Surface Chemistry

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Massively Cooperative Adsorbate-Induced Surface Restructuring and Nanocluster Formation**

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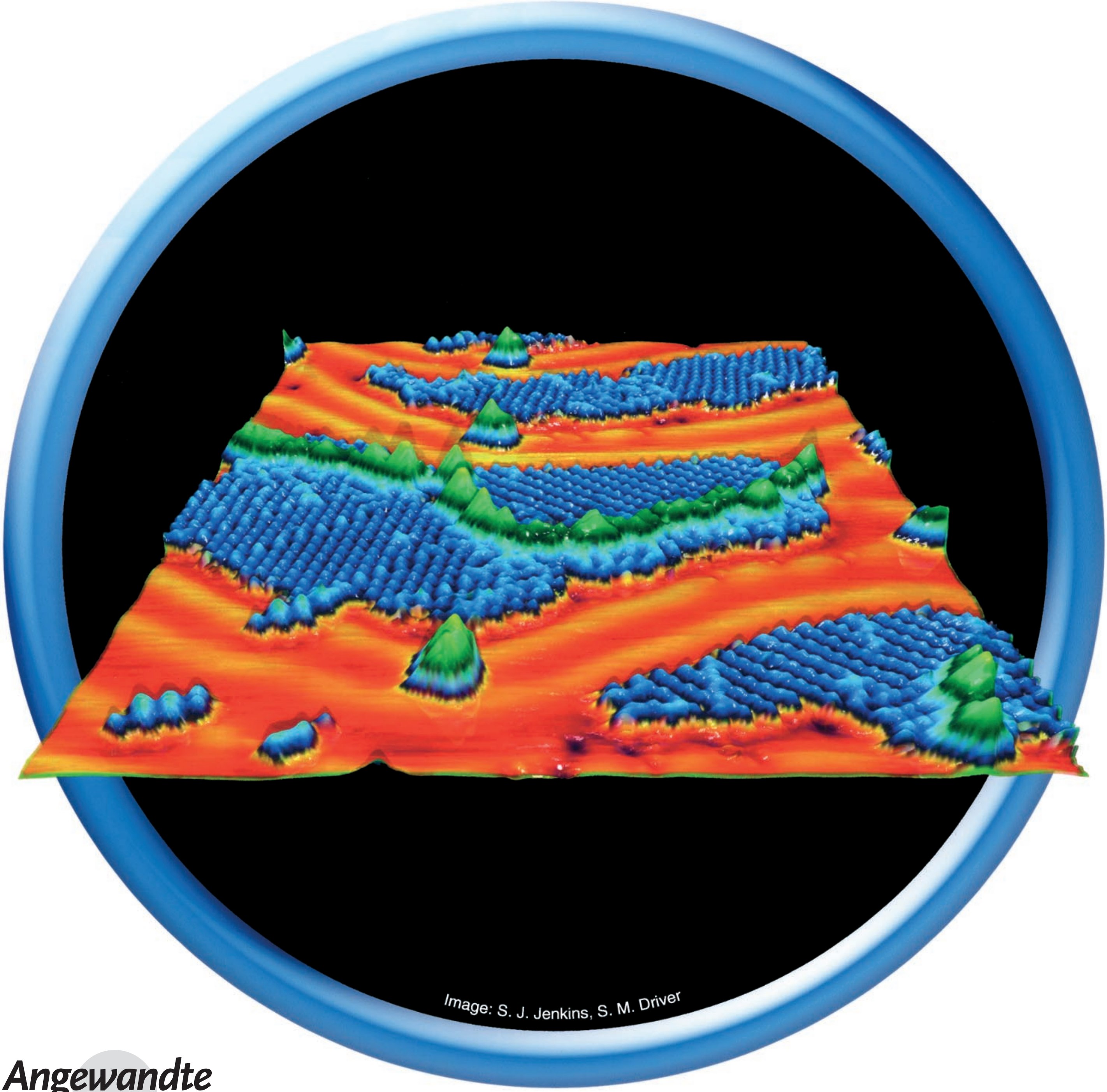
Image: S. J. Jenkins, S. M. Driver

The reconstructions seen at certain clean metal surfaces, such as the Au{111} “herringbone”[1–6] and Pt{100} “hex”[7] phases, are typically lifted by adsorption of small molecular species, with the outermost metal atom layer reverting to (1 × 1). The restructuring process may have important implications for kinetics. In CO adsorption on Pt{100}, for example, an experimentally determined nonlinear power law in the growth rate of (1 × 1)-CO islands from the hex phase implies a “cooperative effect”, in which four CO molecules must coincide for concerted restructuring to (1 × 1) of a small patch comprising about 8–10 Pt atoms.[8,9] This is a key factor in the temporal oscillations observed in the rate of CO_2 production during CO oxidation on this surface.[10,11] However, the cooperative effect is inferred from the kinetics: direct microscopic evidence is currently lacking. Herein we show, using scanning tunneling microscopy (STM), that a massively cooperative effect occurs as growing NO_2 islands locally lift the Au{111} herringbone reconstruction at 78 K in ultrahigh vacuum. The process is triggered when the island size reaches of the order of 300 NO_2 molecules and involves the concerted restructuring of around 20 NO_2 molecules and 80–100 Au atoms. Mesoscopic island ordering driven by local surface stress change[12] is a precursor to this process, and Au nanoclusters form as the restructuring takes place.

Figure 1 shows an STM image of the reconstructed Au{111} surface after a low exposure to NO_2. An extended single stripe domain of the herringbone structure[3] covers most of the visible part of the upper terrace. The bright yellow stripes, usually termed “soliton walls”, mark the transitions between face-centered cubic (fcc) and hexagonal close-packed (hcp) stacking of the outermost layer: Au atoms within these stripes lie close to bridge sites in the second layer.[1,2] The NO_2 molecules have aggregated into substantial ad-islands on the fcc strips of the stripe phase. Smaller NO_2 clusters decorating threading dislocation sites at the soliton wall elbows[13] (extreme left-hand side of Figure 1) nucleate at very low exposures, prior to the islands. A key feature of this image is the lateral curvature of the pairs of soliton walls away from the islands. We attribute this to an NO_2-induced local change in the surface stress in a region centered on each island towards a compressive (or, at least, less tensile) value[12] and a consequent reduction in the slight lattice contraction in the outermost Au layer under the island. Thus, the soliton wall, in which the contraction is greater, is laterally displaced away from the island boundary. Curvature of the soliton wall appears to be a sensitive marker of, and suggests a route towards measuring, local surface stress changes.

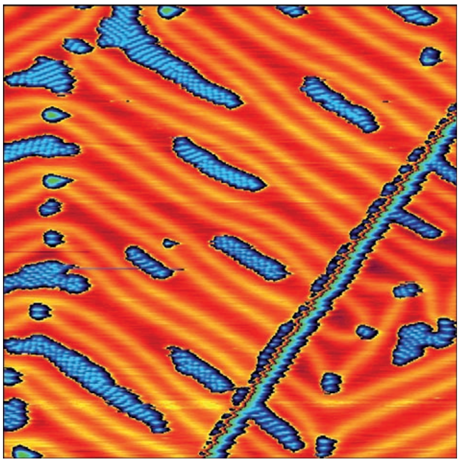

Figure 1. Molecularly resolved topographic STM image (500 × 500 Å^2) of NO_2 islands (blue) adsorbed on reconstructed Au{111} (orange) at 78 K. A step running across the bottom right-hand corner separates the upper (to the left of the step) and lower terraces. Pairs of soliton walls (yellow lines) surround narrow strips of hcp stacking; NO_2 islands are located on the wider fcc strips. Lateral curvature of the soliton walls around the islands and a staggered pattern of mesoscopic ordering of the islands within the stripe domain can be seen.

The islands show marked mesoscopic ordering into either of two distinct patterns. Within a single extended stripe domain (Figure 1 and central terrace of Figure 2), neighboring islands are alternately displaced parallel to the direction of the soliton wall into a staggered arrangement. At domain boundaries (aligned sets of soliton wall “elbows” separating adjacent stripe domains in the herringbone pattern), neighboring islands tend to adopt an alternate-branching configuration, extending to either side of the boundary alternately into one domain and the other, as can be seen in various regions in Figure 2. The interaction between the local

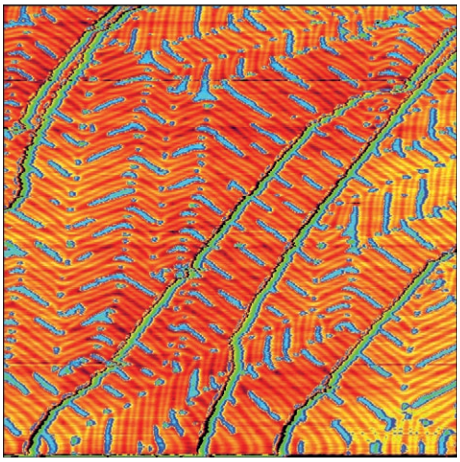

Figure 2. Large-area STM image (2000 × 2000 Å^2) of NO_2 islands (blue) on successive terraces of reconstructed Au{111} (orange) at 78 K. The staggered pattern of mesoscopic ordering of islands can be seen within single stripe domains, and the alternate branching pattern can be seen at domain boundaries.

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compressive stress fields around the islands that drives this ordering[12] is reflected in the complementary way that the soliton walls curve around adjacent islands.

As the islands grow with increasing exposure to NO_2, they start to spread into adjacent fcc strips. A characteristic example of a large island bridging two fcc strips in this way is shown in Figure 3. Locally (i.e. underneath the island), the reconstruction has been lifted. The island does not exhibit the rumpling that would occur if the soliton walls were intact underneath; a U-shaped connection[3] of the soliton wall pair terminates the hcp strip to the left of the island, and a string of nanoscale clusters decorates the island. The clusters evidently contain the excess Au atoms ejected in lifting the reconstruction, and the string has a distinctive S-bend shape. The total number of Au atoms in the cluster string, estimated from the number of discrete features in each cluster (based on those in which resolution of the substructure was achieved) and the number of clusters, matches well with the number of Au atoms that must be ejected in lifting the length of soliton wall covered by the island (80–100 atoms). It is probable that each of the 20 or so clusters in the string is decorated with an NO_2 molecule.

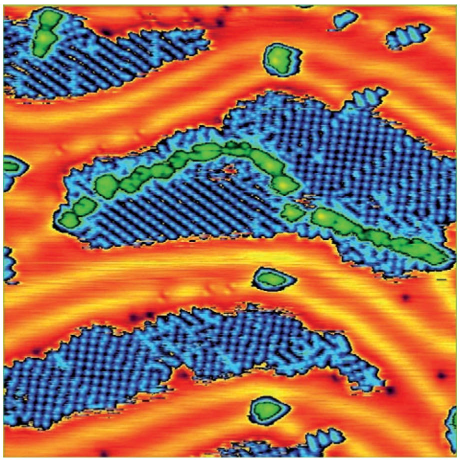

Figure 3. Molecularly resolved STM image (300×300 Å^2) of NO_2 islands (blue) on Au{111} (orange) at 78 K after further exposure to NO_2. The central island has expanded over two successive fcc strips, locally lifting the reconstruction, and is decorated with a string of clusters (green/yellow). The lower island remains confined to a single fcc strip and is undecorated.

We can infer how islands such as that shown in Figure 3 evolved, as illustrated schematically in Figure 4. Initially, two NO_2 islands sit in successive fcc strips on alternate sides of a domain boundary in the alternate branching pattern described above. Their compressive stress fields distort the adjacent soliton walls (Figure 4 a). As the island grows, a point is reached where further distortion of the soliton walls becomes prohibitive. Au atoms are now ejected from the pair of soliton walls sandwiched by the islands, aggregating to form cluster strings marking the approximate positions from which the atoms were ejected (Figure 4 b); the intervening hcp strip reverts to fcc stacking. Because the right- and left-hand islands impinge on the central pair of soliton walls from above and below, respectively, an S bend bisects the cluster string.

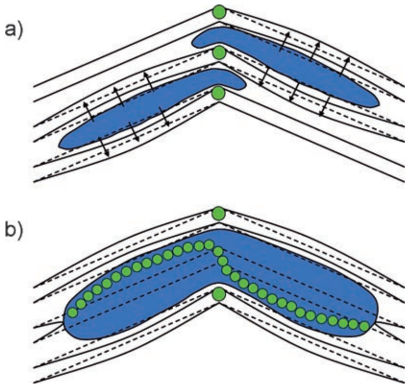

Figure 4. Illustration of the massively cooperative step in the mechanism by which growing NO_2 islands (blue) locally lift the reconstruction, ejecting Au atoms, which form a string of clusters (green). a) Two NO_2 islands in alternate-branching configuration around a domain boundary, causing bowing of pairs of soliton walls. Clusters (green) decorate soliton wall elbows at the domain boundary. b) After coalescence of the two islands. An S bend in a cluster string is a consequence of the islands having impinged on the central hcp strip from opposite sides.

The local lifting of the reconstruction appears to proceed rapidly. At these exposures, a range of island sizes coexist: all of the larger islands that span two fcc strips exhibit cluster strings of comparable length, most containing S bends (the exact configuration will depend on the initial arrangement of islands), whereas smaller islands that remain confined to a single strip do not. Figure 3 shows an example of each of these cases. We found no instances of part-formed cluster strings and no isolated clusters within the islands (except where an island had impinged on one of the initial clusters at the domain wall elbows). Moreover, the fact that the clusters are located very close to the positions at which the Au atoms are ejected from the soliton wall indicates that essentially all of the atoms that form the cluster string are ejected and aggregate before any has time to diffuse away to a surface step.

We conclude that the local restructuring is an all-or-nothing process: once initiated, it proceeds dominolike to completion, rather than occurring progressively as the island grows by attachment of successive molecules. Instead, when the growing island reaches some critical size (on the order of 300 molecules, although the exact value will be affected by the inherent variability of the initial herringbone pattern), the restructuring of the 80–100 Au atoms and the approximately 20 NO_2 molecules at the island boundary, which go to decorate the clusters, occurs as a concerted process. We therefore describe this as a massively cooperative restructuring step (in contrast with Pt{100}/CO, in which four CO molecules and 8–10 Pt atoms restructure cooperatively and the (1×1) island size is not a factor[8,9]). Its rapidity is not surprising: after the first Au atom is ejected, its neighbors will have reduced in-plane coordination and the lattice will be locally distorted. The sequential ejection of successive atoms then becomes facile.

Although there are parallels, this mechanism differs in most details from the restructuring induced by O and S on Cu/Ru{0001},[14,15] for which island formation is not involved, the reconstruction is modified rather than lifted and the restructuring is not reported as rapid or cooperative. The mechanism proposed for alkanethiol-induced lifting of the herringbone reconstruction is also very different; in that case, interestingly, mesoscopic ordering of islands was not seen.[16]

This confluence of mesoscopic island ordering guided by the herringbone pattern, the unprecedented scale of the cooperative effect, and the involvement of nanocluster formation may be unique to Au{111}/NO_2. Much of the recent interest in the unexpected low-temperature catalytic activity of Au concerns nanoparticles, the small size of which is a key factor in their activity,[17–20] although, surprisingly, NO_2 promotes adsorption of CO on Au{111} even in the absence of clusters.[21] The high density of Au nanoclusters that we observe opens up the possibility that Au{111} may exhibit interesting catalytic activity at low temperatures in the presence of NO_2. We plan to explore this possibility, which is of great potential importance in industrial catalysis, in future experiments. By extension from Pt{100}/CO, we anticipate that the massively cooperative nature of the NO_2-induced restructuring of Au{111} will have a profound impact on the kinetics of any reaction based on this system. However, the local nature of the process means that its exact global impact is hard to predict, and careful experiments will be necessary to elucidate this properly.

Experimental Section

The reconstructed clean Au{111} surface was prepared by standard ultrahigh vacuum procedures. It was then exposed at 78 K to gaseous NO_2 in stages, and examined after each exposure by STM, operating in constant current mode at 78 K. In the figures, all terraces are shown artificially co-leveled for clarity; a false color scale enables the soliton walls of the herringbone pattern, individual molecules within the islands, and the clusters to be seen simultaneously.

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