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Pronounced Surface Sensitivity of Hydroxylamine Oxidation on Gold Single-Crystal Electrodes in Acidic and Neutral Aqueous Solutions

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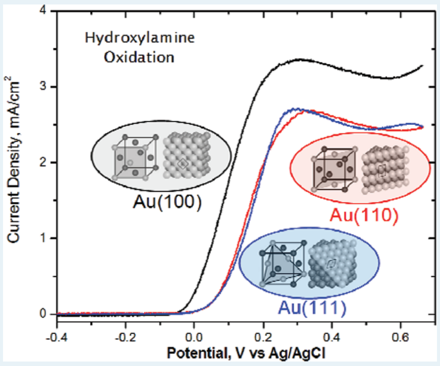
Supporting Information

ABSTRACT: The oxidation of hydroxylamine on the three low index faces of Au single crystal has been investigated by cyclic voltammetry in buffered aqueous solutions in the pH range 1−7 under quiescent conditions. The results obtained have shown that the onset potential for the reaction on Au(100) is more negative, and the current in the region of small overpotentials is higher than for Au(110) and Au(111) regardless of the pH of the solution. Measurements performed in phosphate buffer (pH 7) with single crystal rotating disk electrodes in the hanging meniscus configuration yielded rather linear Tafel slopes in the small overpotential region for Au(111) and Au(110), which were higher than those found for Au(100). This affords clear evidence that the mechanism for this latter surface is different that for the other two faces involving in all likelihood one or more yet to be identified adsorbed intermediates.



KEYWORDS: *Au electrode, single crystal, hydroxylamine, rotating hanging meniscus*

INTRODUCTION

The advent of relatively simple methods to produce well-defined single crystal surfaces of a growing number of metals has made it possible to explore with ever increasing detail the effects of surface orientation on the rates of heterogeneous redox reactions.[1] Most of the emphasis has been focused on metals such as Pt, which are known to exhibit high affinity for a variety of species.[2,3] Rather surprisingly, in view of its general inertness, Au has also been found to exhibit strong electrocatalytic effects as a function of the crystal plane exposed to the electrolyte.[4−10] Among the most striking illustrations is the reduction of dioxygen on Au(100) in alkaline media, a process that displays an onset potential far more positive than that found for the other two low index faces.[4,8] Far more intriguing is the higher activity of Au(100) for the oxidation of hydrazine in aqueous acidic electrolytes reported by the Alicante group about a decade ago.[5] This brief contribution describes the role of the surface orientation on the oxidation of NH_2OH on Au, and represents an extension of electrochemical and spectroscopic studies carried out in our laboratories involving polycrystalline (poly) rotating Au disk electrodes (RDE) in aqueous media.[11−14] Hydroxylamine, NH_2OH, is a reducing agent used most commonly in the synthesis of oximes from aldehydes and ketones. The oxime of cyclohexanone, for example, can be converted to ε-caprolactam, the precursor to the manufacturing of Nylon-6. It addition, NH_2OH is important in biological processes and, as such, has received considerable attention in the scientific literature including electrocatalysis.[15] Particularly noteworthy are the contributions of Karabinas et al.[16] and Rosca et al.[17] who examined the oxidation of NH_2OH on polycrystalline Pt,[17] and, more recently, those of Koper and co-workers on Pt single crystals.[18] On the basis of their studies, there seems to be little doubt that the oxidation of NH_2OH leads to the formation of adsorbed NO, blocking surface sites for the reaction to ensue. Interests in our laboratories have been aimed at exploring NH_2OH oxidation of Au, a metal believed to display no affinity toward adsorption of NO.

As will be shown, the activity of Au(100) surfaces for the process under study is much higher than for the other two low index faces, that is, Au(111) and Au(110), pointing to the possible involvement of one or more adsorbed intermediates in the reaction mechanism.

EXPERIMENTAL SECTION

All of the measurements herein presented were performed with a set of highly oriented Au(111), Au(100), and Au(110) single crystals in the form of flat end cylinders of about 0.3 cm^2 cross sectional area, aligned with their main axes normal to the crystallographic plane of interest (Metal Crystals and Oxides, Ltd. Cambridge, England, 5 N purity). Just prior to the electrochemical experiments these specimens were thermally annealed in a hydrogen-air flame, cooled slowly in an Ar atmosphere until the red color had just disappeared, and subsequently immersed into either ultrapure water or an

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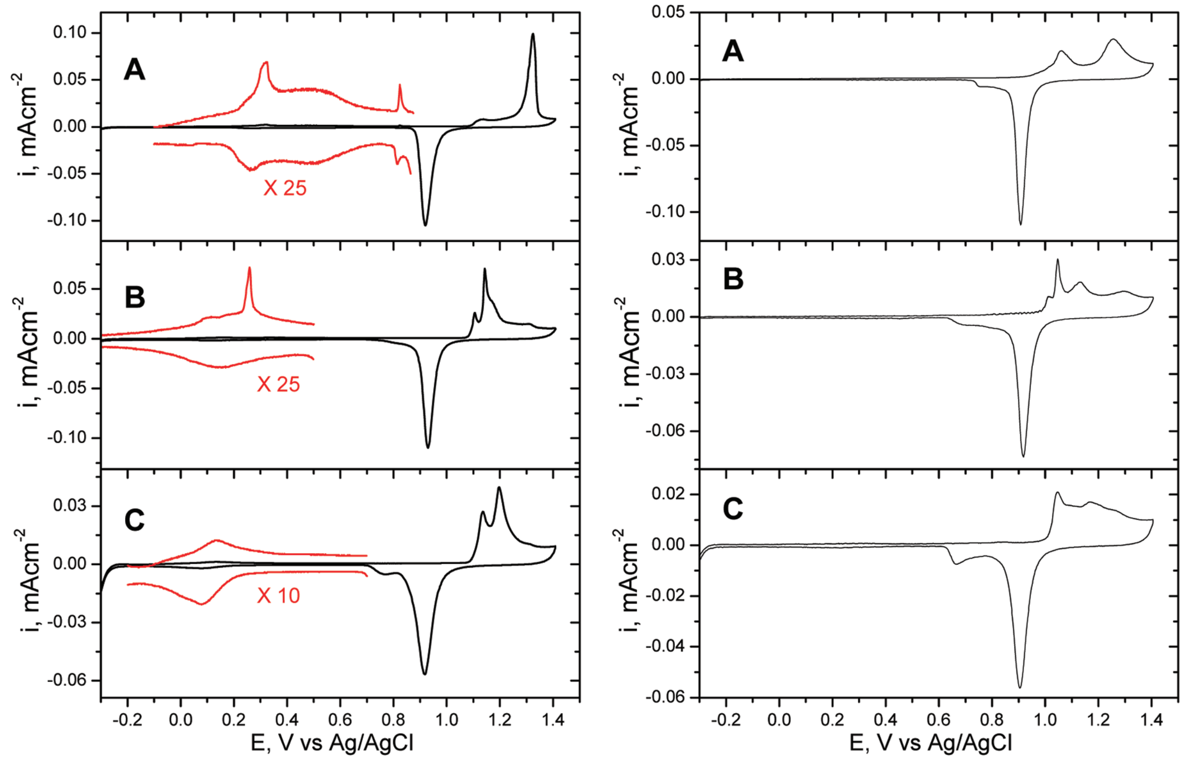

Figure 1. Left panels: Cyclic voltammetry curves for Au(111) (A), Au(100) (B), Au(110) (C) recorded at ν = 10 mV/s in 0.1 M H_2SO_4. Right panels: Same as left panels for data collected in 0.1 M $HClO_4$ under otherwise identical conditions.

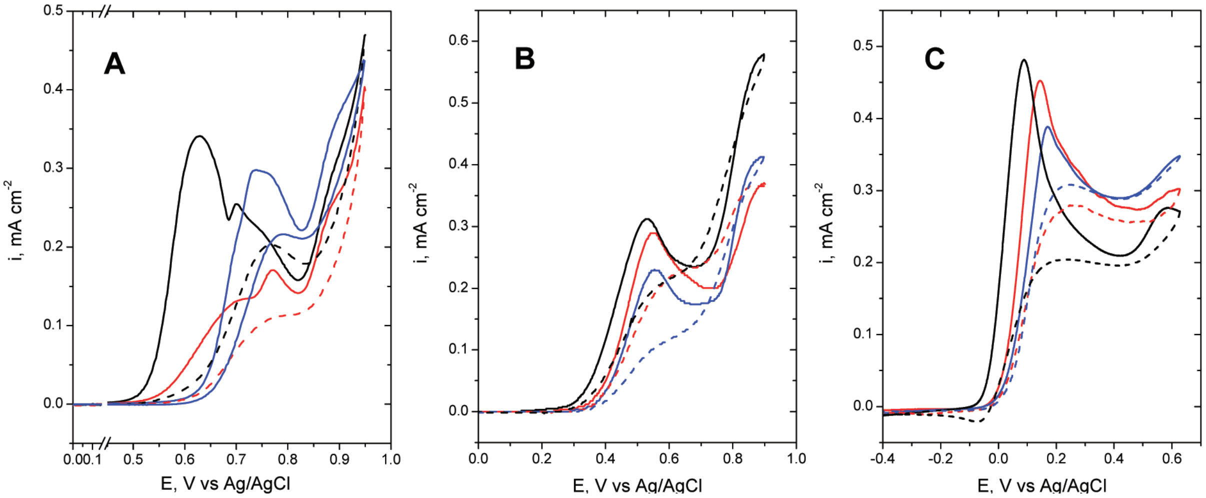

Figure 2. Cyclic voltammograms recorded at a scan rate ν = 10 mV/s for Au(100) (black), Au(110) (red), and Au(111) (blue) in 0.1 M $HClO_4$ (Panel A), and acetate buffer (pH 4, Panel B) with 2 mM NH_2OH and phosphate buffer (pH 7, Panel C) solution containing 2.66 mM NH_2OH. The solid and dashed lines represent scans toward positive and (subsequent) negative potentials, respectively.

aqueous solutions of either 0.1 M $HClO_4$ (Ultrapure, J.T.Baker), acetate buffer (pH 4) made from sodium acetate (Fisher, ACS pure) and glacial acetic acid (Fisher, ACS pure), or phosphate buffer (pH 7) prepared from monosodium dihydrogen phosphate (J.T. Baker Ultrapure Bioreagent 99.9%) and disodium hydrogen phosphate (J.T. Baker Ultrapure Bioreagent 99.7%) using ultrapure water (UPW, 18.3 MΩ cm, EASYpure UV system, Barnstead).[19] A few experiments were also performed in 0.1 M H_2SO_4 (J.T. Baker, Suprapure) to study the effects of a strongly adsorbed anion on the electrocatalytic activity. Hydroxylamine, NH_2OH, was obtained from Aldrich (99.999% pure) and $NaNO_2$ from Fisher (ACS pure). During the transfer through air the surface was protected with a droplet of either ultrapure water or electrolyte.

For rotating disk electrode (RDE) measurements, freshly annealed Au single crystal cylinders covered with a droplet of UPW were mounted on a special Kel-F collet attached in turn to a rotator (Pine Instruments). Following immersion in the electrolyte, the cylinders were slightly lifted to achieve a hanging meniscus configuration and thus avoid contributions to the signal derived from the walls. Cyclic voltammetry and dynamic polarization curves were recorded at scan rate of 10 mV/s using a conventional potentiostat (AFRDE 4, Pine Instruments) at room temperature, that is, about 21 °C,

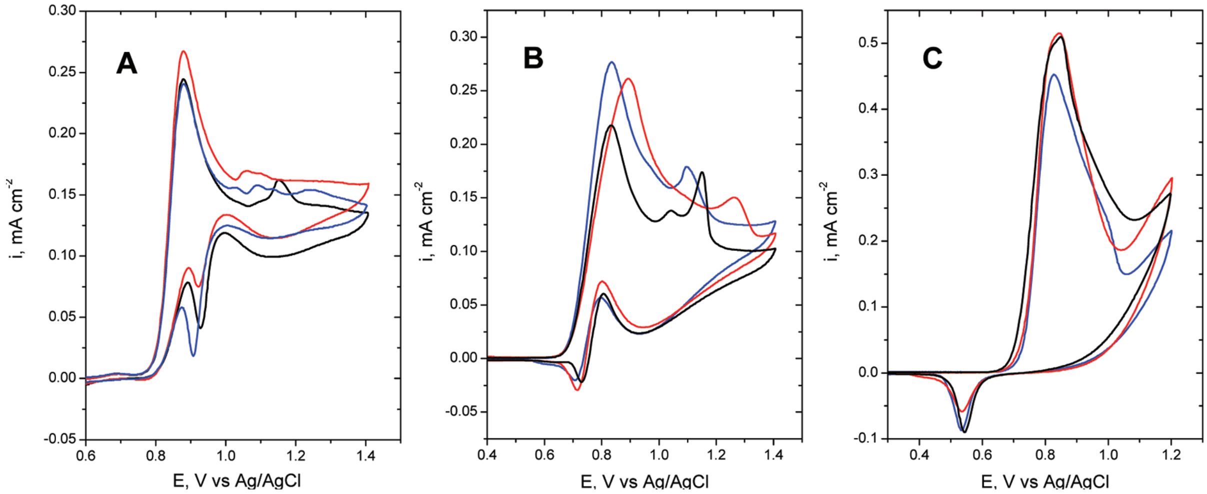

Figure 3. Cyclic voltammograms recorded at ν = 10 mV/s for Au(100) (black), Au(110) (red), and Au(111) (blue) in 0.1 M $HClO_4$ (Panel A) and buffer with 1 mM $NaNO_2$ (pH 4, Panel B) and phosphate buffer (pH 7, Panel C) solution containing 1.33 mM $NaNO_2$. All curves were acquired during the first scan into the oxide region to prevent surface damage (see also Supporting Information).

yielding in the case of 0.1 M H_2SO_4 and 0.1 M $HClO_4$, features believed to be characteristic of the clean, well oriented, low index faces in question (see Figure 1).[19,20] All solutions were deaerated with Ar (UHP, 99.999%, Airgas).

■ RESULTS AND DISCUSSION

Shown in Figure 2 are cyclic voltammograms recorded at a scan rate ν = 10 mV/s for Au(100) (black), Au(110) (red), and Au(111) (blue) in aqueous 0.1 M $HClO_4$ (Panel A) and acetate buffer (pH 4, Panel B) with 2 mM NH_2OH and phosphate buffer (PB, pH 7, Panel C), solution containing 2.66 mM NH_2OH in a potential region negative to the onset of oxide formation in the neat (NH_2OH free) electrolyte (see Figure 1). The thick and dashed lines in these panels correspond to currents recorded during scans toward positive and (subsequent) negative potentials, respectively. On the basis of these data, the activity of the Au(100) surface for small overpotentials, as judged from the more negative onset potential, is much higher than that associated with the other two faces, regardless of the pH of the solution. It should be emphasized that in the potential range in which the oxidation of NH_2OH occurs all three single crystal surfaces are expected to be unreconstructed.[21] Lastly, none of the single crystals displayed activity toward NH_2OH reduction down to onset of hydrogen evolution within the pH range examined.

In stark contrast, the oxidation of nitrite, one of the possible products of oxidation of NH_2OH recorded in PB containing 1.33 mM $NaNO_2$ (and also in acetate buffer and 0.1 M $HClO_4$) appears hardly sensitive to the crystal plane exposed to the solution, that is, the three low index faces display a common onset potential and only minor differences in the observed magnitude of the current. This is illustrated in Figure 3, which displays first voltammetric scans into the oxide region. Curves recorded in the acidic solutions in which the positive potential limit was always negative to the onset of oxide formation under otherwise the same conditions are given in the Supporting Information.

Although informative, the current in cyclic voltammetry represents a convolution of the applied potential and time and, as such, may not provide reliable data regarding the behavior of the system under strict steady state conditions. This becomes particularly important for reactions where the rate at which adsorbed intermediates are formed becomes comparable to the rate at which subsequent or parallel reaction occur. An eloquent illustration of this effect was recently reported for the oxidation of NH_2OH on Pt-, and Pd-modified Au surfaces in neutral aqueous solutions(12), which yielded in cyclic voltammetric experiments under quiescent conditions an onset potential for the reaction more negative than that for bare Au. However, this trend was reversed when the same experiments were performed under forced convection using a rotating disk electrode (RDE). To examine this possibility, RDE measurements for the system under investigation were performed in the so-called hanging meniscus configuration. Shown in Figure 4 are dynamic polarization curves recorded with the three low index single crystals for pH 7. In agreement with the data collected in stagnant solutions, the onset potential was significantly more negative, about 100 mV, and the peak current was markedly larger for Au(100) that for the other two index faces. This is better visualized in Figure 5, which compares curves obtained for the three Au faces at a common rotation rate, that is, ω = 900 rpm.

As was found recently for Au(poly) in PB solutions (pH 7),[13] all these curves are characterized by a current peak followed by a shallow depression, where in that work, the current peak was proportional to $\omega^{1/2}$. A theoretical analysis of the results obtained in that work was consistent with the reaction proceeding via an EEECE mechanism. Support for this model was obtained from the predicted shift in the peak potential as a function of ω. In fact, the same behavior is at least qualitatively displayed by the curves in Figure 4 in this work.

Evidence that the mechanism responsible for the enhanced activity of Au(100) is different than that associated with the other two faces was obtained from the values of the Tafel slopes in the region of small overpotentials, where the currents were found to be virtually unaffected by convection (see Figure 6), about 70 mV^{-1} for Au(100) and 40 mV^{-1} for Au(111) and Au(110). Although somewhat speculative, in view of the lack of spectroscopic evidence, it seems reasonable that the reaction pathway for Au(100) involves one or more adsorbed intermediates, which upon full dehydrogenation would yield NO and/or nitrite as a product. Similar arguments were invoked by Alvarez-Ruiz et al. to explain the higher activity of

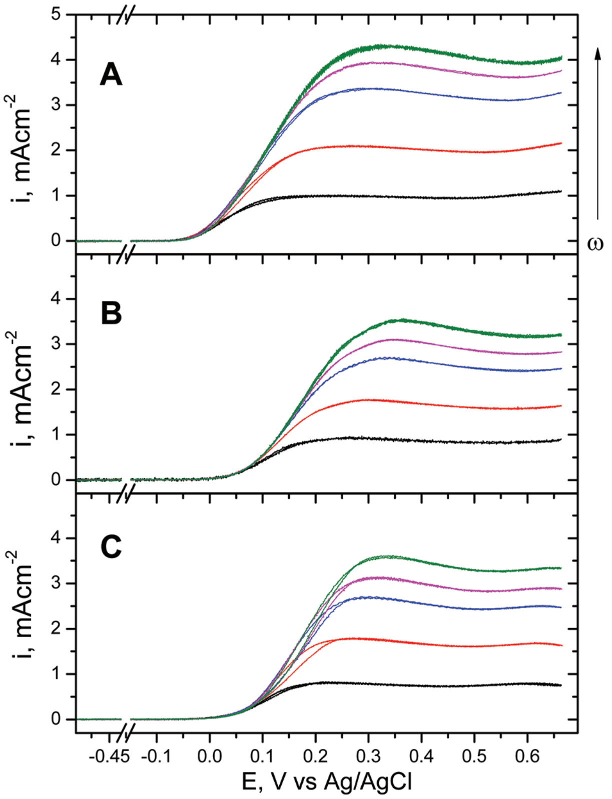

Figure 4. Dynamic polarization curves collected in 2.66 mM NH_2OH in PB (pH = 7) at ν = 10 mV/s for Au(100) (Panel A), Au(110) (B), and Au(111) (C) in the hanging meniscus rotating disk configuration at various rotation rates ω = 100, 400, 900, 1200, and 1600 rpm in the sequence defined by the arrow.

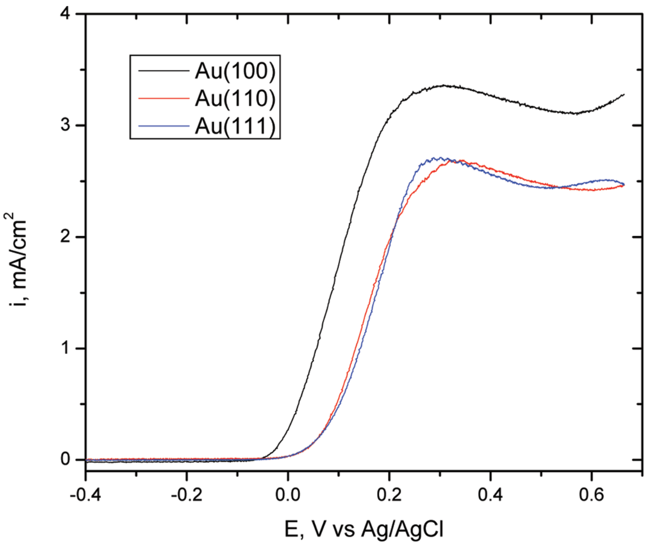

Figure 5. Comparison of polarization curves recorded in 2.66 mM NH_2OH in PB (pH 7) at ω = 900 rpm for Au(100) (black), Au(110) (red), and Au(111) (blue).

Au(100) for hydrazine oxidation in acid media,[5] a reaction that generates dinitrogen as the product. Further support for this view was obtained from experiments performed in 0.1 M H_2SO_4 which, as shown in Figure 7, led to a shift in the onset of NH_2OH oxidation toward positive potentials compared to 0.1 M $HClO_4$, consistent with the blockage of surface sites by adsorbed bisulfate ion.[22]

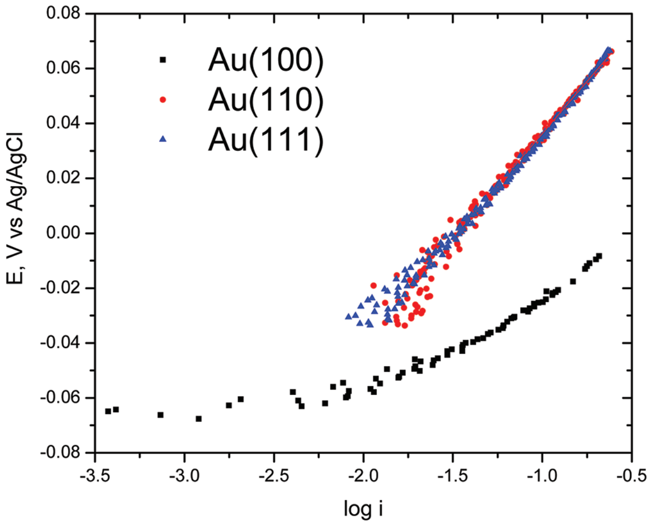

Figure 6. Tafel plots for the oxidation of NH_2OH in PB (pH 7) for Au(100), Au(110), and Au(111) in the small overpotential region based on the data in Figure 5.

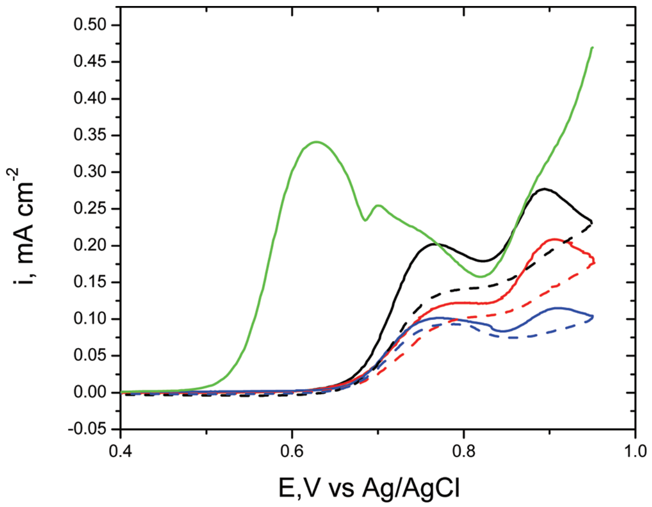

Figure 7. Cyclic voltammetric curves for Au(100) (black), Au(110) (red), and Au(111) (blue) acquired at ν = 10 mV/s in 2 mM NH_2OH in 0.1 M H_2SO_4.The green curve was recorded in 0.1 M $HClO_4$ for Au(100) under otherwise identical conditions.

■ CONCLUSIONS

The onset of oxidation of NH_2OH on Au(100) in the pH range 1−7 occurs at significantly more negative potentials compared to the values observed for Au(111) and Au(110). Measurements performed in phosphate buffer (pH 7) with single crystal rotating disk electrodes in the hanging meniscus configuration yielded linear Tafel slopes in the small overpotential region for Au(111) and Au(110), which were higher than those found for Au(100). This affords clear evidence that the mechanism for this latter surface is different that for the other two faces involving in all likelihood one or more yet to be identified adsorbed intermediates. Efforts are underway in our laboratory to explore the underlying bases of this strong electrocatalytic effect by exploring the interactions of NH_2OH and Au(100) in ultrahigh vacuum.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Further details are provided in Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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