Plasmon-mediated electrochemical reactions: the influence of nanoparticle structure

Technical report due to closeout of award DE-SC0010307 at the University of Texas at Austin upon move from University of Texas at Austin to Temple University

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The goal of this research is to determine whether plasmon excitation can impact redox potentials of molecules at or near nanoparticle electrode surfaces and deduce the relationship between plasmon-mediated electrochemical reactions and the nanoscale structure of the nanoparticle electrodes. Two major accomplishments were made on this work while the PI was at the University of Texas:

1. Bulk electrochemical studies were performed using block copolymer templated nanoparticle arrays to probe redox reactions on nanoparticle array electrodes.

2. Local electrochemical reactivity was probed using super-resolution imaging of single nanoparticle aggregates, finding that "hot spots" were associated with specific redox properties of molecular adsorbates.

The first of these accomplishments focuses on the spectral response of plasmon-mediated electrochemistry, while the second deals with the spatial/structural response of plasmon-assisted electrochemical reactions. Each of these accomplishments will be discussed in more detail below.

Bulk electrochemical studies on nanoparticle arrays

Array development.   Our first task was to create nanoparticle arrays that are (1) inexpensive, (2) wide area, (3) reproducible, and (4) electrochemically addressable. We developed a simple method based on block copolymer templates. Briefly, a poly(methyl methyacrylate)-polystyrene (PMMA-PS) block copolymer is spin coated onto an indium tin oxide (ITO) coated-glass slide and annealed at high temperatures, allowing the block copolymer to self-assemble into PMMA cylinders embedded in a PS matrix. Exposing the film to UV light cross-links the PS while chemically degrading the PMMA, allowing us to rinse the PMMA away and leaving us with a PS hole mask. By depositing the metal of interest through the mask and then removing the PS, we are left with small metal disks on the ITO surface. Figure 1 shows several representative arrays
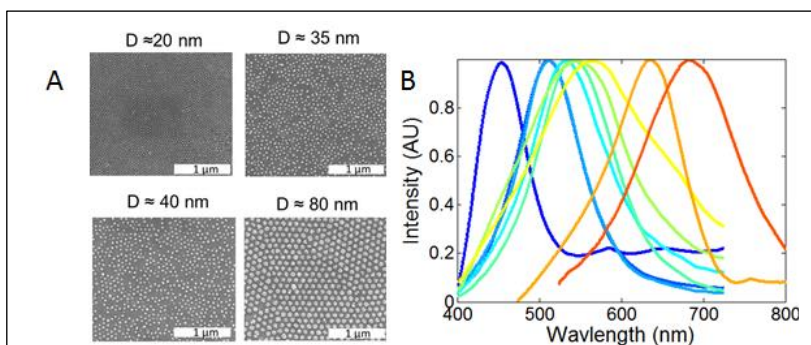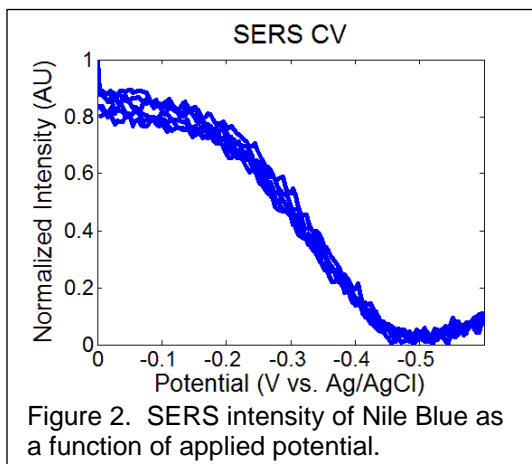

Figure 1. (A) Nanoparticle disk arrays on ITO prepared by block copolymer templating. (B) LSPR spectra of different nanoparticle arrays.
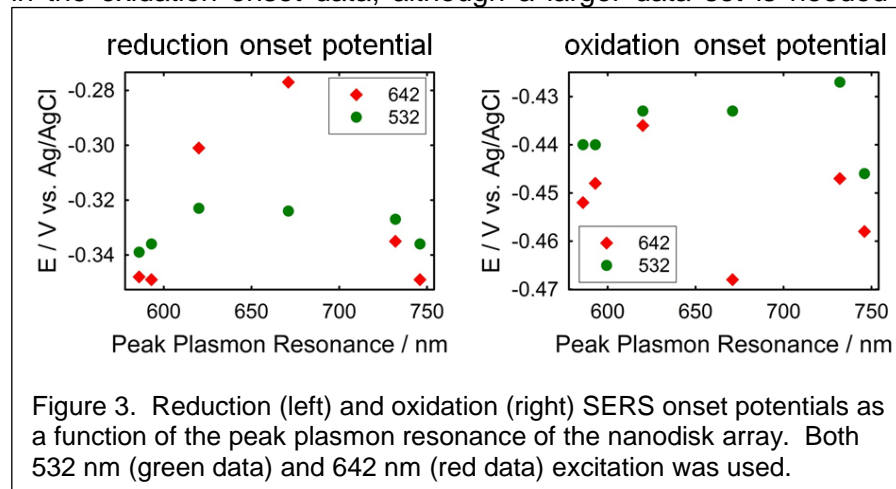
(A-D), as well as localized surface plasmon resonance (LSPR) spectra associated with arrays with varying disk diameter, height, and metal (Figure 1D).

Electrochemical studies on nanodisk arrays. To readout the electrochemical behavior of molecules on the plasmonic nanodisk arrays, we used surface-enhanced Raan scattering (SERS) from Nile Blue as an electrochemical probe. In the oxidized form, Nile Blue has a strong SERS signal, while in the reduced form, the signal is near zero. Thus, we have a simple optical readout of electrochemical reactions on the nanoparticle array surface. Figure 2 shows an example of the SERS intensity modulation of Nile Blue as a function of applied potential.

To extract meaningful electrochemical values, we take the minimum of the first derivative as the SERS half-wave potential and the maximum of the third derivative as the SERS onset potential. We then fabricated a series of nanoparticle arrays with differing plasmon resonances, measured the Nile Blue SERS intensity as a function of potential with both 532 nm and 642 nm excitation, and plotted the SERS half-wave and onset potentials as a function of the array LSPR maximum. Figure 3 shows the results of the reduction and oxidation onset potentials as a function of LSPR.

Figure 2. SERS intensity of Nile Blue as a function of applied potential.

The data shows some interesting trends. First, the SERS reduction onset potential shows a clear response to the plasmon resonance of the array, with the reduction potential shifted towards more positive values when the LSPR of the array is centered around 670 nm. Second, this LSPR-dependent reduction onset potential trend is observed with both red and green excitation, although the magnitude of the shift is larger when the wavelength of the laser is closer to the plasmon resonance of the array. A similar LSPR-dependent trend is not obvious in the oxidation onset data, although a larger data set is needed to confirm the presence or absence of a trend. Thus, preliminary data are suggestive of a plasmon dependent response in the bulk electrochemistry of Nile Blue, although current experiments are focused on expanding the data set and confirming the robustness and reproducibility of the results.

Figure 3. Reduction (left) and oxidation (right) SERS onset potentials as a function of the peak plasmon resonance of the nanodisk array. Both 532 nm (green data) and 642 nm (red data) excitation was used.

<u>Super-resolution imaging of local redox potentials on single nanoparticle aggregates.</u>

<u>Publications</u>:

(1) A.J. Wilson and K.A. Willets. "<u>Visualizing site-specific redox potentials on the surface of plasmonic nanoparticles with super-localization SERS microscopy</u>." Nano Lett. 14, 939-945 (2014).

(2) M.L. Weber, A.J. Wilson, K.A. Willets. "Characterizing the spatial dependence of redox chemistry on plasmonic nanoparticle electrodes using correlated super-resolution SERS imaging and electron microscopy." J. Phys. Chem. C. 119, 18591 (2015).

The next accomplishment involves using super-resolution SERS imaging of Nile Blue on noble metal nanoparticle aggregates to map the spatial dependence of the electrochemical response on plasmonic nanoparticle electrodes. In these experiments, silver or gold nanoparticles are prepared in solution and Nile Blue is either physisorbed or chemically attached to the nanoparticle surface. Then, nanoparticles are aggregated through the addition of salt, and dropcast onto ITO-coated coverslips. The samples are then mounted in an inverted optical microscope and Nile Blue SERS is excited by either 532 nm or 642 nm laser excitation. The resulting SERS from individual nanoparticle aggregates is imaged onto a CCD camera, where each aggregate appears as a single diffraction-limited spot. To extract how the spatial origin of the SERS emission is impacted by the changing in applied potential, we fit each diffraction-limited spot to a 2-dimensional Gaussian, as shown in equation 1.

$$I(x, y) = z_0 + I_0 \exp\left[-\frac{1}{2}\left[\left(\frac{x-x_0}{s_x}\right)^2 + \left(\frac{y-y_0}{s_y}\right)^2\right]\right]$$ (1)

In equation 1, z_0 is the background, I_0 is the peak intensity of the diffraction-limited spot, $s_{x,y}$ are the standard deviations of the Gaussian in x and y, and x_0 and y_0 are the centroid of the fit. We approximate the position of the centroid (x_0, y_0) as the location of the emitter.

Figure 4 shows an example of how the SERS centroid changes as a function of applied potential when roughly 2-10 Nile Blue molecules are adsorbed on the surface of colloidal silver nanoparticles.[1] The SERS intensity modulates as expected as the applied potential changes (Figure 4, left, columns 1-2). More interesting is the reproducible modulation in the SERS centroid position as the potential is swept (Figure 1, left, columns 3-4, and Figure 1, right). We ascribed this behavior to site-specific redox potentials, in which the potential at which a molecule is oxidized or reduced is directly related to its position on the nanoparticle aggregates surface.
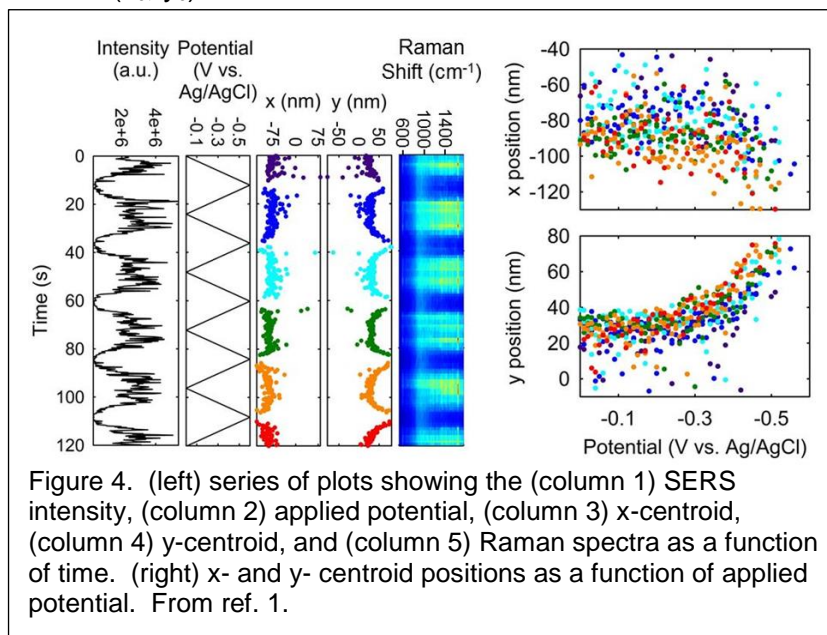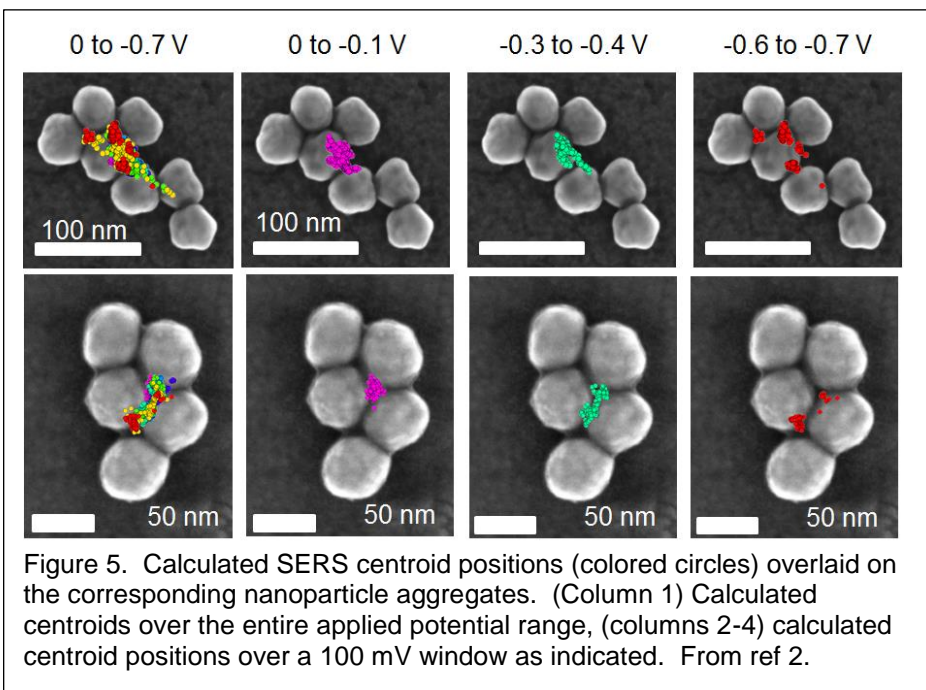

Figure 4. (left) series of plots showing the (column 1) SERS intensity, (column 2) applied potential, (column 3) x-centroid, (column 4) y-centroid, and (column 5) Raman spectra as a function of time. (right) x- and y- centroid positions as a function of applied potential. From ref. 1.

To test this hypothesis, we performed correlated optical and structural studies, in which samples were moved to a scanning electron microscope (SEM) following the optical experiments. This allows us to compare the potential-dependent SERS centroids with the actual structure of the nanoparticle aggregate. Figure 5 shows two examples of Nile Blue SERS centroids, color-coded by the associated potential, and overlaid on the SEM images of the corresponding nanoparticle aggregates.[2] In both examples, the centroid changes position as a

function of the applied potential, as shown in the left column, in which all centroid positions are shown. In the three rightmost columns of Figure 5, the centroid positions calculated when the applied potential was within three representative 100 mV windows are shown. At the most positive potentials, when all Nile Blue molecules are expected to be oxidized and therefore emitting (column 2, pink data), the centroid positions converge to a single position, reflecting a super-position of all of the active Nile Blue emitters. At intermediate potentials (green data, column 3), the centroid is spread out over the nanoparticle, reflecting the changing populations of Nile Blue molecules that are transitioning between oxidized and reduced forms. At the most negative potentials (red data, column 4), the centroid positions converge to highly localized positions associated with junction regions between adjacent nanoparticles in the aggregate. In the SERS community, these junctions are typically known as "hot spots" because they are associated with strong

Figure 5. Calculated SERS centroid positions (colored circles) overlaid on the corresponding nanoparticle aggregates. (Column 1) Calculated centroids over the entire applied potential range, (columns 2-4) calculated centroid positions over a 100 mV window as indicated. From ref 2.

electromagnetic field enhancement in the junctions. Thus, these data suggest a relationship between the redox potential of Nile Blue molecules and their location on the nanoparticle surface, with molecules sitting at hot spots showing the most negative reduction and oxidation potentials.

Conclusions.

The work performed at the University of Texas at Austin suggests both a spectral and spatial dependence of electrochemical reactions on plasmonic nanoparticle electrodes. Understanding how both variables impact observed electrochemical activity on these substrates will be the focus of continued efforts at the Temple University in the remaining three years of this award.