

V.P.11 An *in situ* Electrode-Potential-Controlled Nuclear Magnetic Resonance Investigation of Sulfur-Poisoning Effect on Pt-Based Mono- and Bi-metallic Nanoscale Electrocatalysts

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Objectives

The long-term objectives of our research effort are two folds: 1. Advance significantly our fundamental understanding of sulfur poisoning of Pt-based mono- and bi-metallic nanoscale electrocatalysts through careful interrogation of long and short range electronic effects caused by the poisonous sulfur-metal bonding. 2. Investigate and establish correlations among the surface d band center, the frontier orbitals of the metal surface as represented by the surface local density of states at the Fermi level (E_f -LDOS), and the associated electrochemical reactivity.

Technical Barriers

Lack of detailed molecular level information on how sulfur-metal interaction poisons heterogeneous catalysts in general and electrocatalysts in particular impedes significantly the pace of developing practically viable sulfur-tolerant catalysts. Achieving the aforementioned objectives should help in a significant way the development of sulfur-tolerant catalysts by providing much needed molecular level electronic/geometric structure – functionalities relationships.

Progress Report

In situ Spectroscopic Development. Over the last year, we have developed capability of electrochemical (EC) *in situ* surface-enhanced IR adsorption

spectroscopy (SEIRAS) and surface-enhanced Raman spectroscopy (SERS), as shown respectively in Figure 1 and 2. These spectroscopic developments have broadened significantly our molecular level investigative power in achieving a deeper mechanistic understanding of sulfur poisoning of Pt based electrocatalysts.

Adsorption and Oxidation of Sulfur on Pt Nanoparticles. We have carried out a detailed EC investigation of the adsorption and oxidation of S on commercial Johnson-Matthey (J-M) Pt black (Pt-B) and carbon-supported Pt (Pt/C). These two samples have different size (7 nm vs 4 nm), different boundary condition (inter-grain boundaries due to NP segregation in Pt-B vs NP isolation in Pt/C), and different surface roughness. By carefully analyzing the EC data obtained on 10 consecutive S-electro-oxidation (S-EO) strippings of 7 samples prepared with different S adsorption times, we were able to identify a Pt-S₂ to Pt-S absorption structural transformation.

***In situ* EC ¹⁹⁵Pt NMR Investigation of Ru@Pt and Au@Pt/C NPs.** The first step to delineate how S adsorption alters the structural and electronic properties of bimetallic NPs is to establish what are the starting structural and electronic properties of these NPs. To this end, we have carried out the first *in situ* EC ¹⁹⁵Pt NMR investigation of Ru@Pt and Au@Pt/C NPs that will enable us to move in this direction. The former sample was prepared by scaling up the EG based wet chemistry synthesis we had developed[1] from 5 mg to ~ 100 mg. The starting Ru black had an average particle size of 3 nm. The targeted Pt packing density (PD) was

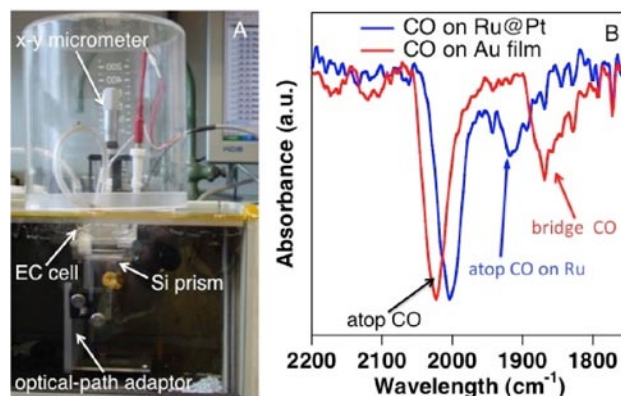


FIGURE 1. A. The fully operational SEIRAS setup. B. The *in situ* SEIRAS spectra of CO adsorbed on Ru@Pt (blue curve) and Au film (red curve).

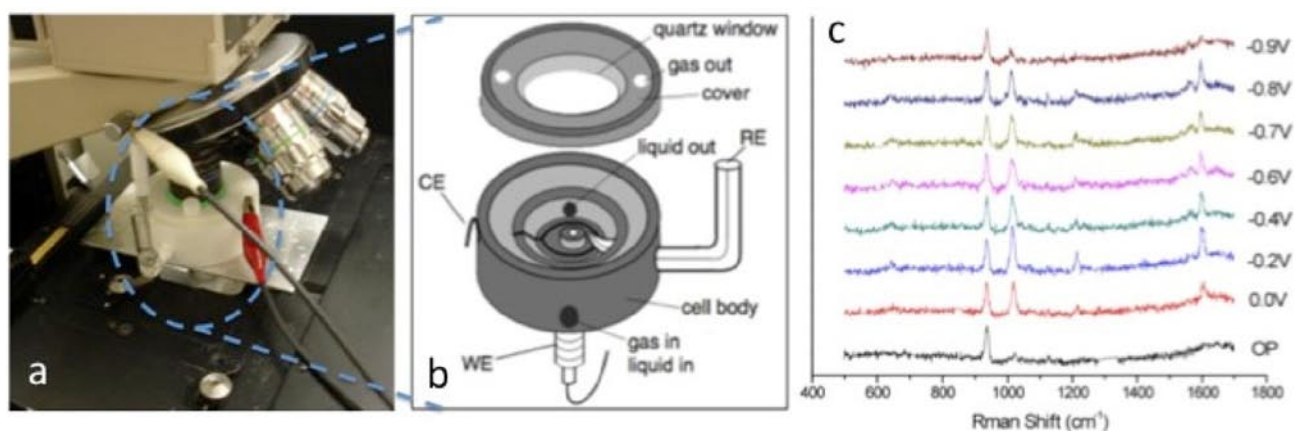


FIGURE 2. a. The fully operational SERS setup. b. The diagram of the in situ SERS cell. c. The SERS spectra of pyridine on roughened Pt electrode at different electrode potentials.

0.4. TEM, XRD, CO stripping and MOR measurements showed results that were in good agreement with the results of the 5mg synthesis[1], demonstrating the feasibility of the scaling-up synthesis. The latter Au@Pt sample was prepared by first synthesizing carbon-supported 30% mass Au NPs. The Au NPs had an average size of 3.5 nm. The Pt was then added in the second step in which the starting Pt ions were reduced by ascorbic acid[2]. The sample studied here had a Pt PD of 3.8. About 80 mg of the NPs were used for NMR measurements.

Figure 3 shows the area-normalized ^{195}Pt NMR spectra of as-prepared and EC-cleaned samples for Au@Pt (a) and Ru@Pt (b) respectively. The spectrum of a 2.5 nm commercial Pt/C is also shown for comparison. The as-received Au@Pt sample had been on shelf for very long time (>12 months) so the spectrum shows clearly a Pt oxide peak at 1.089 G/kHz. After EC-cleaning (by the setup shown in Fig.1), the Pt oxide peak disappeared and the whole spectrum moved up field as happened to pure Pt/C sample[3]. Although still lacking direct spectral evidence, we think that the peak appeared at the low-field side at 1.0975 G/kHz after EC-cleaning is from the surface Pt atoms. The fraction of the area under this peak can be estimated by a Gaussian deconvolution as indicated by the dashed blue line, which gives a value of 0.33, a value of fraction for Pt surface atoms in Au@Pt NPs that is in good agreement with that estimated electrochemically. However, the peak position is low-field shifted from 1.1000 G/kHz, the peak position for the surface Pt atoms in Pt/C NPs. The up-field part of spectrum is compressed towards low field as many alloyed systems do and also is more structured than that of Pt/C.

On the other hand, the as-prepared Ru@Pt sample was very fresh (only had a shelf life of a couple days) so no clear Pt oxide peak appeared. After the EC-cleaning, the spectrum also did not show spectral change as dramatic as that of the Au@Pt NPs. However, as that

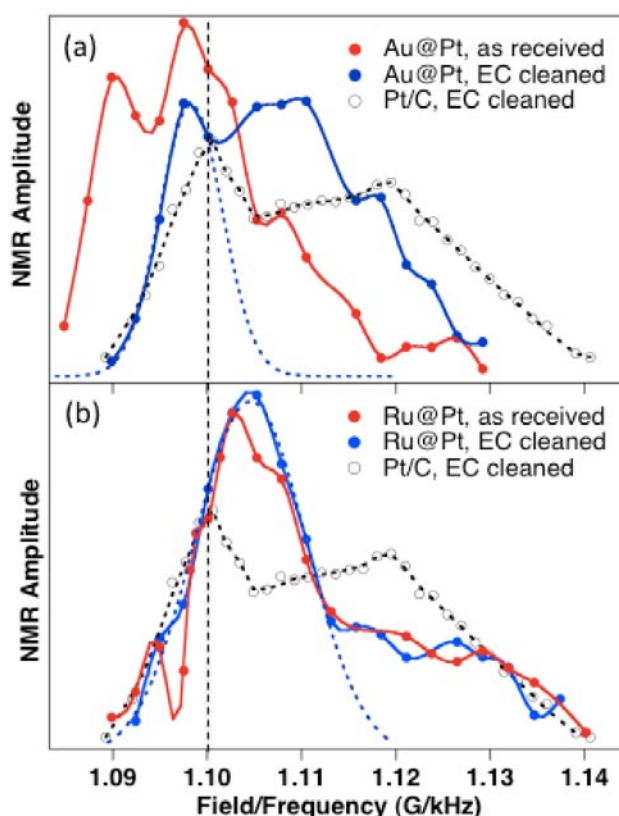


FIGURE 3. *in situ* ^{195}Pt NMR spectra (area-normalized) of Au@Pt (a) and Ru@Pt (b) NPs for as-received (red) and EC-cleaned (blue) samples. The black open circles and dashed line are the spectrum of a 2.5 nm pure Pt/C sample for reference. The vertical dashed line indicates the spectral position of surface Pt atoms for clean pure Pt/C NPs.

of the Au@Pt sample, it is very different from that of the pure Pt/C, with a broad dominant peak centered at 1.1053 G/kHz. Assuming that this is the surface peak, the ratio of the area under this peak can again be obtained by Gaussian deconvolution that gives a value of

0.74. The peak is high-field shifted from 1.1000 G/kHz, in the opposite direction from that of the Au@Pt. The origin of the remaining 26% signals is still unclear but clear difference in spectrum between Ru@Pt and Au@Pt highlights different electronic effect caused by the underlying Ru and Au cores.

If the deposited Pt atoms form mono-atomic islands on the surface of the core NPs, then they should have very similar electronic properties and coordination numbers. This is indeed the case for the Ru@Pt NPs as demonstrated by the spin-lattice and spin-spin relaxation times T_1 and T_2 measurements taken at four different spectral positions of the dominant peak centered at 1.1053 G/kHz (Figure 4). As can be seen, the four T_1 and T_2 data sets are statistically the same with each other. The solid curves are the fits of all four data sets to an exponential saturation-recovery function $A(\tau) = A_\infty - (A_\infty - A_0)\exp(-\tau/T_1)$ for T_1 and to a J-coupling modulated exponential decay function [4] $S(\tau)/S_0 = \exp(-2\tau/T_2)[P_0 + \exp(-(\tau/T_{2j})^2)[P_1\cos(J\tau) + P_2\cos^2(J\tau)]]$ with $P_0 + P_1 + P_2 = 1$ for T_2 respectively. In the former equation, A_∞ is the fully relaxed NMR amplitude, A_0 is the residual amplitude after the saturation pulses, and τ is the time interval between the saturation pulses and the signal reading pulses. In the latter equation, J is the nuclear-nuclear spin J coupling constant, P_0 , P_1 , and P_2 are the probability for a ^{195}Pt nuclear spin having zero, one, and two neighboring ^{195}Pt nuclear spins respectively, T_{2j} is the time constant accounting for the spread in J values due to environmental heterogeneity, S_0 is the equilibrium NMR amplitude (the same as A_0), and τ is the time interval between two Hahn echo pulses. The fits give $T_1 = 1.05 \pm 0.05$ ms, $T_2 = 348 \pm 22$ μs , $T_{2j} = 209 \pm 79$ μs , $J = 3.9 \pm 0.3$ kHz, $P_0 = 0.69 \pm 0.04$, and $P_1 = 0.19 \pm 0.03$. Using

a local Knight shift gradient parameter [4] $\delta = 0.15$, the local Pt atomic fraction estimated from the P_1 value is about 0.37 [5]. Since for a pseudo-morphic Pt monolayer on a Ru(0001) surface, the Pt fraction among all the next-nearest neighbors is 6/9, a local Pt atomic fraction of 0.37 is thus consistent with a Pt PD of 0.4 of mono-atomic Pt islands.

On the other hand, it is a quite different story for the Au@Pt sample whose results of T_1 and T_2 measurements are shown in Figure 5. They are qualitatively different from those of Ru@Pt and varied substantially from a spectral position to the other. Table 1 lists the fitted parameters that give the solid curves in Figure 5. The local Pt atomic fractions estimated from the P_1 values at 1.0975 G/kHz, 1.1001 G/kHz, and 1.1105 G/kHz are 0.14, 0.53, and 0.59 respectively. The T_1 and T_2 were also shorted as the spectral positions moved up-field, indicating that a substantial part of the Pt atoms went inside the Au NPs through exchange with the underlying Au atoms.

Using the two-band model [6], we calculated the s-like and d-like E_f -LDOS for surface Pt atoms in Ru@Pt and Au@Pt. They are $D_{s,E_f} = 3.7 \text{ Ry}^{-1} \cdot \text{atom}^{-1}$, $D_{d,E_f} = 13.3 \text{ Ry}^{-1} \cdot \text{atom}^{-1}$ for the former and $4.3 \text{ Ry}^{-1} \cdot \text{atom}^{-1}$ and $10.1 \text{ Ry}^{-1} \cdot \text{atom}^{-1}$ for the latter respectively. Namely, Pt on Au has higher s-like but lower d-like E_f -LDOS. How these differences in the E_f -LDOS are related to the observed electrocatalytic activity is still unclear at this moment and the Pt PD dependence study should be revealing. Nonetheless, the above EC-NMR investigations demonstrate again the unique investigative power of the technique.

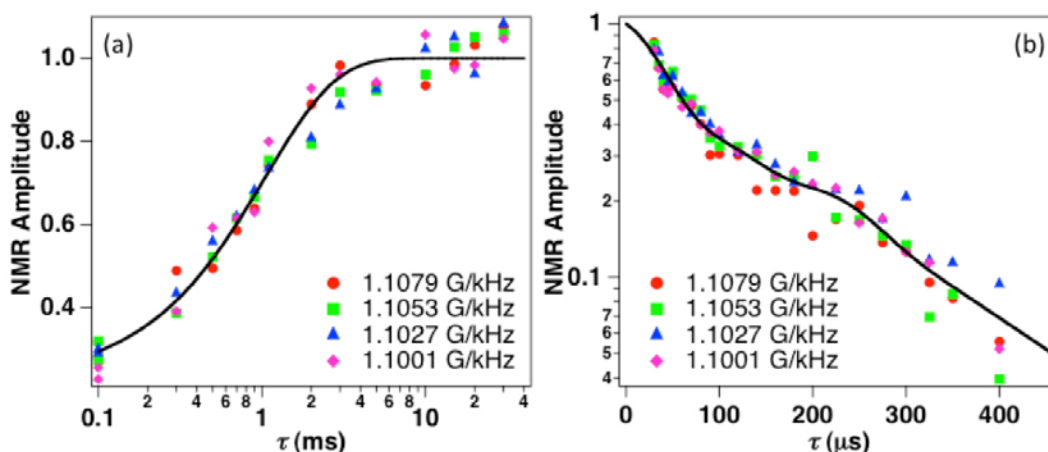


FIGURE 4. The spin-lattice relaxation T_1 (a) and spin-spin relaxation T_2 (b) data of the EC-cleaned Ru@Pt sample measured at different spectral position. The solid curves are the fits to the exponential recovery (a) and J-coupling modulated slow-beat (b) equations.

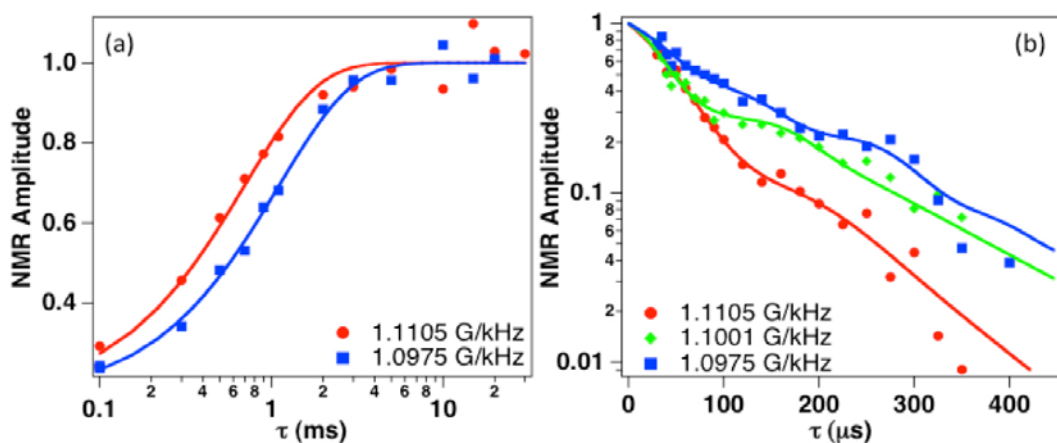


FIGURE 5. The spin-lattice relaxation T_1 (a) and spin-spin relaxation T_2 (b) data of the EC-cleaned Au@Pt sample measured at different spectral position. The solid curves are the fits to the exponential recovery (a) and J-coupling modulated slow-beat (b) equations.

TABLE 1. Fitted Parameters for Au@Pt Sample

Field (G/kHz)	T_1 (ms)	T_2 (μ s)	T_{2J} (μ s)	J (kHz)	P_0	P_1
1.0975	1.10	312	10000*	3.8	0.82	0.081
1.1001	N/A	257	138	5.3	0.70	0.25
1.1105	0.69	193	183	3.6	0.71	0.29

*The large T_{2J} for this position may indicate that the spread in J is small there.

Future Directions

The immediate future directions of research include, but are not limited to, detailed in situ spectroscopic (NMR/SEIRAS/SERS) investigations of Pt/C, Ru@Pt, and Au@Pt NPs as functions of Pt PD and sulfur coverage.

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