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Guided Assembly of 2D Arrays of Gold Nanoparticles on a Polycrystalline Gold Electrode for Electrochemical Surface Enhanced Raman Spectroscopy

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ABSTRACT

Development of a reproducible 2D-array of gold nanoparticles through a guided assembly approach and sequentially using an electrochemical cleaning procedure to remove all capping ligands and surface contaminants for studying gluconate, a weak Raman scatterer, with electrochemical surface enhanced Raman spectroscopy (SERS) is discussed. Here, a unique use of shell-isolated nanoparticles is presented by employing a thin-cell configuration during nanoparticle deposition to obtain a highly reproducible monolayer of gold nanoparticles with spacing by 2x the SiO₂ shell thickness. Upon SiO₂ dissolution and electrochemical cleaning, a well-ordered arrangement of bare gold nanoparticles was achieved. The SERS active electrode modified with nanoparticle arrays was used for characterization of gluconate adsorption. Enhanced spot-to-spot reproducibility of the SERS signal was achieved, allowing for significant reduction in the acquisition time needed for recording SERS spectra and investigation of gluconate adsorption on gold surfaces at short times. The results collected suggest gluconate has undergone some electro-oxidation but remains well hydrated in the interfacial region.

INTRODUCTION

Surface enhanced Raman spectroscopy (SERS) is a common analytical technique employed to nondestructively obtain molecular level information of a desired sample directly adsorbed or in a close proximity to rough surfaces or metal nanoparticles (NPs) made of Ag, Au, or Cu.^{1,2} The use of SERS to characterize molecules at electrode-electrolyte interfaces has considerably grown in the recent past with the ease and reproducibility of substrate fabrication techniques. Combining SERS and electrochemistry can lead to a wealth of additional information, for example, SERS active electrodes have been recently employed for sensing chemical and/or biochemical changes in response to applied potentials (e.g. conformation,

orientation, oxidation state, etc.).³⁻⁷ However, characterizing analytes adsorbed to an electrode with SERS can still be difficult in an electrochemical system as the analytes are often present in monolayer or sub-monolayer coverages ($\sim 10^{-10}$ mol cm⁻²) and are often very weak scatterers ($\sim 10^{-30}$ cm² molecules⁻¹ sr⁻¹).⁸

Gathering SERS spectra with high reproducibility that also accurately represents the electrochemical system requires nanofabrication of the desired electrode with metal NPs that are ideally patterned on the surface to obtain sufficient SERS enhancement.⁹ The roughness or metal NPs support localized surface plasmon resonance (LSPR) induced by the interaction of incident photons of the Raman instrument.¹⁰ Any sample molecules that are located very near the NP surface will experience enhanced electromagnetic fields resulting in larger Raman scattering intensities in the 10^5 - 10^8 range. Surface enhancement of Raman spectra collected of an adsorbate on a metal surface was first observed from a roughened silver substrate.¹¹ Recently, spherical metal NPs have been more commonly used in SERS studies due to their ease of fabrication, susceptibility to chemical modification, and ability to tune the NP size and shape for optimal enhancement.¹² Furthermore, control of the patterning of NPs (the arrangement and/or spacing between NPs) during deposition can vastly improve the intensity and reproducibility of SERS signals and offers critical insight into fundamental plasmonic properties of NPs assembled at a solid-liquid interface.^{2,13-18} This can be especially important for quantitative investigations with SERS,¹⁹ or studying interfacial reactions, e.g. electro-catalytic reactions that may occur very quickly.

Gold nanoparticles (AuNPs) arranged in 2D arrays on electrode surfaces are ideal systems for studying electrochemical processes with SERS as they exhibit superior stability in various electrochemical conditions. Unfortunately, stabilizing ligands, e.g. citrate, that are often

used to prevent agglomeration of NPs in solution, also prevent uniform deposition on an electrode surface required to achieve plasmonically active electrodes. NPs modified with a high surface charge, e.g. citrate, while suspended in solution experience electrostatic repulsion from other nearby NPs. Therefore, during deposition on an electrode surface the NPs will deposit relatively far from one another, or they randomly agglomerate into large 3D structures.¹² Several researchers have reported high sensitivity of SERS measurements using either arrays of NPs formed by evaporation of a thin film of a noble metal,^{17,20} or using hydrophobic capping ligands to form arrays of metal NPs on a solid support.²¹ Recently, deposition of polystyrene spheres onto hydrophilic surfaces producing 2D NP arrays has been employed. A successive thin metal film-over-sphere deposition method gave substrates with large surface enhancement for SERS.^{13,14,22–26} Unlike gold or silver NPs, polystyrene spheres do not require capping ligands to prevent agglomeration in solution. Therefore, the hydrophilic surface results in a very low contact angle resulting in relatively well-ordered 2D arrays upon solvent evaporation. Through varying the polystyrene diameter and the deposited metal thickness, the SERS substrates have shown the ability to tune the LSPR with the wavelength of incident photons.¹⁴

Moreover, recent studies involving shell-isolated nanoparticles (SHINs) deposited on substrate surfaces that were fabricated with inert shell materials, e.g. SiO_x , have been observed to form NP monolayers with improved substrate-substrate and spot-spot reproducibility in SERS signals.^{27,28} Many reports have shown the vast applicability of using SHINs with a wide range of substrate surfaces and the ability to use a range of desired materials and configurations for the NP core and the shell.^{29–31} To achieve optimal SERS enhancement SHINs possess an added advantage of very fine control over the NP core diameter and the shell thickness which may be controlled to within a few nanometers during fabrication.³² However, the inert SiO_2 shell

dampens the SERS signal because the surface enhancement decreases exponentially with shell thickness,³³ and the hydrolyzed (3-aminopropyl)triethoxysilane (APTES) that is required for surface functionalization of the NP core prior to SiO_x deposition may cause spectral interference. Figure 1 shows a comparison of SERS spectra of a thioglucose molecule on AuNPs and SHINs that possess an APTES sublayer. The $\nu(\text{NH}_2)$, $\nu(\text{CH}_x)$, $\delta(\text{CH}_2)$, and $\nu(\text{Au-NH}_2\text{R})$ bands of APTES may be difficult to isolate or background correct from the spectra of glucose due to a pronounced overlap of bands in the 1600 to 1100 cm⁻¹ spectral region where important sugar bands are located. Therefore, pure AuNPs are desired for SERS measurements of sugar molecules. Previously, AuNP modified electrodes, produced by deposition of citrate stabilized AuNPs followed by electrochemical desorption of the citrates, have been employed to characterize adsorbed sugars.¹² However, the AuNPs agglomerated upon deposition giving uneven distribution of particles across the surface. The present work looks to characterize the advantageous use of guided assembly of SHINs to achieve uniform 2D arrays on a gold electrode, followed by SiO₂ shell dissolution to leave clean, evenly distributed AuNPs. The facile method to deposit NPs on a substrate surface should give a uniform enhancement of the Raman signal across the surface. AuNPs nanopatterned in a 2D array on gold surfaces represents an ideal case, however a properly developed method could potentially be applied to a wide range of nanoparticle-electrode systems.

Figure 1: Comparison of the SERS spectra of (A) thioglucose chemisorbed to a AuNPs modified gold electrode and (B) SiO₂ SHINs deposited on a gold electrode.

Experimental Section

Substrate Preparation

SHINs were prepared following previously reported methods.^{2,32–35} First, AuNPs stabilized in an aqueous citrate solution were fabricated using a seed mediated growth procedure. Gold seeds with a target diameter of 40-50 nm were produced using the typical sodium citrate (1.0 wt%, Sigma-Aldrich, >99.5%) reduction method with hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, Alfa Aesar, 99.99%). Further growth to 120 nm diameter was accomplished in a successive step by utilizing a diluted seed suspension with the aid of additional HAuCl₄ and citrate combined with 0.54 wt% hydroxylamine hydrochloride (HONH₃Cl, Sigma-Aldrich, 99%) as a stronger reducing agent. Surface functionalization of the AuNPs was achieved by allowing 20 minutes exposure of the 120 nm citrate stabilized AuNPs to a 0.5 mM hydrolyzed (3-aminopropyl)triethoxysilane solution (APTES, H₂N(CH₂)₃Si(OC₂H₅)₃, Sigma-Aldrich, >98.0%).

Lastly, encapsulation of the AuNP core with a 2-5 nm SiO₂ shell was completed using a sodium silicate solution (Na₂O(SiO₂)_x·xH₂O, Sigma-Aldrich, reagent grade) at ~90.0°C for 60 minutes to ensure a uniform pinhole-free coating. After cooling to room temperature, removal of excess reagents in the suspension of SHINs was accomplished by centrifuging (3000 RPM for 15 minutes) and resuspension in Milli-Q water multiple times. The cleaned SHINs suspension was then vacuum-deposited onto the desired substrate.

To avoid non-uniform deposition of the SHINs, a modified procedure from Bartlett et al. employing a thin-cell configuration was used.²³ A thin Teflon spacer (~0.1 to 0.3 mm thick) gently squeezed between the desired substrate and a glass slide on top was used for all NP depositions as schematically illustrated in Figure 2. The entire thin-cell was placed in a vacuum desiccator to slowly remove the aqueous solvent creating a thin film of solution with suspended NPs present. As the solution evaporate the meniscus moves across the surface where surface forces cause the NPs to densely pack into a monolayer configuration. Complete encapsulation of the AuNPs was confirmed by recording SERS spectra of a minimum of 20 different locations of SHINs deposited on clean silicon wafers immersed in a 0.01 M pyridine solution (C₅H₅N, Fisher Sci., certified ACS reagent grade) with a 100% laser power, 1 s exposure, and 3 accumulations.³²

Figure 2: Schematic illustration of the thin-cell configuration used for guided assembly of NPs on the Au electrode surface. Note: dashed arrow indicates direction the solvent meniscus moves during the solvent evaporation procedure creating a thin film of solution where SHINs will ideally pack into a dense monolayer array (Teflon spacer not drawn to scale).²³

After deposition of the SHINs, the modified electrode was either placed in a 0.1 M NaOH solution for several hours for SiO₂ dissolution and/or directly inserted into a three-electrode glass electrochemical cell to be cleaned in an argon purged 0.1 M sodium fluoride electrolyte (NaF, Sigma-Aldrich, >99%). Repetitive cycling within −0.90 V to +1.25 V vs. SCE was conducted until a stable cyclic voltammogram (CV) with characteristic features of a clean polycrystalline electrode was obtained. A flame annealed gold wire (Alfa Aesar, >99.9%) and a saturated calomel electrode (SCE, Fisher Scientific) that was connected to the electrolyte solution through a salt bridge were used as the counter and reference electrodes, respectively.

Instrumentation

UV-Visible absorption spectra of freshly prepared NPs suspended in Milli-Q water and in air after vacuum deposition on a clean glass slide were recorded using a Cary 300 UV-vis spectrophotometer in the spectral range between 400 to 800 nm. Scanning electron microscope (SEM) images were collected with a FEI Inspect S50 fitted with a tungsten filament and operated with a working distance of ~9.6-10.0 cm, a spot size of 3.5 nm², and a 15-20 kV electron beam energy for collection of all SEM images. A Renishaw Raman imaging microscope (50x objective) equipped with a 785 nm edge StreamLine NIR diode laser (50 mW max power) and a CCD array detector (1024x256) was used for all Raman investigations. A spectral resolution of approximately 1 cm^{−1} was achieved using a slit width of 65 μm and a holographic grating (1200 lines nm^{−1}). The Raman spectrometer was calibrated to the vibrational band of pure silicon at 520 cm^{−1} prior to each experiment.

Results and Discussion

Modification of a Gold Electrode with 2D Nanoparticle Arrays

To determine the plasmonic properties of the AuNPs used in the present study, the extinction spectra of several NP suspensions were measured. Figure 3A plots spectra of the NP suspensions in the visible range of freshly prepared citrate stabilized AuNPs with a diameter of ~50 nm (black curve). The larger 120 nm NPs, synthesized using the 50 nm NPs as seeds, is also displayed in Figure 3A before (red curve) and after (blue curve) coating with the silica shell.³² A single, well-defined extinction maximum at 535 nm is observed for the suspension of Au seeds corresponding well with the independently verified NP diameter of 50 ± 8 nm determined with SEM. For smaller nanoparticles the peak wavelength is predominantly a result of excitation of the NP's LSPR, and is consistent with spectra expected for spherical AuNPs of approximately 50 nm in diameter.^{36,37} In comparison, the extinction spectra of the larger AuNPs (dia. 122 ± 8.5 nm) and the SHINs (dia. 126 ± 8 nm) exhibit broadened peaks that are redshifted, 633 and 607 nm, respectively, with additional peaks that are observed as convoluted shoulders. The broadening, additional peaks, and shift in the LSPR peak position are all commonly reported in the literature for AuNPs larger than 100 nm synthesized using the traditional citrate reduction

Figure 3: (A) Normalized UV-vis spectra of citrate stabilized AuNPs with an average diameter of 50 nm (black line) or 122 nm (red line), and 126 nm_{shell} isolated gold nanoparticles (blue line) suspended in solution. (B) TEM image of a single SHIN with a uniform 4.2 nm shell of SiO₂ (observed as a lighter ring encapsulating the dark AuNP core).

method due to a combination of absorbance and scattering processes that become more prevalent at larger diameters.^{36,37} Additionally, when AuNPs increase in size they may also change their geometric shape, for example elongation into a cylindrical shape where the LSPR can be excited along the short or long axes producing two absorption peaks that may appear in the spectra.³⁶ The TEM image of a single SHIN, Figure 3B, reveals the dark AuNP core modified with a uniform 4.2 ± 0.7 nm (average values obtained from 50-70 SEM/TEM measurements, additional

representative TEM images of SHINs can be found in Figure S1 of the Supporting Information) SiO₂ shell observed as a lighter coating encapsulating the NP core. The SiO₂ shell has lighter shade relative to the gold core due to the large density difference between the two materials.

Similar NPs as those characterized in Figure 3, were deposited onto a planar polycrystalline gold electrode and imaged using SEM as shown in Figure 4. Figures 4A-B show typical 3D agglomeration of the citrate stabilized AuNP seeds upon deposition of the aqueous suspension on a clean gold substrate. The images were collected after the subsequent removal of citrate by electrochemical desorption till a stable CV characteristic of a polycrystalline Au is achieved.¹² This procedure removed the negative surface charge of citrates on the NPs, however non-uniform NP aggregation into clusters is commonly reported for these NPs prior to citrate removal. Figures 4C-D display images of SHINs deposited using the thin-cell modified procedure previously reported by Bartlett et al.²³ before SiO₂ removal. The images show that SHINs are deposited to form a regular, close-packed 2D array on the gold support surface. This guided assembly of the SHINs onto the solid-liquid interface is driven by capillary forces that control the direction of NP deposition on the support surface as shown in Figure 2.³⁸

Spot-to-spot SERS reproducibility can be visualized by tracking the relative spatial variations in the SERS intensity of vibrational bands across the substrate surface using Raman mapping software. The relative SERS intensity map of the CH_x stretching bands originating from the hydrolyzed APTES sublayer of the SHINs in Figure 5A displays the relative spatial distribution of SERS enhancement across the surface.³⁹ APTES is expected to form relatively well ordered layers that are ideal for pinhole-free, uniform SiO_x coatings. Therefore, the observed intensity variation in the SERS map can be expected to be predominantly a result of spatial variations in surface enhancement. The SERS map was produced by collecting spectra in

1 μm step-wise increments and visualizes the distribution of local changes in the surface enhancement of the CH_x vibration intensity.

Figure 4: SEM images of (A + B) 50 nm citrate stabilized Au seeds, and 126 nm SHINs deposited on planar polycrystalline Au electrodes (C + D) before and (E + F) after SiO_2 shell removal.

Figure 5. (A) SERS mapping image generated from 2500-3200 cm^{-1} region collected of SHINs deposited on a clean gold electrode. (B) SERS spectra of select locations from the corresponding map. (C) SERS mapping image generated in the 1000-1600 cm^{-1} region of agglomerated citrate stabilized AuNPs, and (D) SERS spectra recorded of citrates from select locations of the map.

Figure 5B shows the spectra of the CH_x vibrations collected from selected regions of the SERS map. They demonstrate that the 2D array of SHINs reveals high surface enhancement, sufficient for the $\nu(\text{CH}_x)$ region of APTES, and reduced variability in spot-to-spot sampling. This behavior has been reported previously by Chen et al. for highly organized NPs.²¹ For comparison, Figure 5C shows the SERS intensity map generated from the citrate-AuNPs modified surface in the 1000-1800 cm^{-1} region. Due the relatively weak CH_x region for citrate,

Figure 5C is showing the symmetric and asymmetric stretching region of COO^- of citrate. The spatial changes observed within the SERS signal show changes in the surface enhancement at a given point in the image. The SERS map reveals the presence of hot-spots at the surface, which were not observed in Figure 5A to the same extent. Figure 5D plots the SERS spectra recorded in the selected regions of the image in Figure 5C. The data in Figures 5C-D show that in contrast to the electrode covered by SHINs (15 % RSD in SERS signal observed in Figure 5A map), the citrate capped AuNPs display a non-uniform surface enhancement with the presence of intense hot spots and many regions without sufficient enhancement to detect weak scatterers such as citrate (80 % RSD in SERS signal observed in Figure 5C map). This behavior can make the characterization of adsorption of weak Raman scatterers very difficult and time-consuming.

The ability to deposit NPs on an electrode surface in reproducible large-scale 2D arrays furthers the ability of implementing NPs in variety of electrochemical applications, for example electronics, plasmonics, sensing and diagnostics, and catalysis at electrode surfaces. Depositing NPs using a guided assembly approach may give several added advantages, for example; (i) implementation of metal nanoparticles made with differing materials (e.g. Au, Ag, Cu, transition metals, etc.) or different sizes to add versatility and customization for the desired application, (ii) conformation of NPs to various substrate types and morphologies, (iii) tunable spacing between NP cores through control of the shell thickness, and (iv) the ability to remove the SiO_2 if desired. While each of these parameters presents unique opportunities for fundamental investigations, the feasibility of creating large-scale 2D arrays and their use in characterizing adsorbed gluconate is explored here in an attempt to create a foundation for future investigations.

Characterization of the SiO_2 Shell Removal

The SiO₂ shell removal and electrochemical cleaning were performed in separate 0.1 M NaOH electrolyte solutions (pH = 12.2), with copious rinsing. Silica dissolution has been well known to occur in alkaline aqueous solutions, pH > 10.5.⁴⁰ Furthermore, we have previously reported SiO₂ shell dissolution of SHINs occurs in 0.1 M NaOH electrolytes.³⁹ Removal of the SiO_x is further corroborated in Figure S2 of the Supporting Information, where pyridine adsorption is only observed after sufficient exposure of the SHINs to the alkaline aqueous solution. The SEM images of the film of clean AuNPs obtained after SiO₂ removal from the SHINs is shown in Figures 4E-F. The sample was first treated with 0.1 M NaOH and then exposed to repetitive potential cycling between -0.90 V to +1.25 V vs. SCE to ensure successful removal of all contaminants. Independent electrochemical measurements, (Figure S3 of the Supporting Information), were performed to determine the approximate desorption potentials required to remove hydrolyzed APTES and citrate from a planar polycrystalline gold electrode. Despite these treatments, the 2D array structure of the film observed in the film of SHINs is preserved after removal of the SiO₂ shell. However, the EDS analysis of the electrode surface (Figure S4 of the Supporting Information) reveals a clear disappearance of the elements related to the SiO_x coating. In contrast to the film produced by the citrate method (Figures 4A-B), the film of AuNPs obtained by removing the shell from SHINs show significant improvement in the homogeneity of the NPs distribution across the support surface. In theory, sufficient exposure of the SHINs modified gold electrode to a 0.1 M NaOH solution results in relatively stable 2D arrays of AuNPs. However, as revealed from the SEM images in Figures 4F the positions of the AuNPs do appear slightly shifted relative to the 2D array of SHINs shown in Figures 4D but has remained in a stable 2D array. The observed shifted positions of the 2D-NPs may be a consequence of drying in the SEM vacuum chamber prior to image collection, the 2D arrays

used in subsequent Raman investigations in the present study may have remained uniform in the absence of any drying procedures.

Subsequent electrochemical cleaning of the AuNPs modified electrode surfaces was performed by repetitive cycling in a 0.1 M NaF electrolyte between -0.90 and +1.25 V vs. SCE to remove all surface contaminants until a stable CV as shown in Figure 6A and the background SERS spectrum in Figure 6B was obtained. These potential limits were found to be sufficient to remove all remaining contaminants. Figure 6A shows that after removal of the shell, the CV recorded at the 2D array of the clean AuNPs modified electrode surface (Au/2D-AuNPs), has similar shape to the CV recorded at a planar, clean polycrystalline Au electrode. The electrode with NPs exhibits larger Au oxidation and oxide reduction currents relative to the electrode without NPs. This behavior demonstrates an increase in exposed Au surface area due to the 2D array of clean AuNPs that are no longer encapsulated by SiO_x. Since repetitive cycling was performed in a non-complexing electrolyte and the sweep rate was very low, no electrochemical roughening was observed. Once AuNPs were cleaned, no further increase of the electrode area was observed upon further repetitive potential cycling.

Finally, to further confirm that all surface contaminants and background had been successfully removed from the AuNPs modified surface Figure 6B plots the background corrected SERS spectra of the Au/2D-AuNPs electrode before (spectrum 1) and after (spectrum 2) shell dissolution and cleaning. Several bands are observed in spectrum 1 that are positioned at 1128, 1296, 1434, 1456, and 1605 cm⁻¹, and many overlapping bands between 2700 and 3000 cm⁻¹ are characteristic of hydrolyzed APTES and have been assigned as $\nu_{as}(\text{SiOSi})$, $\omega(\text{CH}_2)$, $\delta(\text{SiCH}_2)$, $\delta(\text{CH}_2)$, $\delta(\text{NH}_2)$, and $\nu(\text{CH}_x)$, respectively.^{39,41-43} Spectrum 2 collected at the Au/2D-

AuNPs electrode after electrochemical cleaning does not display any characteristics of hydrolyzed APTES that were present in spectrum 1.

Figure 6: (A) CV curves (5 mV s^{-1}) of a polycrystalline gold electrode in an argon purged 0.10 M NaF electrolyte before (curve 1) and after (curve 2) modification with a 2D array of AuNPs. Inset displays the double layer region (-0.90 to +0.40 V vs. SCE) of the same electrodes. (B) Background corrected SERS spectra collected in Milli-Q water at the nanoparticle modified polycrystalline gold electrode surface before (spectrum 1) and after (spectrum 2) SiO_2 shell removal and electrochemical cleaning.

Electrochemical desorption upon sweeping the potential to -1.0 V vs SCE is sufficient to remove all traces of surface contaminants. Without any remaining species to impede sample molecule adsorption onto the clean gold surface or characterization with SERS, spectra of high quality and reproducibility can now be obtained without the tedious effort of searching for randomly located hotspots as required using the citrate-AuNPs modified electrode. To reveal the spatial reproducibility in surface enhancement of Raman scattering signals that result from 2D array of “bare” or electrochemically cleaned AuNPs, Figure 7 plots a 2D SERS map collected by tracking the intensity of the 1011 cm^{-1} ring breathing mode of pyridine that had been allowed to adsorb to the modified substrate surface as a Raman reporter molecule.^{11,34} SERS mapping was accomplished by scanning the laser ($\sim 1\text{ }\mu\text{m}$ spot dia.) across the surface in $4\text{ }\mu\text{m}$ increments. Areas that are observed to have larger intensities at 1011 cm^{-1} appear brighter than areas with lower intensity. In comparison to the citrate stabilized AuNPs modified surface, Figure 5C which resulted in small localized hot-spots that can be difficult or time consuming to locate, Figure 7 of the 2D-AuNPs present an example of the ability to reliably detect pyridine across the 2D-AuNPs surface. The %RSD of the signal in the image Figure 7B is 55%. It is higher than for the film of SHINs (Figure 5A) but lower than for citrate stabilized AuNPs (Figure 5C). These numbers indicate that the film of bare AuNPs gives less uniform signal than the film of SHINs but more uniform than for citrate stabilized AuNPs. However, %RSD of the image in Figure 5c averages sharp signals from hot spots and signals from regions with very low enhancement. The SERS map in Figure 7A reveals a fairly uniform distribution where all locations reveal two ring breathing modes of pyridine located at 1011 and 1035 cm^{-1} (see Figure 7B). The uniformity in the SERS substrate can lead to vast improvement in spectral collection variability and improve quality of spectra obtained of catalytic reactions that occur very quickly as there is no longer a

need to search for optimal hot spots. To highlight this achievement, electrochemical SERS will be used to investigate gluconate oxidation on the Au/2D-AuNPs substrate.

Figure 7: (A) SERS map of the 1011 cm^{-1} ring breathing mode of pyridine adsorbed on the Au/2D-AuNPs electrode surface after passive incubation for 10 mins, and (C) individual SERS spectra from indicated areas of the SERS map. Mapping parameters: 1% laser power ($\sim 0.3\text{ mW}$), 785 nm laser, 2 s exposure time, 1 accumulation.

Application of Au/2D-AuNPs Electrode for Identifying Gluconate Physisorption

The motivation to study gluconate adsorption at gold originated from our earlier studies of a self-assembled monolayer of thioglucose.¹² That study indicated that thioglucose is oxidized and a thio-derivative of gluconate was a possible candidate for the oxidation product but this was not confirmed. Figure 8-A plots Raman spectrum of concentrated D-gluconate solution. Figure 8-B plots the SERS spectrum of gluconate collected of the Au/2D-AuNPs electrode in 0.05 M calcium D-gluconate solution. After a short assembly time sufficient quantity of gluconate has adsorbed at the electrode so that it has become easily detectable with SERS. The SERS spectrum was determined with a better S/N than the Raman spectrum of gluconate in solution. There are visible differences between the two spectra. In the SERS spectrum, the bands are narrower, their

positions are shifted and their amplitudes are changed. The shift in frequency may be caused by coordination of gluconate to the gold surface. For a molecule at the electrode surface, bands

Figure 8: (A) Baseline corrected Raman spectrum of a sodium D-gluconate solution. SERS spectra collected in a sealed spectroelectrochemical cell using (B) a Au/2D-AuNPs electrode in a 0.1 M NaF + 0.05 M sodium D-gluconate solution at E_{OCP} , and (C) a Au electrode with randomly distributed AuNPs in a 0.1 M NaF electrolyte with an externally formed self-assembled monolayer of β -D-thioglucose averaged between E_{OCP} and $E = -0.6$ V vs SCE. (D) Baseline corrected Raman spectrum of a β -D-thioglucose solution.

which have strong components of the polarizability tensor in the direction normal to the surface are enhanced and those with weak components are attenuated.⁴⁴ For NP modified electrode surfaces, analyte molecules may completely or partially lie within a localized hotspot resulting in SERS spectra with varying intensities. In both spectra the most prominent bands are observed in the 1450-1650 cm^{-1} region characteristic of the gluconate asymmetric carboxylic stretches, $\nu_{\text{as}}(\text{COO}^-)$. In the SERS spectrum, splitting of the bands is likely attributed to a number of possible adsorption sites and orientations of the gluconate on different surface crystallographic facets and step edges. Water molecules are also expected to be present at the interface in this spectral region combined with the gluconate adsorption. Convolved with the gluconate carboxylic stretches, a broad band at ~ 1600 cm^{-1} and a shoulder at ~ 1640 cm^{-1} are characteristic for the bending vibrations of water, $\delta(\text{H}_2\text{O})_{\text{interface}}$ and $\delta(\text{H}_2\text{O})_{\text{bulk}}$, respectively.⁴⁵ This suggests water molecules may remain in close vicinity of the gold interface. The 1450–1200 cm^{-1} region contains bands corresponding to coupled vibrations of methylene and hydroxyl groups. SERS bands observed at ~ 1403 , 1345 and 1322 cm^{-1} correspond to a combination of CH_2 , COH , and CH bending modes, $\delta(\text{CH}_2, \text{COH}, \text{CH})$, as well as $\omega(\text{CH}_2)$. The SERS bands in the 1200–950 cm^{-1} region are mainly a result of C–O stretching with a small contribution from C–C stretching and bending of the OH functional groups, e.g. 1162, 1141, 1100, and 1000 cm^{-1} .^{12,46} In this region, band intensities in the SERS and solution spectra differ significantly, most likely due to surface orientation effects.

The Au/2D-AuNPs SERS spectrum for gluconate could be now compared to the SERS spectrum of thioglucose collected on the Au electrode modified with randomly deposited AuNPs and the normal Raman spectrum of a β -thioglucose solution which are presented in Figures 8C and 8D, respectively. Firstly, the calculated SERS EF value for gluconate on the Au/2D-AuNPs substrate is observed to be ~ 5 x times larger than the thioglucose spectrum collected with the randomly distributed AuNPs, estimated at 4×10^9 and 8×10^8 , respectively, determined using procedure published previously.⁴⁶ However, the main significance results from the ability to reliably collect spectra with an approximately similar EF value over a much greater spatial range when employing the 2D-AuNPs fabricated with the guided assembly approach. This substrate is significantly reducing the time required to find a suitable enhancement. When the Raman spectrum of a solution of thioglucose (Figure 8D) is compared to the Raman spectrum of a solution of gluconate (Figure 8-A) one notices several significant differences. The most apparent is the absence of bands in the $1500\text{--}1700\text{ cm}^{-1}$ in the spectrum Figure 8C which indicates an absence of the carboxylic group in thioglucose. In contrast, the Raman spectrum of thioglucose has strong bands below 700 cm^{-1} which are assigned to out-of-plane ring deformations of the lactol ring.⁴⁷ These bands are absent in the Raman spectrum of gluconate (Figure 8A) which is a linear molecule.

In a striking difference to the Raman spectrum (Figure 8D), the SERS spectrum of thioglucose (Figure 8C) displays strong bands in the $1500\text{--}1700\text{ cm}^{-1}$ characteristic for the presence of the carboxylic group. The presence of this band indicates that adsorbed thioglucose molecules are at least partially oxidized at the gold electrode surface with the presence of interfacial water. In fact, the SERS spectrum of thioglucose (Figure 8C) has some similarities to the SERS spectrum of gluconate (Figure 8B). However, in spectrum Figure 8C, the presence of strong lactol ring vibrations in the $1100\text{--}1000\text{ cm}^{-1}$ region, typical vibrations of the lactol ring of

the glucose moiety indicates that the oxidation of adsorbed thioglucose is only partial.¹² This is confirmed by the presence of strong bands below 600 cm⁻¹ due to out-of-plane ring deformations of the lactol ring. These bands are present in the SERS of thioglucose (Figure 8C) but they are absent in the SERS spectrum of linear gluconate (Figure 8-B). In summary, the comparison of the SERS spectra of gluconate to the SERS spectra indicates that the SAM of thioglucose is partially oxidized. However, a significant fraction of the adsorbed molecules retain its original lactol ring structure. This information is significant for the application of SAMs of thioglucose as hydrophilic support for construction of floating bilayers in biomimetic studies.^{48,49}

Conclusions

A novel method for depositing bare gold nanoparticles on a substrate surface in 2D arrays with increased reproducibility has been discussed with its implementation to study gluconate adsorption on gold surfaces. Shell-isolated nanoparticles were found to deposit in uniform 2D-arrays with increased reproducibility when employing a thin-cell configuration during deposition. Upon dissolution of the SiO₂ shell, the exposed AuNPs were found to remain in 2D-arrays that were spaced by ~2x the shell thickness with fairly consistent stability. The modified Au electrode was found to have increased spot-to-spot reproducibility combined with the increased spatial distribution of nanoparticles in a given area. While not systematically studied here, it is expected this method can lead future studies of tuning the spacing between each NP for better sensitivity through plasmonic coupling effects and to investigations of the possibility of employing a wide range of NP materials (e.g. Au, Ag, Cu, transition metals, etc.). While gold substrates were studied in the present manuscript it is expected that 2D arrays of various SHINs could be deposited on a wide range of desired substrates. The increased sensitivity and lower variability of these novel Au/2D-AuNPs electrodes was employed to successfully characterize gluconate physisorption to a gold electrode surface. Several characteristic bands for gluconate

have been identified and can be used to further characterize glucose electro-oxidation in a range of electrolyte media.

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Supporting Information

Additional figures detailing further investigations into the cleaning procedure and characterization of the 2D-AuNPs is given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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