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Using Catalytic and Surface-Enhanced Raman Spectroscopy-Active Gold Nanoshells to Understand the Role of Basicity in Glycerol Oxidation

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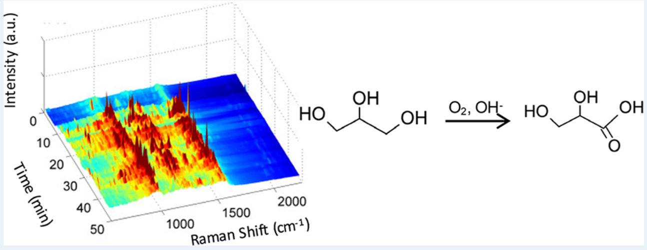
Supporting Information



ABSTRACT: The origin of oxidation activity of gold catalysts has been a subject of great interest, particularly with the discovery of selective glycerol oxidation under water-phase alkaline conditions, for which neither small gold nanoparticles nor a catalyst support is necessary for activity. Little is known about the interactions among the catalyst surface, reactant, and hydroxyl species, which have never been examined spectroscopically because of a lack of developed in situ methods. In this work, we studied the room-temperature, water-phase reaction of glycerol oxidation using gold nanoshells (Au NSs), in which the gold substrate was active for surface-enhanced Raman spectroscopy (SERS) and catalysis. Analysis of glycerol solutions at high pH values and with oxygen content indicated that glycerol and glycerolate species did not bind directly to the catalyst surface in the absence of oxygen. However, glycerate surface species formed very rapidly when oxygen was present, suggesting an Eley−Rideal-type reaction mechanism with O_2 (and/or O_2-activated OH^-) as the adsorbed species. SERS analysis of carbon monoxide chemisorption on Au NSs indicated that higher pH values progressively weakened the C−O bond as the Au negative charge increased. The importance of high alkalinity to Au-catalyzed alcohol oxidation may result from both the activation of glycerol via deprotonation and the weakening of the adsorbed O_2 double bond via induced Au negative charge.

KEYWORDS: *glycerol oxidation, surface-enhanced Raman spectroscopy, gold, catalysis, nanoshells*

INTRODUCTION

First reported by Hutchings and co-workers in 2002,[1] the selective oxidation of glycerol in alkaline solution by Au catalysts, a reaction pertinent to the synthesis of biomass-derived chemicals, has been studied fairly extensively by others.[2−5] Basic conditions are preferred for glycerol oxidation, with the rate limiting step presumed to be deprotonation of glycerol ($pK_a = 14.5$[2]) to glycerolate anion.[1,6] This is followed by oxidation to glyceraldehyde, which further oxidizes selectively to glyceric acid. Reducing glycerol concentration, increasing catalyst amount, or increasing O_2 partial pressure led to trace amounts of further oxidized products. The two-carbon species oxalic acid was also found as a byproduct, indicative of carbon−carbon cleavage during the reaction. Smaller Au particles produced other reaction products, like dihydroxyacetone and glycolic acid,[4,6−8] similar to supported monometallic Pt and Pd[6,9] and bimetallic Pd−Au,[10] The Au catalyst size is a subject of some contention; Demeril-Gulen et al. reported relatively small 3.7-nm Au particles to be most selective to glyceric acid,[4] while Porta and Prati found that catalysts with larger (>20 nm) Au particles were optimum.[5]

Several reports have addressed the mechanism of glycerol oxidation, variously considering possible adsorbates[7] and the possible generation of H_2O_2 as an oxidant.[11,12] Claus and co-workers showed that the reaction using small Au NPs (2−5 nm) was consistent with a Langmuir−Hinshelwood reaction mechanism in which glycerol, glyceric acid, and tartronic acid were significant absorbate species.[7] They detected dihydroxyacetone and glyceric acid as direct oxidation products of glycerol. Davis and co-workers proposed that glycerol oxidation proceeded through glyceraldehyde and/or dihydroxyacetone surface intermediates.[8,12] These then further oxidized to glyceric acid (and other products if in situ-generated H_2O_2 was present[11−14]). In a recent density functional theory and isotopic labeling study, Davis and co-workers reported that the oxygen of hydroxide ions participated directly in the oxidation of alcohols, with O_2 replenishing the consumed hydroxide ions via peroxide species formation.[15]

In all cases, the surface reaction intermediates involved were not detectable because the aqueous nature of the reaction

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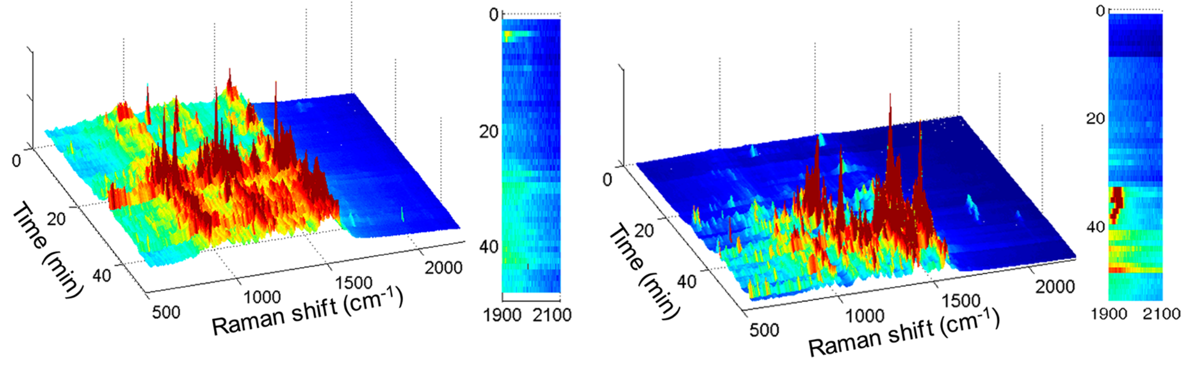
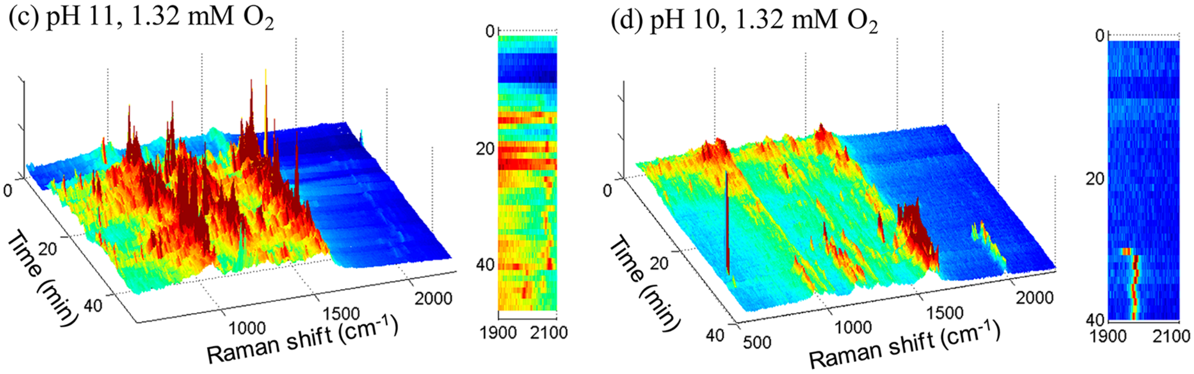

(a) pH 11, 0.26 mM O_2

(b) pH 10, 0.26 mM O_2


(c) pH 11, 1.32 mM O_2

(d) pH 10, 1.32 mM O_2

Figure 1. Time-resolved NS-based SER spectra of 1.3-mM glycerol solutions (a) at pH 11 with 0.26 mM O_2, (b) at pH 10 with 0.26 mM O_2, (c) at pH 11 with 1.32 mM O_2, and (d) at pH 10 with 1.32 mM O_2.

precluded the use of traditional spectroscopic techniques used for the identification of surface species. Surface enhanced Raman spectroscopy (SERS) is well-suited for studying aqueous-phase catalysis because of the small Raman signal of water, the inherent surface selectivity, and greater intensity than conventional Raman scattering.[16−20] However, this technique is not generally sensitive enough to detect low concentrations of transient surface adsorbates using roughened metal substrates. In this work, we show that SERS can be suitably applied to study aqueous-phase glycerol oxidation by using Au nanoshells (NSs) as a simultaneously SERS-active and catalytically active version of a Au catalyst. We further show that NS-based SERS can be used to monitor the pH effect on the Au surface using carbon monoxide as the probe molecule, providing new insights into the reaction mechanism and the roles of high alkalinity.

■ METHODS

Preparation of Au NS Substrate. Au NSs were synthesized as described previously (see ref 21 and Supporting Information). To immobilize the NSs for SERS experiments, a silicon wafer was first prepared by plasma-cleaning for 5 min to remove surface impurities. Afterward, the wafer was placed in a 5 wt % solution of poly(diallyldimethylammonium) chloride, and left for 11 min for self-assembly of the polymer to the silicon surface. Then, 20 μL of concentrated solution of Au NSs was placed on the wafer, and allowed to self-assemble for 30 min. After thoroughly rinsing with deionized water, the wafer was adhered to an 18 mm round microscope coverslip NS side up for use in the SERS analysis chamber.

NS-Based SERS of Glycerol. Similar to our study on the SERS of dichloroethene,[22] the sample was then plasma cleaned under vacuum (Harrick Plasma Cleaner/Sterilizer, PDC-32G) for ~1 min to remove any possible surface impurities, before placing it in the sealed analysis chamber. The analysis chamber (Warner Instruments RC-43, volume of 213 μL without Au NS sample, complete with inlet and outlet ports) was then mounted inside the Raman spectrometer, and the sample pretreated to ensure no surface oxygen was present (see Supporting Information).

We analyzed the interaction of glycerol with the catalyst surface at 2 different pH values. Because the surface SiO_x layer of the silicon substrate dissolves at ~pH 12 (causing the detachment of the self-assembled NSs), we chose pH 11 as an upper limit for our analyses. Solutions used to pretreat the Au NSs were prepared by adding 180 mL of deionized water each to Boston Round screw top bottles (Alltech, 250 mL), and then sealed. Three bottles (for catalyst rereduction, rinsing with inert, and reactive removal of chemisorbed reaction products) were bubbled with UHP H_2, N_2, and O_2 respectively, for 1 h.

To perform each experiment, 3 mL of one of the prepared glycerol solutions (see Supporting Information for more detail) was flowed over the NS substrate, and spectra was acquired using a Renishaw inVia micro-Raman spectrometer. To ensure that the collected spectra were representative, several precautions were undertaken. One, the microscope spot was kept constant for both solutions. Two, the substrate surface was cleaned without removing it from the SERS chamber, by flowing 3 mL of O_2-saturated deionized water to desorb any surface species remaining at the end of the experiment, and

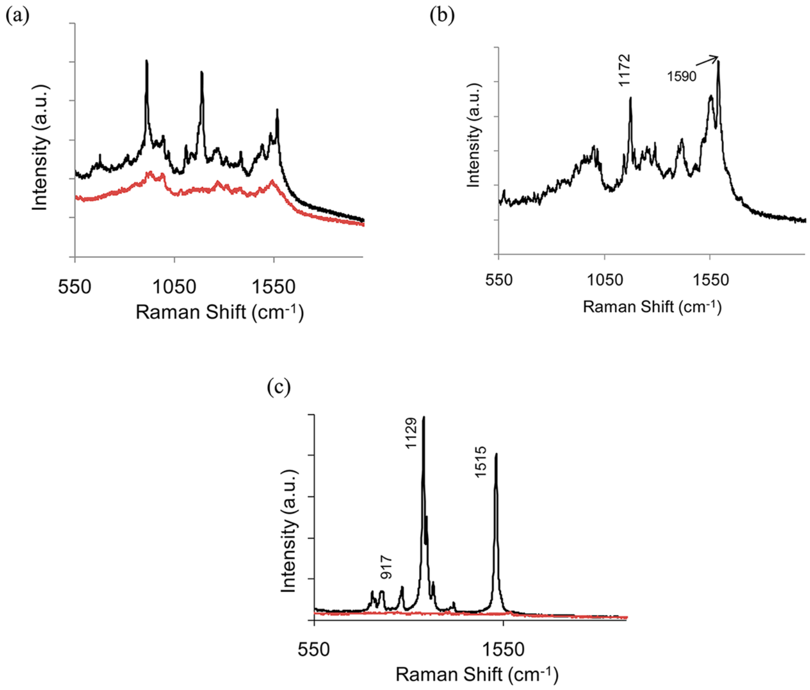


Figure 2. NS-based SER spectra of several oxygenated hydrocarbons: (a) 1.3 mM glycerol solution at pH 11 with and without 0.026 mM O_2, (b) 1.3 mM glyceric acid solution at pH 11 with no O_2, and (c) 1.3 mM ethylene glycol at pH 11 with and without 0.026 mM O_2. Spectra of no-O_2 cases are red colored.

flowing 3 mL of N_2-saturated deionized water as a rinse step. Experiments were repeated using the same Au NS substrate. The initial scan time (t = 0) marked the first integrated spectrum taken immediately after sealing the analysis chamber. To ensure there was no hysteresis effect that would indicate irreversible structural damage or catalytic deactivation of the SERS substrate, we ran the SERS experiments at alternating pH values.

NS-Based SERS of Carbon Monoxide. To further understand the role of hydroxyl in the oxidation reaction, we investigated the adsorption of CO to the surface as a function of pH. The pretreatment of the samples was similar to that given in the previous section. Five different pH solutions were tested, at pH 11, 10, 9, 8, and 7. The bottles were then sealed as before, and sparged with ultrahigh purity CO gas in a fume hood. To perform the experiments, the solutions were added to the NS substrate as before, and 8 spectra (at a given spot) for each sample were recorded and averaged. Between the introduction of the CO saturated solutions, 3 mL of N_2 saturated deionized water (neutral pH) was used to clean the surface. Spectra were obtained to ensure the surface was once again clean. To make sure the effect was not due to changes in ionic strength, the results were repeated using samples treated with NaCl to ensure constant ionic strength (0.001 M) between the samples (Supporting Information, Table S1).

■ RESULTS AND DISCUSSION

SERS with Au NSs was used to assess in aquo (i) the nature of chemical reaction intermediates formed during glycerol oxidation and (ii) the surface charge state of the gold as a function of solution pH. Au NSs, consisting of a 100−200 nm silica particle surrounded by a complete shell of Au metal several nm's thick,[23,24] offer much higher SERS enhancement factor than roughened metal surfaces (10^8−10^9 vs 10^4). Their resonant optical properties can be tuned through rational control of the nanostructure, allowing them to be optimized for strongest SERS enhancements for specific pump laser wavelengths.[25] Using Au NSs partially coated with Pd metal, we collected the first in situ spectroscopic evidence to support a multistep reaction mechanism for the catalyzed hydrodechlorination of dichloroethene, a model reaction for groundwater decontamination.[22,26,27] The study of water-phase reactions through SERS has been limited to the chemisorption of simple compounds using roughened noble metal surfaces and SERS-active nanoparticles coated with catalytic metal.[28−32]

Analysis of Deoxygenated, High-pH Glycerol Solutions. An aqueous glycerol solution (1.3 mM) was prepared at pH 11 (with a calculated glycerolate concentration of 920 nM), sparged with inert N_2, and introduced to the Au NSs immobilized on a silicon wafer enclosed within a sealable SERS cell. With weak Raman peaks observed at ~1000 cm^{-1} and 1550 cm^{-1} for the oxidized silicon wafer surface and carbonaceous residue, respectively, no prominent signals were found over the course of SERS collection time (Supporting Information, Figure S1a). A similar result was found for a deoxygenated glycerol solution at pH 10 (glycerolate concentration of 90 nM, Supporting Information, Figure S1b). In the absence of O_2, there was no spectroscopic evidence for glycerol or glycerolate chemisorption onto the Au surface.

Analysis of O_2-Containing, High-pH Glycerol Solutions. Introduction of O_2 (at a concentration of 0.260 mM) to a pH-11 glycerol solution led to the rapid appearance of SERS features between 800 and 1600 cm^{-1}, with persistent and sharp peaks at ~1000, 1200, and 1500 cm^{-1} (Figure 1a). A pH-11 glycerol solution containing 10 times less O_2 was spectrally similar, displaying prominent SERS peaks at ~900, 1189, and 1566 cm^{-1} (Figure 2a). These features did not match the SER spectrum of neat glycerol, indicating the presence of non-glycerol surface species (Supporting Information, Figure S2a).

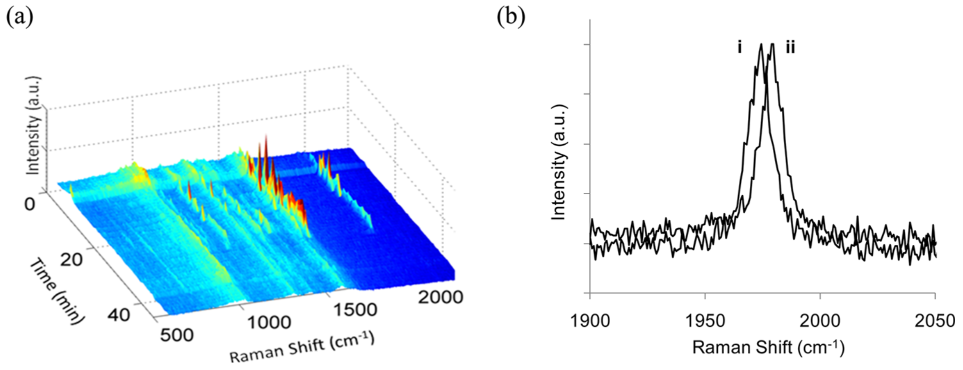


Figure 3. NS-based SER spectra of 0.13 mM glycerol solution at pH 11 with 1.32 mM O_2 (a) collected over 45 min, with (b) the spectrum collected at 20 min shown as curve i. The spectrum collected at 20 min for 1.3 mM glycerol solution at pH 10 with 1.32 mM O_2 (from Figure 1d) is shown as curve ii.

In contrast, a glyceric acid solution gave SERS spectra with strong features at 1172 and 1590 cm^{-1}. While these peak positions were similar to those of oxygen-derived species, like superoxide (∼1100 cm^{-1}) and physisorbed O_2 (∼1500 cm^{-1}),[33] control experiments using water at pH 11 saturated with O_2 showed no evidence of these bands. Hence, the observed modes were assigned to C−O stretching modes of a carboxylate (R-COO$^-$) group (Figure 2b). The large separation of these modes (418 cm^{-1}) was consistent with unidentate binding to Au metal.[34] No vibrational modes for the C═O double bond of the carboxylic acid (R-COOH) group (∼1710 cm^{-1}[35]) were found, as the carboxylate form of glyceric acid exists at high pH. The modes around ∼900 cm^{-1} could be ascribed to C−C−OH modes[35] or to the O−C−O stretch of adsorbed carboxylate (Figure 2a,b).

A higher concentration of O_2 (1.32 mM) led to a small, persistent, well-defined peak between 1900 and 2100 cm^{-1}, which we ascribed to the C−O stretching of chemisorbed CO (Figure 1c). Most studies of glycerol oxidation reported the formation of one- and two-carbon intermediates (like glycolic acid, oxalic acid, formaldehyde, and CO_2) but not CO.[8,12,36,37] This carbon−carbon cleavage reaction likely resulted from the surface-mediated oxidation by H_2O_2, which is formed during glycerol oxidation.[8,12] Mechanistically, CO_2 can form from the gold-catalyzed oxidation of CO, a reaction well-known to occur at room temperature in vapor[38] and water phases.[8,11,12]

To compare to other alcohol oxidations, we tested ethylene glycol, a diol with a pK_a (14.2) comparable to that of glycerol. Alcohol species such as methanol, ethanol, and propanol have pK_a's (∼16) that were too high for our experimental setup to handle and were not studied. A basic solution of ethylene glycol did not have discernible SERS peaks without O_2, but it showed definite SERS features with O_2 (Figure 2c). These features did not match the SER spectrum of neat ethylene glycol, indicating the presence of nonglycol surface species (Supporting Information, Figure S2b). The large modes at ∼1200 and ∼1500 cm^{-1} were assigned to the ν_s and ν_{as} carboxylate stretches of deprotonated glycolic acid, respectively. Calculations on glycolate anion in continuum water solvent gave ν_{as} and ν_s carboxylate stretches at 1630 and 1360 cm^{-1} for the isolated species and 1620 and 1300 cm^{-1} for the ion bound to an Au_4 cluster. These are significantly shifted from the 1740 cm^{-1} ν(C═O) and 1130 cm^{-1} ν(C−O) stretches calculated for glycolic acid.

Observing the pH Effect on Glycerol Oxidation. Glycerol conversion increases with increasing pH.[1,12] In our experimentation, the reaction occurred at pH 10, but not at pH 9 or below. At an O_2 content of 0.26 mM and pH 10, a small SERS peak at ∼2000 cm^{-1} (assigned to CO) transiently appeared after approximately 20 min, suggesting the extent of CO oxidation decreased during the course of SERS analysis such that adsorbed CO was occasionally observed (Figure 1b). Increasing O_2 content by ∼5 times to 1.32 mM had little effect on the emergence of the CO peak (Figure 1d). This peak was not observed at the higher pH of 11 (Figure 1a), consistent with faster CO oxidation rates at higher pH values.[8] The CO band was very weakly present at the same pH when O_2 content was increased (Figure 1c).

Changing the pH also changed the concentration of glycerolate, the presumed activated form of glycerol. To isolate the effect of pH better, the SER spectra of two different solutions (1.3 mM glycerol solution at pH 10, and 0.13 mM glycerol solution at pH 11) with the same calculated glycerolate amount (90 nM) were analyzed and compared. The resulting spectra differed greatly (cf. Figures 1d and 3a). Peaks appeared faster at higher pH than lower pH, as shown by the near immediate appearance of the strong ∼1550 cm^{-1} peak characteristic of the carboxylate functional group. These SERS results indicated that there was a pH effect on glycerol oxidation catalysis at constant glycerolate concentration.

Analysis of CO Chemisorption. A closer inspection of the CO stretching band showed a peak position of 1975 cm^{-1} at pH 10 and 1970 cm^{-1} at pH 11 (Figure 3b), both of which we ascribe to CO bound to two Au atoms at a bridging site on the Au surface.[39] While such band position range is typical of bridging CO for many transition metals,[40,41] this is not typically observed in gas-phase experiments on monometallic Au catalysts. However, in a study on CO adsorption on gold electrodes in alkaline solution, peaks ranging from 1900 to 1988 cm^{-1} were observed and ascribed to CO in a bridging position.[39,42]

Intrigued by the subtle red-shift between the pH 11 and pH 10 systems, we performed a more systematic SERS analysis of CO chemisorption (in the absence of glycerol) on Au NS surfaces at different solution pH values. We found that regardless of pH, the CO was linearly bound to Au atoms with modes of wavenumbers >2000 cm^{-1},[39,40,42,43] and was not in a bridging configuration. The CO band red-shifted from 2094 cm^{-1} to 2077 cm^{-1} as the pH increased from 7 to 11, indicating the C−O bond weakened at higher pH values (Figure 4). From extensive studies of CO adsorption on Au, a red-shift in CO stretching band frequency is indicative of a

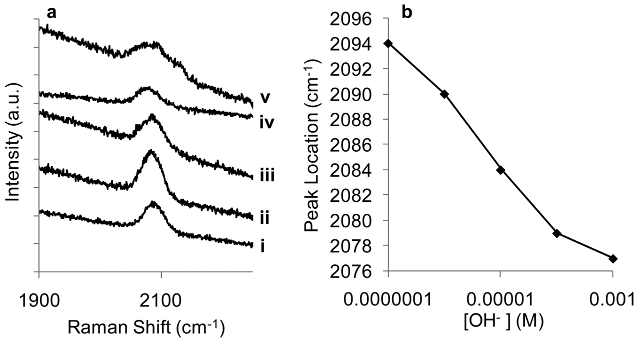


Figure 4. (a) NS-based SER spectra of chemisorbed CO in water solutions (not adjusted to a constant ionic strength) at (i) pH 7, (ii) pH 8, (iii) pH 9, (iv) pH 10, and (v) pH 11 (offset for clarity). (b) CO peak location as a function of hydroxyl concentration (log scale). These spectra were nearly identical to those of solutions at different pH values and a constant ionic strength.

more negative charge state of the Au.[43−45] Mulvaney and co-workers demonstrated that Au particles can accommodate excess electrons in water.[46] We therefore propose that the observed CO band red-shift at higher pH values results from the greater extent of hydroxyl anion chemisorption and donation of electron density to the Au, and that the subtle red-shift observed in Figure 3b (the glycerol oxidation experiments) is also due to this effect.

Spectral modes can also shift when adsorbates are exposed to an electric field, for example, from the electric double layer (EDL) at an Au electrode surface (the Stark effect).[44,45,47] To eliminate this as a possible source for the observed CO band shifts with pH, we repeated the CO SERS experiments using solutions at a constant ionic strength of 1×10^{-3} M, adjusted using NaCl, and found no difference in the CO band shifts (Supporting Information, Figure S3).

The role of OH groups in glycerol and other oxidation reactions has been studied theoretically and experimentally by many groups. Calculations by Landman and co-workers[48] showed that coadsorption of O_2 and H_2O on free and supported Au clusters involved hydrogen bonding between O_2 and H_2O, yielding increases in chemisorption energy, O−O bond length, and bond activation. A more recent study by Davis and co-workers concluded that free and adsorbed OH^- was involved in both glycerol oxidation and O_2 reduction, after finding that labeled $^{18}O_2$ was not incorporated into the glycerol oxidation product.[15] They proposed that the glycerolate anion bound directly to the surface prior to reaction with chemisorbed OH as an initial step.[15]

Throughout this study, the SERS results showed no evidence for glycerolate adsorption to the gold surface under inert conditions, consistent with zero glycerol conversion. In the presence of O_2, surface reaction intermediates were observed, suggesting the surface reaction proceeded via an Eley−Rideal-type mechanism, that is, free glycerolate reacting directly with adsorbed O_2 or surface bound OH activated by the presence of the electron scavenging O_2.

Haruta commented that Au particle size may not be critical to activity in general, and that other mechanisms, like the interaction of Au with metal-hydroxyl species or H_2O,[49] are important to Au catalysis. Whether the Au catalysts were in supported form (e.g., Au/carbon) or in unsupported form (e.g., Au nanotubes), both reaction systems presumably involved interactions with hydroxyl anions and water. The Au/C catalysts of Ketchie et al. were in contact with liquid water in the presence of hydroxyl anions.[8] In the Au nanotube experiments of Sanchez-Castillo et al., it was noted that the addition of water vapor for the gas phase experiments or the addition of hydroxyl for the aqueous phase experiments increased the reaction rate by 70 times.[50] It has been theorized that the presence of hydroxyl groups (from water or a metal-hydroxyl support) helps to stabilize chemisorbed O_2 in these oxidation reactions, hence accelerating the reaction.[48] Davis and co-workers surmised that adsorbed hydroxyl groups enhanced O_2 chemisorption, based on their high-alkalinity CO and glycerol oxidation batch reaction experiments.[12] Our CO adsorption experiments suggest that the electronic effect of OH^- on Au may also weaken the O−O bond of chemisorbed O_2 during glycerol oxidation, thereby increasing catalytic activity of the Au.

■ CONCLUSIONS

Using SERS on Au nanoshells, we have gained spectroscopic support for the mechanism of glycerol oxidation on Au in solution. Glycerolate does not directly adsorb to the surface, but undergoes reaction before returning as a carboxylate. Furthermore, increased O_2/glycerolate led to increased reactivity and production of CO. Further investigation of the data and additional experiments showed a weakening of the CO bond with increasing pH. Hence, we suggest an additional role of hydroxyl in the reaction, which was once largely thought to only deprotonate the starting reactant. The observed frequency shifts of adsorbed CO indicate that adsorbed hydroxyls increase the surface negative charge of the Au, which may be leading to enhanced adsorption and activation of O_2, and may help to explain the catalytic activity of many Au-based catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental protocols; Figure S1 (time-resolved SER spectra of pH 10 and pH 11 solutions in the absence of oxygen); Figure S2 (SER spectra of neat glycerol and neat ethylene glycol); Figure S3 (SER spectra of chemisorbed CO in water solutions); Table S1 (Aqueous conditions used for NS-SERS study of CO chemisorption). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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