM, photoemission, and ab initio density functional theory calculations. These Ni-Rh nanowires have specific electronic properties that lead to a significantly enhanced chemical reactivity towards oxygen. As a result, the Ni-Rh nanowires can be oxidized exclusively, generating novel quasi-one-dimensional oxide structures.

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Nanometer-scale materials in low dimensions possess novel physical and chemical properties that distinguish them from their respective macroscopic bulk counterparts. Finite size effects and the dominance of surface and interface phenomena conspire to generate the observed particular electronic, magnetic, and chemical properties of nanoscale systems that have prompted much scientific excitement and high-level expectations for future nanotechnology applications recently [1–5]. An area where nanoscale systems are already in use with commercial success is the field of advanced heterogeneous catalysis [6,7]. Successful metal–oxide catalysts consist of metallic nanoparticles, of size \( \leq 10 \) nm, dispersed on an oxide support [8]. The particular reactivity and selectivity of nanoscale catalysts and the underlying physico-chemical principles are an area of intensive scientific endeavor. There is general consensus that the presence of low-dimensional structures in the form of under-coordinated atoms at steps, corners, or at other defect sites is of paramount importance for the reactivity of nanoparticle catalysts [9,10], but a detailed understanding of the structure-reactivity relationship is not yet reached. The active components of these nanocatalysts are difficult to characterize at the atomic level because of their inherent disorder, heterogeneity, and structural complexity. Atomistic and related chemical information thus often relies on indirect methods employing, for example, the adsorption behavior of probe molecules to derive structural characterization.

To explore the reactivity of low-dimensional metal systems with atomic precision, we have fabricated a unique prototypical model system consisting of quasi-one-dimensional (1-D) Ni nanowires that decorate the regular monatomic array of steps on a vicinal Rh surface. The system has the character of bimetallic nanowires, because the stripes of Ni adatoms are coupled electronically and elastically to the Rh step atoms, leading to a strained quasi-one-dimensional lattice of Ni rows [11]. It is shown in this letter that the Ni-Rh nanostructures exhibit a modified chemical reactivity with enhanced oxidation kinetics and that the Ni stripes can be oxidized preferentially, yielding 1-D nickel oxide structures as the reaction product. The nickel oxide nanowires formed appear to grow partially pseudomorphic on the Rh substrate with an anisotropically strained lattice. These strained Ni oxide nanowires are interesting structures because of the question of their magnetic state [12] and of their catalytic behavior.

Here we have combined state-of-the-art experimental and theoretical methods to investigate the oxidation reaction of 1-D bimetallic Ni-Rh nanowires formed by one to several atomic row-wide Ni stripes grown on stepped Rh(111) surfaces [11]. We have employed scanning tunneling microscopy (STM) and high-resolution X-ray photoelectron spectroscopy (HR-XPS) with use of synchrotron radiation to follow the oxidation of Ni decorated Rh(15 15 13) and Rh(553) surfaces. The energetics of oxygen adsorption on Rh and Ni-Rh sites, the structure of surface oxide phases, and the surface core-level shifts (SCLS) of metal and oxygen atoms have also been calculated by ab initio density functional theory (DFT). Both the vicinal Rh surfaces expose (111) terraces separated by monoatomic steps with (111)-type microfacets, the terraces being 15 atoms (\( \sim 33.5 \) Å) and 5 atoms (\( \sim 10.4 \) Å) wide for the (15 15 13) and (553) surfaces, respectively. The Rh(15 15 13) surface has been investigated in the STM measurements because more stable tunneling conditions could be obtained on the larger terraces, while the Rh(553) surface has been probed in the HR-XPS experiments to enhance the step derived emission intensity in the core-level photoelectron spectra. The DFT simulations have also been performed on the Rh(553) surface. Consistent results have been obtained on the two vicinal surfaces, indicating that nanowire-specific processes are dominant and are being probed.

The STM experiments were carried out in a custom-designed, variable-temperature STM system as described previously [13]. HR-XPS spectra were recorded at beamline I311 in the Swedish synchrotron radiation laboratory MAX-lab, Lund; the beamline and the electron spectrometer end station have been specified in Ref. [14]. The total energy resolution employed in the present experiments was \( \sim 200 \) meV. The vicinal Rh surfaces were cleaned by heating in oxygen and by cycles of Ar ion sputtering and
annealing. Ni nanowires on Rh (15 15 13) and (553) surfaces have been fabricated by physical vapor deposition of submonolayer quantities of Ni atoms (~0.1–0.2 ML) on to the substrates at 420 K [11]. Figure 1(a) shows an STM image of the Rh(15 15 13) surface, whose straight step edges are decorated by Ni nanowires consisting of stripes of one to several atomic rows wide. The Ni wires are distinguished from the Rh surface atoms by the brighter appearance in the STM (see inset) [11].

The DFT calculations have been performed with the Vienna ab initio simulation package (VASP) [15] using PAW potentials [16] and the PW91 GGA corrections for the exchange correlation (xc) functional [17]. The Rh(553) surface was modeled by a slab consisting of 7 Rh layers parallel to the (111) terraces. For each coverage, the energetically most stable adsorption configuration was determined by a comparison of selected structures. Possible magnetic effects were taken into account by the spin-polarized calculations. The STM images were simulated using the Tersoff-Hamann approach [18]. For the comparison with the experimental data, the calculated height contrast is given perpendicular to the terraces. The core-level binding energy shifts have been calculated in the initial state approximation [19].

The STM images of Fig. 1(b)–1(e) have been recorded after exposure of the Ni-wire decorated Rh(15 15 13) surface to 60 L O₂ (1Langmuir(L) = 1 × 10⁻⁶ torr · s) at 470 K. The large-scale image of Fig. 1(b) shows the straight step structure of the vicinal surface and indicates that the morphology of the Ni decorated Rh steps remains stable under oxidizing conditions [20]. The higher resolution images of Fig. 1(c)–1(e) demonstrate that the oxygen exposed Ni wires display lines of individual bright maxima following the step directions with a separation of maxima of ~5.2 Å (see the line scan of Fig. 1(f), upper panel), which is only slightly shorter than ~2\( \times \)\( a_{Rh} \) (= 5.38 Å). Directly at the Ni step edges, and also between the lines of maxima and the rows of Rh step atoms, continuous broad lines are visible without distinct corrugation resolved. These line structures appear to follow both step and kink edges at the surface [see Fig. 1(c)]. The wire in Fig. 1(d) shows a single row of maxima at its center, but the somewhat broader wire of Fig. 1(e) shows two rows of maxima, which are separated by ~9.7 Å as shown by the line scan in Fig. 1(f) (lower panel). This distance is not commensurate with the Rh(111) unit cell parameter, but considering the Ni(111) unit cell vector of 2.49 Å gives an approximate fourfold periodicity. Moreover, the widths of the oxidized Ni wires as measured with the STM in Figs. 1(d) and 1(e) are ~15 ± 0.5 Å and ~25 ± 0.5 Å, respectively, corresponding to 6 and 10 atomic Ni rows on the basis of the relaxed Ni nearest-neighbor bulk distance. The oxidized Ni wires thus appear to reflect a strained lattice situation, with approximately pseudomorphic behavior to Rh along the step direction but contracted to the Ni lattice perpendicular to it. In a way, this may be regarded as an oxygen decoration of the Ni wires with little relaxation of the Ni structure. We note parenthetically that the weak corrugation visible on the lower left hand part of image 1(e) corresponds to a (2 × 2) structure on the Rh terrace, which is due to chemisorbed oxygen and some adventitiously coadsorbed CO [22].

The DFT calculations of the Ni decorated Rh(553) surface allow us to follow the crucial steps of the oxidation in detail. A systematic overview over the relevant adsorption sites shows that in the low coverage case [Fig. 2(a)] the adsorption of oxygen is clearly dominated by the presence of steps. While the adsorption energy on the terrace is \( E_{ads} = -2.05 \text{ eV} \), i.e. the same value as for adsorption on a flat Rh(111) surface, it is increased to a value of \( E_{ads} = -2.60 \text{ eV} \) in the vicinity of the Ni decoration. This increase can be explained by two contributions: on the one hand by a steric effect, that is an increase in the adsorption energy due to the reduced coordination of Ni atoms at the step, and on the other hand by a chemical effect due to the Ni-Rh alloy formation. A comparison to the adsorption of oxygen on the clean Rh(553) surface [21] allows one to quantify these aspects. While the steric effect results in an increase of the adsorption energy of roughly \( \Delta E = -0.2 \text{ eV} \), the main contribution (\( \Delta E = -0.4 \text{ eV} \))
arises from the change of the chemical environment, that is the formation of the Ni-Rh nanostructure. As a direct consequence, even adsorption sites that are energetically disfavored on the clean surface, like the step facets, become more attractive. The latter observation helps to understand the oxygen configurations at higher coverages: in contrast to the oxygen adsorption on the undecorated Rh(553), the additional oxygen is predicted to adsorb exclusively in the vicinity of the Ni step decoration, leading to a zigzag pattern [Fig. 2(b)] and finally the formation of 1-D Ni oxide stripes [Fig. 2(c)].

In order to mimic the adsorption on the broader (15 15 13) terraces, the adsorption of oxygen on broader Ni stripes, consisting of 3 rows (0.6 ML), on Rh(553) has been investigated. Considering the experimental conditions, we have focused on the high oxygen coverage regime with a completely covered Ni structure [Fig. 2(d)]. Although the significantly smaller terrace width of Rh(553) allows for only a qualitative comparison, the main features of the experimental STM images are reproduced by the simulation of the unoccupied states [Fig. 2(e)]. That is, the oxygen decorated Ni step is seen as a homogenous bright region, while the larger circular maxima separated by twice the Rh lattice constants correspond to the oxygen atoms adsorbed on the Ni terrace region.

While the STM images clearly demonstrate the oxidation of the Ni-Rh nanowires, more specific chemical site information may be obtained from HR-XPS. Figure 3 displays O 1s (a) and Ni 2p$_{3/2}$ (b) core-level spectra of the Rh(553) surface decorated by 0.2 ML Ni as a function of oxygen exposure at room temperature. The experimental data (circles) have been fitted with components given below the data points, the line through the data points is the resulting fit. Bars indicate DFT calculated SCLS. The Rh 3d spectral components in (c)–(f) derived from the decomposition analysis and the DFT calculations (bars) are labeled according to the cartoon in the middle and are explained in the text.

The Rh 3d HR-XPS spectra are more complex because many spectral components have to be considered; here, the theory is crucial to extract chemical information. Figure 3(c) shows the Rh 3d$_{5/2}$ spectrum of the pristine 0.2 ML Ni on Rh(553) surface (data points: open circles) with the spectral components obtained by the curve fitting decomposition analysis given below the data points; the calculated SCLS are included in Figs. 3(c)–3(f) in the form of bars. The components T$_1$–T$_3$ correspond to the Rh terrace atoms, F to the Rh atoms at the lower step
edge in contact with the Ni adatoms (which form the step edge on the Ni decorated surface), and $B$ to the Rh bulk atoms—see the cartoon at the middle of Fig. 3. At low $O_2$ exposures (0.5 L, Fig. 3(d)), the oxygen adatoms occupy one half of the upper-step, threefold hollow sites (see model in Fig. 2(a), IO situation), and the corresponding core-level component $T_1 + O$ shifts to higher BE. Further O$_2$ exposure (1 L, Fig. 3(e)) leads to oxygen adsorption at the lower step edges as well, resulting in a zigzag arrangement as shown in Fig. 2(b) (20), and the $F + O$ component shifts to higher BE. Interestingly, component $T_1$, the oxygen-free Rh atoms at the Ni-Rh boundary, shifts to lower BE at this stage, and this is clearly borne out by the experimental data with the increased intensity at 306.5 eV BE [Fig. 3(e)]. After 2 L O$_2$ [Fig. 3(f)], all upper and lower step sites are occupied by O adatoms (4O, Fig. 2(c)], and the $T_1 + O$ and $F + O$ components equally contribute to the central intensity maximum at 307.1–307.2 eV. Note that the $T_2$ and $T_3$ terrace sites are unoccupied by oxygen at this stage, indicating the increased reactivity of the Ni-Rh nanowires towards oxygen.

The valence band photoemission spectra (see auxiliary material [24]) confirm the preferential oxidation at the Ni rows. The Ni decoration results in a massive increase of the density of states (DOS) close to the Fermi level, which is due to Rh-Ni hybridization. A comparison with the calculated projected local density of states close to the Fermi level, which is derived, in the region 4.5–6.5 eV. The DFT calculations confirm a shift of the Ni $d$ derived core levels. For Ni, final state effects tend to facet under oxygen exposure at elevated temperatures (Ref. [21]).

Test calculations including final state effects have been performed showing that the latter were insignificant for the Rh $3d$ and O $1s$ core levels. For Ni, final state effects are more important leading to a less good agreement with the experiment.

This cannot be taken for granted, since vicinal Rh surfaces tend to facet under oxygen exposure at elevated temperatures (Ref. [21]).

To conclude, we have demonstrated that simple templates like stepped surfaces allow the creation of bimetallic nanostructures. As shown by photoemission data and density-of-states calculations, these nanowires have specific electronic properties, which lead to a significantly enhanced reactivity. A detailed analysis indicates that the main contribution to this phenomenon is the shift of the $d$-band of the step atoms, which facilitates an interaction with the anti-bonding oxygen states. Indeed, surface core-level spectroscopy measurements and DFT calculations agree that a nanowire of 0.2 ML Ni/Rh(553) can be exclusively oxidized with increasing oxygen pressure. Therefore, these nanowires are not only promising new candidates of tailored catalysts for reactions involving the adsorption or dissociation of oxygen, but they also offer the possibility to fabricate quasi-1D oxide structures with novel electronic and catalytic properties, which open up a whole new field of nanocatalysis for further study.

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[19] This cannot be taken for granted, since vicinal Rh surfaces tend to facet under oxygen exposure at elevated temperatures (Ref. [21]).
[23] See EPAPS Document No. E-PRLTAO-97-033638 for (a) Valence band spectra of the clean Rh (553) surface (top curve), after decoration with 0.2 ML of Ni at 420K, and after exposure to oxygen at room temperature. Note that the top spectrum has been amplified by a factor of 2 for better display. (b) Corresponding calculated projected densities of states. Rh(1–3) and Rh-f designate the Rh atoms as indicated in the cartoon at the top of Fig. 5. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.