Nitrate Reduction Pathways on Cu Single Crystal Surfaces: Effect of Oxide and Cl⁻

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Graphical Abstract

$\text{Cu}_2\text{O}(100)$

Abstract

The origin of different nitrate reduction activity between the (100), (111), and (110) faces of Cu is examined using vibrational spectroscopy and calculations. Shell isolated nanoparticle enhanced Raman spectroscopy (SHINERS) reveals a suite of intermediates from the nitrate reduction process on Cu(100), Cu(111), and Cu(110) including NO_2^- and HNO . All three faces show similar intermediates, suggesting the same mechanism is operative on all of them. Critical to the reduction pathway on the bare Cu surfaces is the reduction of nitrate to nitrite concomitant with partial oxidation of the Cu surface. This priming action facilitates nitrate reduction and reduces overpotentials, particularly on the Cu(111) and Cu(110) faces, which are more susceptible to oxidation. Decoration of the surfaces with Cl^- suppresses nitrate reduction, resulting in higher overpotentials and lower current density. NH_3 is observed by SHINERS as a direct nitrate reduction product in the presence of Cl^- , rather than NO_x species observed on the bare Cu surfaces, indicating a reaction pathway unique from the bare, undecorated surface.

Keywords: nitrate reduction, copper, Raman spectroscopy, surface oxidation, electrocatalysis

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I. Introduction

Nitrate contamination of groundwater poses serious health risks at high levels of exposure including methemoglobinemia (blue-baby syndrome in infants) and increased incidence of certain gastrointestinal cancers.[1-3] This contamination is mostly the byproduct of agricultural runoff from fertilizers and animal waste.[3-5] Remediation of nitrate in nuclear waste is also a critical issue for the nuclear industry.[6] Additionally, nitrate is used as a starting material to produce useful chemicals such as ammonia, hydroxylamine, hydrazine, and azides.[7] Thus, effective methods and materials to reduce nitrate is of considerable interest. Electroreduction is considered ideal as a method to reduce nitrate in water because reduction products can be tuned by altering pH, concentration, electrode material, and applied potential.[2; 8; 9] Nitrate reduction electrocatalysis is of interest in numerous contexts, but like the electrocatalysis associated with energy, such as that involving oxygen or CO₂ reduction, a detailed understanding of the interplay between the reactant, intermediates, and the substrate is required. Many metal surfaces have been investigated, with Cu representing one of the most active nitrate electrocatalysts available either alone [10; 11] or in combination with other materials[12-15]

On copper surfaces in acidic media, nitrate reduction occurs through an eight electron reduction as shown in equation 1.[16; 17]

$$E^\circ = 0.68 \text{ V vs. Ag/AgCl}$$

Previous investigations observed intermediates to reaction 1, particularly nitrite (NO₂⁻)[16; 17] and gaseous nitric oxide (NO)[10] in aqueous acidic conditions. A full suite of intermediate reactions are considered as possibilities for nitrate reduction to ammonia on Cu,

similar to reactions studied on Pt surfaces and Cu decorated Pt.[8; 9; 11; 18] The rate determining step on all surfaces is considered the initial two electron reduction of nitrate to nitrite as seen in equation 2.[7; 8; 16; 17]

Reduction of nitrite to nitric oxide through a one electron reduction has been demonstrated on Pt as in equation 3.[7; 8]

Adsorbed NO is then reduced to NH_3 comparatively fast according to equation 4.[8]

Nitric oxide reduction to ammonia can be further broken down into a three step sequence as demonstrated by equations 5 through 7.

Direct protonation of adsorbed NO results in an equilibrium between NO and HNO. [7] This is followed by a rate determining step of the one electron reduction of HNO to H_2NO , followed by the rapid three electron reduction of H_2NO to NH_3 . [7]

While the intermediate situation is well-described for *Pt surfaces*, there is not yet a full understanding regarding the nature of intermediates on *Cu* and how these intermediates influence

the electroreduction activity.[9] We demonstrated previously that Cu(111) is more active for nitrate reduction than Cu(100).[17] The origin of this different reactivity is not yet clear, in part because it is not known whether the same intermediates occur on both Cu faces. On polycrystalline Cu electrodes SERS data shows the presence of adsorbed nitrate and nitrite, while DFT calculations and STM observations suggest a two O atom binding mode to bridge sites of the Cu surface for nitrate and nitrite on both Cu(111) and Cu(100).[16] Dima et al. compared nitrate reduction on multiple transition metal surfaces and found using differential electrochemical mass spectrometry (DEMS) that NO desorbs from Cu into the solution because it exhibits a weaker binding energy than NO bound to Pt or other metals.[10] As a result, neither N_2O nor N_2 were observed as products of reduction on bulk Cu.

Shell-isolated nanoparticle enhanced Raman spectroscopy (SHINERS) expands the domain of adsorption and reaction processes that can be spectroscopically monitored at a surface.[19-25] Typically, such studies using surface enhanced Raman spectroscopy (SERS) or tip-enhanced Raman spectroscopy (TERS) are limited by low detection sensitivity and having a substrate whose localized surface plasmon resonance lies at visible wavelengths (Cu, Ag, or Au).[26-29] Additionally, these techniques lack the surface specificity achieved by SHINERS because of electrochemical roughening or interference from deposited nanoparticles to achieve enhancement.[20] SHINERS eliminates these drawbacks by coating a Au nanoparticle, active for Raman enhancement, with a SiO_2 shell to prevent signal from analyte adsorbing to the Raman enhancing Au core.

In order to probe the reaction intermediates on the different faces of Cu to determine the origin of the differential reactivity observed and provide insight into the overall reaction mechanism, we here use SHINERS to interrogate nitrate reduction on Cu(100), Cu(111), and

Cu(110). The higher sensitivity attendant the SHINERS technique means that different intermediates may be observed. In particular, nitrite can associate with Cu in several different ways, as depicted in Figure 1. Figure 1 shows the N-bound nitro, O-bound nitrito, doubly O-bound chelating nitrito, N- and O-bound bridging nitro, N-bound nitroxyl, and N-bound nitrosyl (nitric oxide) modes of association. Nitric oxide and nitroxyl are considered to bind through lone pairs of the nitrogen atoms at bridge sites on Cu while nitrate may bind through two O atoms to bridge sites on the Cu surfaces.[16]

II. Experimental Details

Solutions in this work were prepared from ultrapure nitric acid (J.T. Baker – Ultrex II), sodium nitrate (99.999%, Fluka), sodium nitrite (ReagentPlus, Aldrich), or hydrochloric acid (ACS Reagent 37%, Aldrich). Electrolytes were made from ultrapure HClO_4 (J.T. Baker – Ultrex II) and Milli-Q water (18.2 M Ω cm, Millipore Inc.).

Before electrochemical and SHINERS experiments, 10 mm diameter discs of Cu(100), Cu(110), and Cu(111) (Monocrystals, Inc.) were polished to a mirror finish using 9, 3, 1, and 0.25 μm diamond suspensions (Buehler), sequentially. The crystals were sonicated after each level of grit. The crystals were then electropolished in 50/50 v/v% $\text{H}_3\text{PO}_4/\text{H}_2\text{O}$, [30] and then rinsed with copious amounts of Milli-Q water. Crystallinity was confirmed via X-ray diffraction studies on an X'Pert MRD System (Philips). For SHINERS and some electrochemical experiments, the SiO_2 -coated Au nanoparticles, whose synthesis was described previously, [20] were then dropcast onto the Cu electrodes and allowed to dry under gently flowing Ar.

Cyclic voltammetric data (CV) were obtained in a two-compartment, glass electrochemical cell, as previously reported.[31] The copper crystal was placed in the cell in a

hanging meniscus configuration. The solutions were purged with Ar prior to use, and an Ar atmosphere was maintained in the cell during all electrochemical measurements. Scan rates for measurements were 50 mV/s. Tafel plots were generated from rotating disk electrode (RDE) CV experiments using a rotator (Pine) at 400 rpm and a Kel-F collet to hold the Cu crystals.

Raman spectra were collected using previously described cells[32] and instrumentation.[19; 33] A HeNe laser (632.8 nm) was used as the excitation source. The acquisition time at each potential was 120 s with 0.05 V potential steps controlled using staircase voltammetry. Potential control was achieved using a CHI760D (CH Instruments) bipotentiostat with the copper working electrodes, a no-leak Ag/AgCl reference, and Au wire counter electrode. All potentials are reported versus the Ag/AgCl reference electrode.

Adsorption energies were calculated by Density Functional Theory (DFT)[34] using the ab-initio total-energy and molecular dynamics program VASP 5.2 (Vienna ab-initio simulation program)[35]. A graphical user interface program, GoVASP 1.0.1 (Windiks Consulting), was used to generate the models. Cu and Cu₂O surfaces were generated as a slab two layers thick with a 10 Å vacuum layer. The surface was extended as 3×3×1 for Cu and a 2×2×1 supercell for Cu₂O onto which NO₂⁻ and NO₃⁻ molecules were brought into close contact. For the calculations, atoms within the Cu and Cu₂O lattice were frozen in place. To determine adsorption energies, the energy of the minimized bare surface and the NO_x molecule is subtracted from the energy of the minimized surface/NO_x configuration.[16] For all calculations, the generalized gradient approximation (GGA)[36; 37] using the Perdew-Burke-Ernzerhof (PBE)[38] exchange-correlation functional and projector augmented wave (PAW) potentials[39; 40] were employed along with a 400 eV planewave cutoff, 1e⁻⁵ eV SCF convergence tolerance, and fast Davidson and RMM-DIIS algorithm.

III. Results

Figure 2 displays the linear sweep voltammogram of nitrate reduction collected without convection in a solution containing 0.1 M HClO_4 + 0.05 M HNO_3 on Cu(100), Cu(111), and Cu(110) during cathodic polarization from 0 V to -0.8 V. Starting at 0 V, near the open circuit potential, very low current density is observed. As the system is subjected to more negative potentials, negative current density becomes apparent, most notably for Cu(111) and Cu(110). A small peak in the voltammogram from -0.05 V to -0.2 V is present for these surfaces, but not for Cu(100). This peak is attributed to NO_3^- reduction to NO_2^- through a 2e^- reduction, as reported previously.[16] The onset for nitrate reduction on Cu(100) is around -0.2 V. We also note the difference in voltammetric behavior between the Cu(100) and Cu(111) surfaces, as Cu(100) demonstrates a more negative potential onset reduction than Cu(111).[17] By -0.2 V, all three surfaces exhibit negative current density, with Cu(111) and Cu(110) retaining slightly higher overall current densities than Cu(100) until -0.8 V. By comparison, voltammograms collected on Cu surfaces in a solution of 0.1 M HClO_4 (not shown) reveal an onset of H^+ reduction around -0.7 V. Thus, reduction current observed at less negative potentials can confidently be attributed to nitrate and nitrite reduction processes.

Using the same potential range, 0 V to -0.8 V, SHINERS spectra were collected for each surface during cathodic polarization to investigate the nature of adsorbed intermediates during nitrate reduction. Table 1 compiles and identifies the peaks observed during nitrate reduction on Cu(100), Cu(111), and Cu(110) as well as normal Raman spectra of $\text{NaNO}_{2(\text{s})}$, $\text{NaNO}_{2(\text{aq})}$, $\text{NaNO}_{3(\text{s})}$, $\text{NaNO}_{3(\text{aq})}$, and $\text{HNO}_{3(\text{aq})}$ for comparison.

SHINERS spectra were also collected on Cu(100), Cu(111), and Cu(110) during cathodic polarization in a solution containing only 0.1 M HClO₄. Figure S1 displays these spectra and on all three surfaces; there are no discernible peaks related to nitrate or to Cu₂O.

Figure 3 presents SHINERS spectra obtained during nitrate reduction on Cu(100) from 0 mV (bottom) to -800 mV (top). At the positive potential extreme, the only peaks apparent result from the Cl-O stretch from perchlorate in solution at 931 cm⁻¹ (peak **F**), the symmetric NO₃⁻ stretch at 1044 cm⁻¹ (peak **G**) from solution nitrate, and symmetric (1350 cm⁻¹, peak **K**) and antisymmetric (1372 cm⁻¹, peak **L**) N-O stretches from the NO₂ moiety associated with adsorbed NO₃⁻.^{12, 38, 63}

As the potential is scanned to more negative potentials, a suite of peaks associated with intermediates of nitrate reduction begin to appear by -300 mV. Peaks at 1200 cm⁻¹ (peak **I**, N-O stretch) and 1372 cm⁻¹ (peak **M**, N=O stretch) are associated with nitrito binding to the Cu surface due to the similarity of these energies with that found in complexes such as K₄[Ni(NO₂)₄(ONO)₂].[41; 42] Peaks at 1180 cm⁻¹ (peak **H**, symmetric NO₂⁻ stretch) and 1281 cm⁻¹ (peak **J**, antisymmetric NO₂⁻ stretch) are also assigned to NO₂⁻ in the chelating nitrito configuration from comparison to Co(Ph₃PO)₂(NO₂)₂ and Ni(α-pic)₂(NO₂)₂ complexes.[42; 43] The N=O stretch of the bridging nitro conformation appears at 1434 cm⁻¹ (peak **N**) and compares well to the ν(N=O) from bridging nitro groups in [Ni(β-pic)₂(NO₂)₂]₃•C₆H₆.[42; 44] A final strong peak at 1528 cm⁻¹ (peak **O**) is assigned as the N=O stretch of HNO by comparison with free HNO[45] and the N=O stretch in [Ru(HNO)(‘py^{bu}S₄’)][46]. There is also evidence of a low intensity shoulder around 1535 cm⁻¹ (peak **P**) growing in by -800 mV, assigned as a HNO stretching and bending combination mode. Assignment of peak **P** is based upon the presence of HNO bending and stretching combination mode at slightly higher frequency than N=O stretching

in the SPARTAN calculated Raman spectrum of HNO shown in Figure S2. The nitroxyl peak (**O**) exhibits the highest relative intensity of this group on Cu(100). An additional NO_2^- bending mode appears at 801 cm^{-1} as peak **D** at -400 mV .⁶¹⁻⁶³

Figure 4 displays the SHINERS spectra obtained during nitrate reduction on Cu(111) from 0 mV (bottom) to -800 mV (top). At 0 mV , as on Cu(100), only peaks associated with perchlorate and nitrate are observed. Peak **F** appears at 931 cm^{-1} , Peak **G** at 1044 cm^{-1} , and peaks **K** and **L** at 1353 cm^{-1} and 1373 cm^{-1} , respectively. Upon scanning to negative potentials, intermediates associated with nitrate reduction, including nitrite and nitroxyl, begin to appear. At -250 mV , peaks assigned to nitrito, chelating nitrito, bridging nitro, and nitroxyl begin to grow in as nitrate is reduced on the surface. Nitrito peaks grow in at 1202 cm^{-1} (**I**) and 1374 cm^{-1} (**M**). Chelating nitrito peaks grow in at 1181 cm^{-1} (**H**) and 1288 cm^{-1} (**J**). The bridging nitro orientation presents at 1435 cm^{-1} (**N**). Nitroxyl peak **O** first grows in at 1528 cm^{-1} , then by -450 mV , a second peak associated with nitroxyl bending (**P**) appears at 1534 cm^{-1} and continues to become more prominent until -800 mV . On Cu(111), peaks **I**, **O**, and **P** have the highest relative intensity of this set of peaks, indicating a preference for the adsorption of NO_2^- in the nitrito configuration as well as adsorption of nitroxyl. The NO_2^- bending mode (**D**) appears with a strong relative intensity by -300 mV at 800 cm^{-1} .

Figure 5 presents the SHINERS spectra obtained during nitrate reduction on Cu(110) from 0 mV (bottom) to -800 mV (top). Peak **F** appears at 931 cm^{-1} , Peak **G** at 1027 cm^{-1} , and peaks **K** and **L** at 1349 cm^{-1} and 1373 cm^{-1} , respectively. Additionally, moderate intensity peaks at 509 cm^{-1} (**A**) and 619 cm^{-1} (**B**), assigned as Cu_2O , indicate that the surface of the Cu(110) is partially oxidized.

Upon scanning to negative potentials, intermediates associated with nitrate reduction, including nitrite and nitroxyl, begin to appear. At -200 mV, peaks assigned to nitrito, chelating nitrito, bridging nitro, and nitroxyl begin to grow in as nitrate is reduced on the surface. Nitrito peaks grow in at 1208 cm^{-1} (**I**) and 1374 cm^{-1} (**M**). Chelating nitrito peaks grow in at 1183 cm^{-1} (**H**) and 1272 cm^{-1} (**J**). The bridging nitro orientation presents at 1431 cm^{-1} (**N**). Nitroxyl peak **O** first grows in at 1531 cm^{-1} , and peak **P** does not appear as on Cu(100) and Cu(111). On Cu(110), peaks **I** and **J** have the highest relative intensity of this set of peaks, indicating a preference for the adsorption of NO_2^- in the nitrito and chelating nitrito configuration. The NO_2^- bending mode (**D**) appears with a strong relative intensity by -250 mV at 801 cm^{-1} . An additional peak at 817 cm^{-1} (**E**) also appears as a shoulder of peak **D** by -250 mV. This is assigned as a second NO_2^- bending mode.

In order to examine the effect of surface adsorbates on the course of the nitrate reduction reaction, we added Cl^- to the reaction mixture. Cl^- is known to form overlayer arrays on Cu over a potential region starting at -300 mV vs. RHE (roughly -500 mV vs. Ag/AgCl) and through the anodic potential range.[47-49] Cl^- has also been demonstrated to poison the nitrate reduction process on copper and cause a negative nitrate reduction potential shift.[50; 51] Linear sweep voltammetry from a solution containing 0.1 M HClO_4 + 0.05 M HNO_3 + 10 mM HCl is presented in Figure 6. In contrast to the Cl^- free situation in Figure 2, the onset for nitrate reduction occurs at much more negative potentials as a result of Cl^- adsorption on the Cu surfaces. Cu(111) and Cu(110) display reduction beginning near -0.4 V. Interestingly, in the presence of Cl^- , there is no initial onset of current (associated with nitrate to nitrite reduction) before nitrate reduction occurs. Cu(100) exhibits reductive current density beginning around -0.5 V. As in the Cl^- free case, Cu(100) nitrate reduction onset is more negative than on Cu(111)

and Cu(110). Overall current densities reach a maximum between -1.5 and -2 mA/cm² at -800 mV. This is significantly lower than the current densities of approximately 9 mA/cm² at -800 mV from Figure 2 for Cl⁻ free Cu surfaces.

Figure 7 shows SHINERS spectra of nitrate reduction on Cu(100), Cu(111), and Cu(110) in a solution containing 0.1 M HClO₄ + 0.05 M HNO₃ + 0.01 M HCl, in panels A, B, and C, respectively. As in Figures 2, 3, and 4, peaks associated with free perchlorate and free nitrate (**F** and **G**) are apparent around 930 cm⁻¹ and 1040 cm⁻¹ on each surface. In contrast to the Cl⁻ free systems, there is no evidence of adsorbed nitrite or nitroxyl species as the potential is scanned from 0 mV to -800 mV. Instead, on Cu(100) there are faint peaks associated with NH₃ and NH₄⁺ that appear by -500 mV. Peaks at 765 cm⁻¹ (**Q**, $\rho_r(\text{NH}_3)$ rocking), 1307 cm⁻¹ and 1377 cm⁻¹ (**S**, $\delta_s(\text{HNNH})$ deformation) and 1582 cm⁻¹ (**V**, $\delta_a(\text{HNNH})$ of NH₃) are attributed to NH₃ formation at potentials more negative than -500 mV. Cu(111) differs and only shows a faint product peak at 1479 cm⁻¹ (peak **U**) associated with the $\nu(\text{T}_4)$ antisymmetric NH₂ deformation of NH₄⁺.

Cu(110) exhibits much stronger peak formation as the potential is scanned in the cathodic direction, with similar frequencies to Cu(100). Peaks at **Q**, **S**, **T**, **U**, and **V** all indicate the formation of NH₃ and protonation to NH₄⁺ near the surface. Peaks at **V** are particularly complicated as several vibrations overlap and do not allow full identification. In addition to the $\delta_a(\text{HNNH})$ of NH₃, vibrations of $\delta(\text{E})$ antisymmetric NH₂ def. of NH₄⁺ also fall in the 1560 cm⁻¹ to 1614 cm⁻¹ range.

Density Functional Theory (DFT) calculations were performed to determine the adsorption energies of NO₂⁻ and NO₃⁻ to Cu(100), Cu(111), Cu(110), Cu₂O(100), Cu₂O(111),

and $\text{Cu}_2\text{O}(110)$. The adsorption energies are displayed in Table S1 for comparison. Adsorption energies for NO_3^- and NO_2^- adsorption have previously been reported by us on $\text{Cu}(111)$ and $\text{Cu}(100)$.^[16] The results reported here closely follow those calculations and suggest a valid computational model has been established for evaluating nitrate and nitrite adsorption on $\text{Cu}(hkl)$. NO_2^- adsorption energies were determined on each surface in both the nitrito and chelating nitrito configurations on $\text{Cu}(100)$, $\text{Cu}(111)$, and $\text{Cu}(110)$. For both conformations, as well as for nitrate, the adsorption energy of nitrite decreases in the sequence $\text{Cu}(110) > \text{Cu}(100) > \text{Cu}(111)$.

Adsorption energies of nitrate and nitrite on $\text{Cu}_2\text{O}(100)$, $\text{Cu}_2\text{O}(111)$, and $\text{Cu}_2\text{O}(110)$ differ from the trend from the Cu surfaces. These models were constructed using the same modeling methodology as for the $\text{Cu}(hkl)$ surfaces and thus should reveal any relevant trends in nitrate and nitrite adsorption to $\text{Cu}_2\text{O}(hkl)$. The oxide surfaces are indexed to the corresponding Cu surfaces during growth, making such comparisons relevant.^[52] In the case of both nitrate and nitrite, the adsorption energies follow the trend of $\text{Cu}_2\text{O}(111) > \text{Cu}_2\text{O}(110) > \text{Cu}_2\text{O}(100)$. Figure 8 presents a picture of the orientation of nitrate and nitrite on each oxidized surface. In each case, the adsorbing molecules orient themselves to most effectively bind O atoms to exposed Cu atoms on the surface. Qualitatively, the $\text{Cu}_2\text{O}(100)$ surface has Cu atoms that are less accessible to nitrate and nitrite O atoms than are either $\text{Cu}_2\text{O}(111)$ or $\text{Cu}_2\text{O}(110)$. The oxide surfaces shown here are consistent with those suggested by Besenbacher for oxidized single crystal Cu surfaces.^[53]

IV. Discussion

The results presented in this work deliver a new level of detail concerning the reduction of nitrate in acidic conditions on Cu(100), Cu(111), and Cu(110). The work suggests that there are a number of different intermediate species occurring during nitrate reduction on these surfaces. Additionally, the work provides insight into the origin of the different reactivity observed between Cu(100) and the other two low Miller index faces of Cu. Finally, this work provides insight into other catalysts exhibiting nitrate reduction activity.

Reaction Intermediates on Bare Cu Surfaces

The higher signal to noise available with the SHINERS technique and the ability to perform this technique on single crystal surfaces provides an opportunity to fully inventory intermediates attending the electroreduction of NO_3^- on Cu surfaces. The nitrate to nitrite process is well understood to be catalyzed by copper, thus making it a good candidate for overall nitrate reduction.[10; 18; 50; 54]

On the basis of STM images and calculations, we suggested previously that nitrate and nitrite preferentially adsorb in a chelating configuration through 2 oxygen and 2 copper atoms.[16] The data here, however, suggest that the intermediate situation is substantially more involved as there are indications of adsorption of nitrite through the singly bound nitrito, bridging nitro, chelating nitrito, and nitroxyl conformations. In particular, SHINERS spectra shown in Figures 3, 4, and 5 provide extensive detail regarding the nature of the intermediates on the low Miller index Cu surfaces. Peaks **H** and **J** are assigned as the chelating nitrito configuration, peaks **I** and **M** as the singly bound nitrito configuration, peak **N** as the bridging nitro configuration, and peaks **O** and **P** as the nitroxyl molecule. This observation may provide some rationale for the dispersion of products seen during nitrate reduction on Cu[9], which

generally results in formation of NO and NH₃. For example, a DEMS study [10] shows evolution of nitric oxide from an acidic solution from a Cu surface as a byproduct and Pletcher demonstrated NH₃ production in solution electrochemically[50], while other electrode surfaces like Pd or Pt can yield N₂O, NH₂OH and N₂. [11] We suggest that the presence of these intermediates and adsorption to the surface may lead to different products and suggest the origin of the multiple pathways for nitrate reduction on Cu.

The relative intensities of peaks related to the configurations of intermediates differed between the surfaces. From Figure 3, peaks **H**, **J**, **I**, and **M** as well as peak **D**, associated with nitrite configurations, all feature lower relative intensity than the same sets of peaks from Figures 4 and 5 for Cu(111) and Cu(110). Assuming an identical Raman cross section, this could be explained by a lower density of nitrite on the Cu(100) surface, (vide infra). Given the uncertainties in SiO₂@Au particle loading densities and the Raman cross sections of the adsorbed molecules, we can't quantitatively assess a difference in adsorbed nitrite density. However, we note that the Cu(100) surface is less active for nitrate reduction relative to the other two faces.

Peak **O** from nitroxyl grows strongly on the Cu(100) and Cu(111) surfaces. Additionally, as potential is scanned to more negative potentials, peak **P** from the HNO bending and stretching combination mode begins to appear, and is rather prominent for the Cu(111) surface in particular. An additional difference between the reaction intermediates between the surfaces is that a second NO₂⁻ bending mode appears with peak **E** only on Cu(110). We speculate that this second bending mode is visible because of a higher density of NO₂⁻ on Cu(110), as suggested by the high relative intensities of both the nitrito and chelating nitrito vibrations in Figure 5. It is not clear that these interesting observations directly affect the reduction activity, but simply show

slightly different configurations that are favored on each unique face and whose identification is accessible using a sensitive technique like SHINERS.

Reaction Intermediates in the Presence of Cl^-

From the spectra in Figure 7, there are also unique molecules and configurations generated in the presence of Cl^- . All three surfaces exhibit at least some peaks attributed to NH_3 or NH_4^+ . In particular, Cu(110) reveals a suite of strong peaks attributed to both species. We propose that the reduction yields NH_3 as a product that is loosely bound to the surface in the presence of a protecting layer of Cl^- . Protonation and coordination with the Cl^- then leads to a surface bound adduct of NH_4Cl that is detected primarily on the Cu(110) surface, but whose presence cannot be excluded on the Cu(100) or Cu(111) surfaces. No oxygenated species are evolved on a Cl^- protected surface, likely because these species can't be effectively stabilized by the electrode in the presence of Cl^- . STM investigations have revealed that bare Cu surfaces can only be imaged beyond the potential of Cl^- desorption (-500 mV vs. Ag/AgCl).[47; 49] Because nitrate is not stabilized by the surface, the reduction does not occur until more negative potentials relative to the case where nitrate and nitrite reduction are facilitated by adsorption to the Cu surface and interaction with surface Cu_2O that is present on Cu surfaces near the anodic potential extreme.

Origin of Different Surface Reactivity

Among the most interesting results presented here is the fact that nitrate reduction on Cu(100) occurs at more negative potentials compared to Cu(111) and Cu(110). This trend is observed in the electrochemistry[17] and in SHINERS spectra where peaks associated with adsorbed nitrite and nitroxyl begin to grow in on Cu(111) and Cu(110) at potentials more

positive than on Cu(100). The work function for Cu(100) is 4.59 eV which is in between and not that different from the work function for Cu(111) (4.94 eV) or Cu(110) (4.48 eV).[55] Thus work function (and hence pzc) differences between the three faces likely is not the origin of the differential reactivity.

The origin of this different reactivity is also not immediately obvious from DFT calculations of the energetics of NO_3^- and NO_2^- adsorption to bare Cu surfaces. Specifically, Table S1 shows that both the reactant and product, nitrate and nitrite, bind most strongly to Cu(110), then to Cu(100) and finally most weakly to Cu(111). Models of reaction rate dependence on surface association strength, invoking the principle of Sabatier, suggest that intermediate strength association of both reactant and product to a surface should yield the highest rate.[56] However, exactly the opposite trend is observed here, where Cu(110) and Cu(111) are more active than Cu(100) toward nitrate reduction. This experimental trend also cannot be reconciled with the nearly identical reactivities of Cu(110) and Cu(111), which exhibit different energies of nitrate and nitrite adsorption. Duca[18] and Dima[10] have previously shown the importance of the Sabatier principle in regards to nitrate reduction on Cu by demonstrating a tendency for an NO byproduct to form during the reduction process because of weak association of NO with the metal. Because of this, there is also a conspicuous absence of N_2O and its reduction product N_2 , which ordinarily appears during the reduction process on other metals.

There are two possible ways to reconcile the observed trend with the calculation. First, it is possible that the nitrate reduction event is more complicated than indicated here, and perhaps involves species different from the nitrate and nitrite used in the calculation. In particular, the experimental observation of different nitrite orientations and coordination geometries suggests

that these must all be considered. However, different nitrate and nitrite geometries follow the same calculated trend described above. This calculation, coupled with the experimental observation of both nitrate and nitrite on the surface, suggests that these are the correct species to be used here. Thus, the adsorption energies of nitrate and nitrite to bare Cu, and by extension the relative ability of the surface to stabilize these ions, do not determine the observed difference in reduction activity.

The second possibility to reconcile calculation and experiment is that a bare Cu surface might not be the correct site of reduction activity. We note in particular the presence of features in the SHINERS of Cu(110) in Figure 5, as well as previous SERS studies of electrochemically roughened Cu(poly), indicating the formation of Cu₂O arising as a consequence of nitrate exposure to the Cu surface. Even in strong acid, features ascribed to oxide species were observed in AFM studies of Cu(*hkl*) interfaces interface were observed.[17] Thus, we consider the relative association energies of nitrate and nitrite with Cu₂O grown on each of the three Cu faces considered here. Table S1 shows that both nitrate and nitrite exhibit significantly higher adsorption energies on Cu₂O(111) and Cu₂O(110) relative to the same molecules on Cu₂O(100). The increased affinity of these molecules to the Cu₂O(110) and Cu₂O(111) surfaces in relation to the Cu₂O(100) surface is a potential driving force behind the increased reduction activity observed on Cu(110) and Cu(111) relative to Cu(100).

While DFT derived adsorption energy trends alone do not confirm the critical role of surface oxidation on reactivity, the association between nitrate reduction activity and the presence of special surface features, including oxides, at the reactive interface is well established. For example, hydrided Ge adsorbed on Pt or Pd increase the nitrate reduction activity and improve selectivity toward hydroxylamine by inhibiting adsorption of poisoning anions.[57] Sn

coated surfaces have been shown to increase activity on Pt by providing a favorable site for binding O from NO_3^- , resulting in partial oxidation of the Sn.[58] In has also been demonstrated as a promoter on Pd.[59] While the association of nitrate (or nitrite) with each of these complex interfaces is not yet clear, the work here suggests an important role for oxide and oxophilic surfaces for facilitating nitrate reduction.

We next consider the rate of formation of the Cu_2O active surface. It is known that the corresponding Cu_2O oxide grows epitaxially on the underlying Cu surface for each of the three faces considered here.[52; 53] However, oxidation of Cu(110) to form regions of Cu_2O occurs at a faster rate than on Cu(100) because higher surface energy leads the Cu(110) surface to be less stable; an additional factor is that the close packed nature of Cu(100) relative to Cu(110) allows less O diffusion into the metal and encourages more Cu_2O island growth.[52] Cu(111) oxidizes by a more layer by layer deposition because it serves as a perfect template for oxide layer formation, which allows for a faster rate of Cu_2O island nucleation than on either Cu(100) or Cu(110)[9].[52] Thus, the different susceptibilities of the surfaces to oxidation differentiate their activity toward reduction of NO_3^- to NO_2^- , leading to the difference in potential onset of reductive current observed in Figure 2. We showed previously that oxide like features were present on Cu(111) in the presence of nitrate, but that these features were largely absent on Cu(100).[17]

Similar formation in aqueous systems of thin Cu_2O layers on Cu(100)[30], Cu(111)[60], and Cu(110)[61] has been demonstrated, even at potentials and pH not amenable to bulk Cu_2O formation.[60] Given the tendency of Cu(110) and Cu(111) to oxidize more readily than Cu(100), we suggest that another origin of the differential reactivity observed relates to the rate of oxide formation on these surfaces upon exposure to nitrate. Thus, we propose that an oxygen

atom from the nitrate is transferred to these particular copper surfaces, resulting in a reduction to nitrite by the equations below at potentials greater than -0.2 V vs. Ag/AgCl.

The Cu_2O surface then forms the catalytically active site. SHINERS spectra from Figures 3, 4, and 5 bolster this argument by demonstrating no noticeable Cu_2O formation on Cu(100) and strong oxidation on Cu(110) with Cu_2O vibrations present at 509 cm^{-1} and 619 cm^{-1} . The Cu(111) case was spectroscopically inconclusive, though previous voltammetric and probe microscopy experiments on Cu(111) have indicated a strong presence of Cu_2O formation under identical conditions.

Poisoning the Cu surface with adsorbed Cl^- leads to significant changes to nitrate reduction activity. First, the potentials for nitrate reduction in Figure 6 occur some 300 mV more negative relative to that absent halide. Additionally, the current density for the reduction of nitrate is significantly reduced at the negative potential extreme. Second, species seen in the SHINERS during nitrate reduction from the Cl^- decorated surface are different from those seen absent the halide. In particular, peaks observed in Figure 7 do not match those of any known NO_x or other partially oxygenated nitrate reduction species. There is no observation of Cu_2O , adsorbed nitrate, nitrite, or nitroxyl groups in the SHINERS spectra on Cu(100), Cu(111), or Cu(110). Instead, peaks in Figure 7 are associated with NH_3 and NH_4^+ species, possibly coordinated through Cl^- to the Cu electrode surface. Cl^- is known to inhibit the formation of Cu_2O on Cu surfaces. Only once Cl^- is desorbed from the copper surface around -500 mV[47;

49] will nitrate be reduced. Since Cu_2O will not form at such negative polarization according the Pourbaix diagram, the reaction is prevented from occurring via pathways requiring NO_x species.[62]

In the Cl^- free situation, Cu_2O can linger because the surface has access to nitrate, which reacts to form an oxide and adsorbed nitrite as the reaction proceeds. Eventually even this process breaks down, as is observed prominently in Figure 5 of nitrate reduction on Cu(110) where peaks associated with Cu_2O largely disappear by -500 mV. We thus conclude nitrate reduction follows a direct formation pathway to yield NH_3 when the Cu is decorated with Cl^- , but at greater overpotentials because the surface is not available to be oxidized to facilitate the reaction. This observation supports the notion that an oxidized surface is a key component to nitrate reduction catalysis. Cl^- effectively blocks the Cu surface and prevents the adsorption of NO_3^- on each surface and the reduction to nitrite on Cu(111) and Cu(110). Since the NO_3^- to NO_2^- reduction is the key intermediary step, Cl^- blocking of the surface has a significant effect on the overall activity. The bare Cu(100) surface still experiences the lowest activity toward nitrate reduction because of its greater relative stability, meaning fewer Cu^+ ions will be present to catalyze the reduction; Cu^+ is known to catalyze the reduction of nitrate.[63] The Cl^- layer on the Cu(100) may also be slightly more stable than on the (111) or (110) surfaces, resulting in delayed Cl^- desorption.

V. Conclusions

We show that the SHINERS technique provides insight into reactivity on different faces of Cu with and without the presence of Cl^- . Nitrate reduction proceeds via formation of different modes of association of nitrite to the electrode surface, particularly the nitrito and nitroxyl

geometries. All three faces show similar intermediates, suggesting the same mechanism is operative on all of them. Absent Cl^- , nitrate reduction proceeds with concomitant surface oxidation, the rate of which controls subsequent reactivity and provides an explanation for the differential reactivity seen between Cu(100) and the other two low Miller index faces. The early onset of cathodic current density, along with earlier onset of SHINERS peaks associated with nitrite, on Cu(111) and Cu(110) compared to Cu(100) are associated with the different rates of surface oxide formation. The importance of the oxidized Cu surface for nitrate reduction activity is also made apparent by the extra overpotential required for Cu surfaces protected by Cl^- . SHINERS observations indicate a unique reaction mechanism from the Cl^- free situation, featuring direct reduction to NH_3 . That the presence of Cu_2O modulates activity gives additional direction for the engineering of effective nitrate reduction catalysts.

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Tables

Table 1: Raman scattering peaks for nitrate and nitrite species.

Peak	Raman Shift (cm ⁻¹)								Assignment	Ref.
	NaNO ₂ (s)	NaNO ₂ (aq)	NaNO ₃ (s)	NaNO ₃ (aq)	HNO ₃ (aq)	Cu(100)	Cu(111)	Cu(110)		
A							502	509	Cu ₂ O	[16]
B							621	619	Cu ₂ O	[16]
C			723	778	782					
D	826	814				801	800	801	NO ₂ ⁻ bending	[16; 64-66]
E								817	NO ₂ ⁻ bending	
F						931	931	931	v(Cl-O)	
G			1066	1031 1047	1031 1047	1044	1044	1027	v _s NO ₃ ⁻ stretch	[42; 67-72]
H						1180	1181	1183	v _s NO ₂ ⁻ , chelating nitrito	[42; 43]
I				1269	1291	1200	1202	1208	v(N-O), nitrito orientation	[41; 42]
J						1281	1288	1272	v _a NO ₂ ⁻ , chelating nitrito	[42; 43]
K						1350	1353	1349	v _s NO ₂ of NO ₃ ⁻	[16; 66; 73; 74]
L			1384	1408	1427	1372	1373	1373	v _a NO ₂ of NO ₃ ⁻	[16; 64; 66; 74]
M	1324	1326				1372	1374	1374	v(N=O), nitrito orientation	[41]
N						1434	1435	1431	v(N=O), bridging nitro	[42]
O						1528	1528	1531	v(N=O), nitroxyl	[45; 46; 75]
P							1534		HNO bend and stretching, nitroxyl	

*v_s is symmetric stretch, v_a is antisymmetric stretch

Table 2: Raman scattering peaks for ammonia and ammonium products of nitrate reduction in a solution containing Cl^- .

	Raman Shift (cm^{-1})				
Peak	Cu(100)	Cu(111)	Cu(110)	Assignment	Ref.
Q	765		763	$\rho_r(\text{NH}_3)$ rocking	[42]
F	933	931	931	$\nu(\text{Cl-O})$	
R	1018	1015	1013	$\nu_s(\text{NO}_3)$ adsorbed NO_3^-	[42; 67-72]
G	1047	1045	1045	$\nu_s(\text{NO}_3)$	[42; 67-72]
S	1307		1309	$\delta_s(\text{HNNH})$ deformation	[42]
T	1377		1374	$\delta_s(\text{HNNH})$ deformation	[42]
U	1481	1479	1480	$\nu(\text{T}_4)$ antisymmetric NH_2 def. of NH_4^+	[76-78]
V	1582		1560, 1591, 1614	$\delta_a(\text{HNNH})$ of NH_3 and $\delta(\text{E})$ antisymmetric NH_2 def. of NH_4^+	[42; 76-78]

Figures

Figure 1: Conformations for the adsorption of NO_2^- , NO , and HNO onto a Cu surface

Figure 2: Linear sweep voltammetry collected from Cu(100), Cu(110), and Cu(111) in a solution containing 0.1 M HClO₄ + 0.05 M HNO₃ from 0 V to -0.8 V vs. Ag/AgCl

Figure 3: SHINERS obtained from a Cu(100) crystal in a solution containing 0.1 M HClO₄ + 0.05 M HNO₃ during cathodic polarization from 0 mV to -800 mV vs. Ag/AgCl

Figure 4: SHINERS obtained from a Cu(111) crystal in a solution containing 0.1 M HClO_4 + 0.05 M HNO_3 during cathodic polarization from 0 mV to -800 mV vs. Ag/AgCl

Figure 5: SHINERS obtained from a Cu(110) crystal in a solution containing 0.1 M HClO_4 + 0.05 M HNO_3 during cathodic polarization from 0 mV to -800 mV vs. Ag/AgCl

Figure 6: Linear sweep voltammetry collected from Cu(100), Cu(110), and Cu(111) in a solution containing 0.1 M HClO₄ + 0.05 M HNO₃ + 10 mM HCl from 0 V to -0.8 V vs. Ag/AgCl

Figure 7: SHINERS obtained from (A) Cu(100), (B) Cu(111), and (C) Cu(110) in a solution containing 0.1 M HClO₄ + 0.05 M HNO₃ + 10 mM HCl during cathodic polarization from 0 mV to -800 mV vs. Ag/AgCl.

Figure 8: Minimized structure of nitrate and nitrite on $\text{Cu}_2\text{O}(hkl)$ surfaces from VASP calculations.