

## In situ Spectroscopic Identification of Surface Intermediates in Aqueous-phase Metal-catalyzed Reactions

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### Introduction

Characterization of the binding and/or reaction of adsorbates at the surfaces of platinum group metals is of great importance to the understanding and improvement of catalytic reactions. Electron energy loss spectroscopy (EELS), for example, is highly satisfactory in detecting molecules bound to model surfaces, but suffers from the need for expensive equipment and ultra-high vacuum environments. Hence, it cannot be used to replicate actual behavior of catalytic reactions that occur at or above atmospheric pressure or in the presence of a liquid. Fourier-transform infrared spectroscopy (FTIR), often coupled with the use of attenuated total reflectance (ATR) techniques and Raman spectroscopy, have also been used to characterize adsorption processes, but the technique is not surface selective and signal-to-noise ratios often suffer from solvent effects. Moreover, with the growing trend toward greener aqueous-based reactions, the technique is especially limited by the strong IR absorption of the O-H stretching modes of water [1]. Additionally, current techniques often require integration times much longer than actual reaction times. There is a critical unmet need for sensitive, surface-selective, and easy-to-implement methods to provide detailed molecular-level information on heterogeneous catalytic reactions while they occur under realistic reaction conditions [2].

The surface reaction intermediates are studied and the likely reaction mechanisms are determined for two metal-catalyzed water-phase reactions using surface-enhanced Raman spectroscopy (SERS). With recent developments in understanding structure effects on plasmonic behavior in metal nanostructure synthesis, SERS substrates with higher and more highly reproducible enhancements in the form of gold nanoshells (Au NSs) are used [3]. The room-temperature, aqueous-phase hydrodechlorination of chlorinated ethylenes was analyzed using palladium (Pd)-coated Au NSs (10% Pd coverage), in which the Pd provides the catalytic activity and the Au provides SERS activity and catalytic enhancement of the Pd metal [4]. Room-temperature, Au-catalyzed, aqueous-phase glycerol oxidation served as the second model reaction of study, in which Au NS's were used.

### Materials and Methods

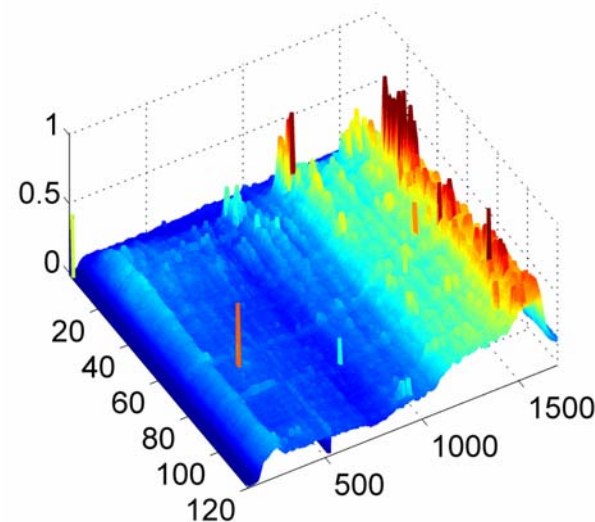
Au NS's and Pd-coated Au NS's were synthesized and assembled into SERS substrates, according to procedures published by us recently [4]. The substrate was inserted in a sealed analysis chamber with inlet and outlet ports, and SERS spectra were obtained using a Renishaw inVia micro-Raman spectrometer with a 785-nm excitation laser and a 40 $\times$  working distance objective. Spectra were obtained using 0.05 mW power and 10 second integration times.

### Results and Discussion

Spectroscopic changes during 1,1-dichloroethylene hydrodechlorination with H<sub>2</sub> over Pd/Au NSs were observed (Fig. 1). Raman bands were identified with known surface intermediates and corroborated with *ab initio* molecular modeling calculations. The changes in band position and intensity were correlated to stepwise chemisorption, dechlorination, and subsequent hydrogenation [4]. For glycerol oxidation, there is now spectroscopic evidence that indicate oxygen and basic pH were necessary for the reactive chemisorption of glycerol on Au NS surface.

### Significance

Nanoshell-enabled SERS is a new approach for elucidating the chemical reaction pathway of liquid-phase catalytic reactions through the in situ detection of surface intermediates.



**Figure 1.** Waterfall plot of time-resolved spectra gathered from the reaction of 50.9  $\mu$ M 1,1-DCE and 16.3 mM H<sub>2</sub> on Pd-coated Au NSs, after injection of 1,1-DCE/H<sub>2</sub> solution..

### References

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