

Investigation of the Surface-Electrolyte Interface of Semiconductors and Metals

Dennis P. Butcher

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To address the low detection sensitivity and poor surface selectivity of surface-enhanced Raman scattering (SERS) and tip-enhanced Raman scattering (TERS), Li, et al.¹⁻² developed a new technique, shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), consisting of a gold nanoparticle Raman probe that is chemically isolated from the analyte by an insulating thin SiO₂ shell. This arrangement allows for the long-range electromagnetic (EM) enhancement to provide Raman enhancement while excluding any interfering signal from molecules adsorbing to the particles. This unlocks a wide range of surfaces and solid/liquid systems for investigation by SHINERS, of which several are presented in this seminar.

The adsorption dynamics of 2,2'-bipyridine on Au single crystals have been studied extensively. Several transitions are anticipated during potential scanning based upon differential capacity measurements performed by Lipkowski, et. al.³ and STM by Dretschow and Wandlowski⁴. Of particular interest is the nature of adsorption at negative potentials, since previous studies of pyridine and 2,2'-bipyridine on Au using IR are limited by selection rules that only allow in plane vibrations to be seen, which prevents observation of π -flat oriented molecules since the molecular dipole is not affected by electrode polarization.³

SHINERS is employed to explore the adsorption dynamics of 2,2'-bipyridine on Au single crystals, with broader applicability to other solid/liquid interfaces. By means of visual inspection, it is hard to assign the spectral pattern of 2,2'-bipyridine in the ring breathing modes C-C inter-ring modes upon potential cycling. Thus, two dimensional correlation analysis is performed to deconvolute these complicated and sensitive spectral regions to link vibrations observed to the molecular orientation on the surfaces. These relations are used to determine the adsorption dynamics of 2,2'-bipyridine during electrochemical perturbation on Au(111) and Au(100), with a schematic of the results of anodic polarization summarized in Figure 1.

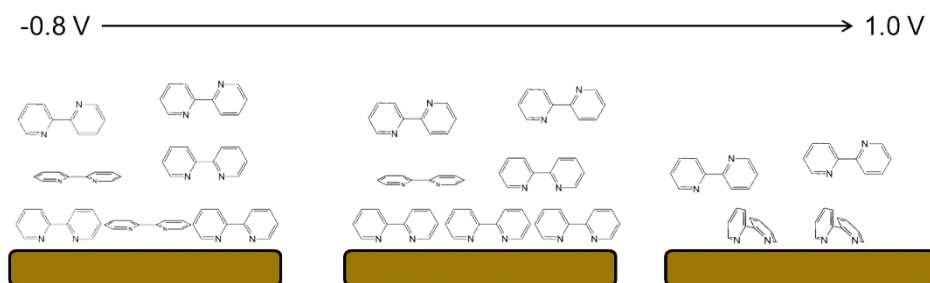
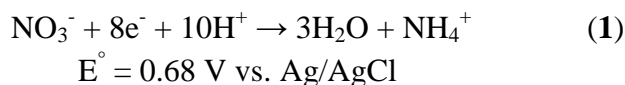


Figure 1: Schematic of 2,2'-bipyridine on Au(111) and Au(100) under anodic polarization.

Nitrate contamination of groundwater, mostly the byproduct of agricultural runoff, poses serious health risks at high levels of exposure including methemoglobinemia (blue-baby syndrome) and increased incidence of certain gastrointestinal cancers.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 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.⁸⁻⁹ Many metal surfaces have been investigated, with Cu representing one of the most active nitrate electrocatalysts available.¹⁰⁻¹¹

On copper surfaces in acidic media, nitrate reduction occurs through an eight electron reduction as shown in equation 1.¹²⁻¹³



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 The highly sensitive SHINERS technique is used to probe the reaction intermediates of nitrate reduction on Cu(100), Cu(111), and Cu(110) and to help determine the origin of differential reactivity previously reported.¹³ Cu(111) and Cu(110) exhibit higher activity and lower reduction overpotential than Cu(100), as seen in Figure 2A. Additionally, comparison of nitrate reduction on bare Cu to surfaces decorated with Cl⁻ reveal a stark difference in reaction products with bare Cu yielding a series of NO_x products and the Cl⁻ coated surface producing NH₃ directly; furthermore, reduction onset is delayed by 300 mV, as seen in Figure 2B. Taken together, the data point to a critical role for Cu₂O as a facilitator for reduction of nitrate, as this species is observed on Cu(110) and Cu(111), but not Cu(100).

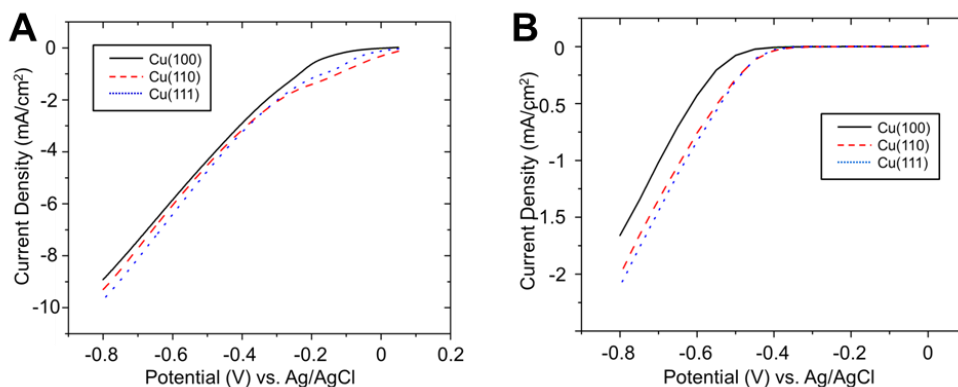


Figure 2: Linear sweep voltammograms from 0 V to -0.8 V vs. Ag/AgCl on Cu(100), Cu(111), and Cu(110) in a solution containing (A) 0.1 M HClO₄ + 0.05 M HNO₃ and (B) 0.1 M HClO₄ + 0.05 M HNO₃ + 1 mM HCl.

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