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Effect of Ligands and Their Removal on the Au Nanoparticle-Catalyzed Reduction of 4-Nitrophenol

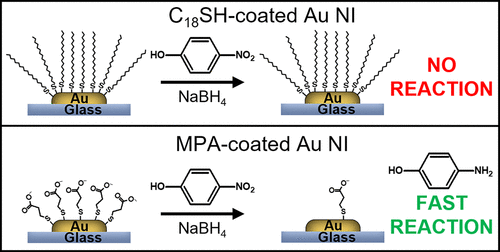
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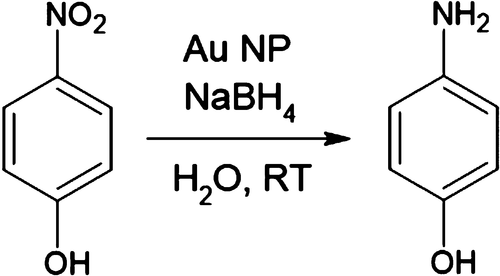
# Abstract



The catalytic activity of gold nanoparticles (Au NPs) is strongly affected by the organic ligands coating them, which afford colloidal stability and are most commonly attached during the synthesis of the Au NPs. However, different ligands also produce Au NPs of different sizes and morphologies, complicating the study of the impact of the ligands themselves. Alternatively, postsynthetic ligand exchange risks incomplete exchanges and a mixed ligand shell, as well as colloidal instability. Here, Au NPs are immobilized on glass supports to afford truly ligand-free, solvent-stable Au nanoislands (NIs). The catalytic activity of Au NIs, uncoated and coated with a variety of ligands, is evaluated for the catalytic reduction of 4-nitrophenol to 4-aminophenol, a common model reaction. The modification of stable, immobilized NIs ensures identical size and shape distributions across all cases and isolates the effect of ligands to reveal their absolute impact versus uncoated Au. All molecules are found to inhibit catalysis to varying degrees, with longer-chain molecules having a stronger influence. Ligands are partially removed by borohydride during the reaction, as confirmed by X-ray photoelectron spectroscopy measurements, leading to significantly less inhibition when the catalysts are reused. Kinetic analysis of the reaction for various ligand-coated catalysts shows that the reaction rate increases over time due to ligand removal, demonstrating the value of longer conversion studies versus the method of initial rates. These direct cross-class ligand comparisons, using the same NP core, provide valuable insights into complex NP–ligand–reactant interactions.

# Introduction

Gold nanoparticles (Au NPs) catalyze a variety of reactions, including hydrogenations, oxidations, and coupling reactions such as Suzuki–Miyaura.1−6 In colloidal systems, the NPs are generally coated with a shell of organic ligands, which stabilize the NPs to prevent aggregation and precipitation. These ligands may reduce the fraction of sites open for catalysis on the NPs’ surface, although the nature of the specific ligand and its mode of binding to the NP will affect the result greatly. The reduction of 4-nitrophenol (4-Nip), shown in Scheme 1, is widely studied as a model reaction to assess the catalytic performance of Au NPs.2,3,7−17 The appeal of the reaction is that there are few-to-no side products, no reaction occurs without a catalyst, and the reaction proceeds at standard temperature and pressure in an aqueous environment. The progress of the reaction can be monitored via the decrease in absorbance at 400 nm, corresponding to the consumption of 4-nitrophenolate, the predominant form under the common reaction conditions.18−21



**Scheme 1.** Reduction of 4-Nip by Sodium Borohydride Catalyzed by Au NPs

The relative impact of the ligands on the reaction has been isolated and explored in several studies, each focusing on a specific ligand or class of ligands, which were attached to the NP cores as stabilizers during NP synthesis or by using postsynthetic ligand exchange procedures. For small molecules such as mercaptopropionic acid (MPA) and mercaptoundecanoic acid (MUA), inhibition increased with chain length,21 while an opposite trend was observed for the lengths of larger poly(ethylene glycol) ligands.12 Electrostatic interactions were also shown to modulate the activity, with a negatively charged ligand inhibiting the reaction compared to a similarly sized positively charged ligand.22 In some studies, different ligands were used in the NP synthesis step itself, resulting in size and shape variations, confounding the impact of ligands.18,20,22,23 Furthermore, since the colloidal NPs used were always coated with some ligand, studies were not able to measure the absolute impact of the ligand on the activity but rather only their impact relative to one another.

An important factor complicating the study of ligand effects on 4-Nip reduction is the ability of sodium borohydride to remove ligands (Scheme 2) with various binding groups including thiols.20,24,25

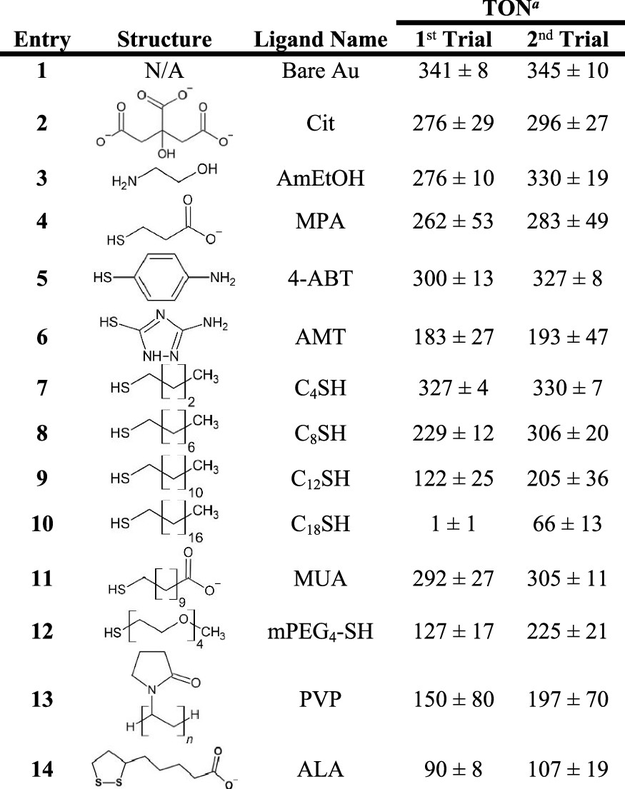
Scheme 2. Equation of chemical reaction, explained in caption below.

**Scheme 2.** Removal of a Thiolated Ligand from a Au NP by Sodium Borohydride, Leaving a Hydride-Coated Au NP Surface

Álvarez Cerimedo et al. demonstrated that higher borohydride concentrations alleviate the blocking effect of PVP ligands and increase NPs’ catalytic rate.14 Neal et al. demonstrated the ability of borohydride to remove ligands, although the authors still found significant differences in the catalytic rate between NPs coated with different ligands, showing that some ligands remained.20 These observations, combined with those noted above, show that borohydride’s ability to remove ligands is limited, and bound ligands still exert a strong influence on catalytic performance. Furthermore, ligand removal from colloidal NPs risks aggregation, which would lower the observed activity. Therefore, to study and accurately quantify the impact of ligands, their identity must be isolated from NP size and stability.

In this work, we measured the rate of 4-Nip reduction with sodium borohydride, catalyzed by gold nanoislands (Au NIs) partially embedded in glass─bare, or coated with a variety of ligands. We chose ligands commonly used in Au NP studies: (i) citrate, a common native ligand in aqueous Au NP synthesis, bound via carboxylate groups;26−29 (ii) aminoethanol, a ligand that binds through the amine group;30 (iii) several short-chain thiolated ligands, which are expected to bind strongly; (iv) a series of alkanethiols of different lengths to test the impact of hydrophobic forces on the permeability and stability of the ligand shell; (v) long-chain thiols with hydrophilic functionalities; (vi) a neutral polymer; and (vii) a small disulfide molecule with bidentate coordination to the Au NIs (for full names and chemical structures, see the Materials section and Table 1). The use of Au NIs allows us to isolate and quantify the absolute impact of various ligand coatings versus one another and versus bare Au (due to the removal of organic ligands or contaminants following annealing and UV/ozone treatment) while keeping all structural properties (NP size, morphology, and concentration) constant, with the exception of potential ligand-induced restructuring. The use of supported NIs prevents aggregation, a common issue with in situ ligand exchange in colloidal systems, and enables the study of hydrophobic ligands, such as alkanethiols, for this aqueous reaction. Additionally, in situ ligand exchange procedures have been shown to yield mixed monolayers, as common native ligands such as citrate31 or oleylamine32 can prove difficult to completely remove via exchange alone. Starting from bare Au surfaces, as we do here, ensures only a single ligand type is present. The comparison with truly ligand-free NIs tests the common claim that ligands such as citrate are appropriate comparisons to bare NPs12 and provide an effectively unobstructed surface. We focus on turnover numbers (TONs) for 3 h reactions, which allows time for ligands to desorb, a process that is not captured well by relying solely on initial rates. Kinetic trials support this notion by providing insight into the ligand removal process over the course of the reaction.

**Table 1.** TONs for 3 h 4-Nip Reduction by Sodium Borohydride Catalyzed by Various Ligand-Coated Au NI Slides



aTON, turnover number, represents the number of 4-Nip molecules converted per nm2 of the exposed gold catalyst over the course of the reaction. Means are of four samples each, and uncertainties are standard deviations.

# Methods

## Materials

Vistavision #2 22 mm × 22 mm glass coverslips were purchased from VWR. Hydrogen tetrachloroaurate(III) trihydrate (Alfa Aesar), trisodium citrate dihydrate (Sigma), ethanol (absolute, Supelco), methyl alcohol (AR ACS, Macron), nitric acid (Macron), hydrochloric acid (Macron), hydrogen peroxide (30%, J.T. Baker), sulfuric acid (95−98%, Macron), 3-aminopropyltrimethoxysilane (“APTMS”; TCI) 4-nitrophenol (“4-Nip”; TCI), sodium borohydride (Acros Organics), 4-aminobenzenethiol (“4-ABT”; TCI), 2-aminoethanol (“AmEtOH”; TCI), 3-amino-5-mercapto-1,2,4-triazole (“AMT”; TCI), 1-butanethiol (“C4SH”; Acros), 1-dodecanethiol (“C12SH”; Alfa Aesar), 3-mercaptopropionic acid (“MPA”; BTC), 11-mercaptoundecanoic acid (“MUA”; Synthonix), 1-octadecanethiol (“C18SH”; TCI), 1-octanethiol (“C8SH”; TCI), poly(ethylene glycol) derivative (“mPEG4-SH”; PurePEG), polyvinylpyrrolidone 50 kDa (“PVP”; Acros), and DL-α-lipoic acid (“ALA”; TCI) were used as received. Water for solutions was obtained from a Milli-Q purification unit at a resistance of 18.2 MΩ or was ASTM Type I/II water (Ricca Chemical). Solutions containing sodium borohydride were prepared fresh as needed to avoid decomposition.

## Synthesis and Characterization of Colloidal Au NPs

Au NPs were synthesized using the Turkevich method, as detailed below.27,48 All glassware and stir bars were cleaned with freshly prepared aqua regia (1:3 volume ratio of nitric acid and hydrochloric acid) prior to synthesis to remove potential nucleation sites. Chloroauric acid trihydrate (95 mL, 0.68 mM) and a stir bar were added to a 3-neck 250 mL round-bottom flask equipped with a reflux condenser. The solution was heated to boiling while stirring and refluxing. Trisodium citrate dihydrate (5 mL, 0.17 M) was rapidly injected directly into the vortex of the boiling Au solution, upon which the solution turned clear. After approximately 30 s, the solution turned dark-purple, slowly changing to red over the course of a few minutes. Five minutes after the addition of the sodium citrate, heating was terminated and the solution was allowed to stir and reflux for an additional 40 min while cooling down. Once the solution reached room temperature, it was transferred to a 120 mL Boston round glass bottle. A sample of the particle solution was diluted by a factor of 5 with MilliQ water for UV/vis and dynamic light scattering (DLS) analysis. DLS was performed using a Malvern Zetasizer Nano ZS; the refractive index and absorption of the Au NPs were set to 0.2 and 3.320, respectively; the dispersant was set as water at 25 °C with a viscosity of 0.8872 cP and a refractive index of 1.330; three measurements, each with an average of 11 runs, were recorded at 25 °C using a backscatter angle of 173°.

## Silanization of Glass Supports

Glass coverslips (henceforth referred to as “slides”) were cut to 8.5 mm × 22 mm using a diamond scribe and placed in a custom-made PTFE multislide holder. The holder was placed in a glass jar and cleaned in piranha, a 1:3 solution of hydrogen peroxide (30%) and sulfuric acid. (*Caution: piranha solution is extremely corrosive and boils upon mixing*. *It continues to outgas for days and so should be kept in an open or vented container before neutralization or disposal*.) After the mixture cooled down (30 min to 1 h), the slides were rinsed in Milli-Q water three times, rinsed in MeOH three times, and dried under a nitrogen stream. The slides were then silanized to provide a positively charged surface: a solution of 0.1% v/v APTMS in water was prepared, and the slides (held in the PTFE holder) were incubated in the solution for 15 min. Although the interaction of trimethoxysilanes with water may lead to polymerization, the short duration and low concentration prevent this undesirable outcome; previous studies have shown that low concentrations of silane in water do not lead to polymerization, (49) and we did not observe a white residue, indicative of polymerization. The slides were then rinsed in water three times and MeOH three times and dried under a nitrogen steam.

## Immobilization of Au NPs

The silanized slides were each placed in individual shell vials containing 3 mL of the as-synthesized Au NP solution (19 nM with respect to the number of Au NPs, see the Supporting Information for the concentration calculation), and incubated for 2 h. The negatively charged Au NPs attached electrostatically to the positively charged surface of the slides. Following deposition, the slides were rinsed thoroughly in water. The UV/vis transmission spectra of the slides were then recorded in water, and the slides were dried under a nitrogen stream. Adsorbed Au NPs were removed from the backs of the slides by wiping them with a wet cotton swab; similarly, a small section on the top front of the slides was cleared of Au NPs to afford a place to grip the slide using tweezers (Figure 1b)─in order to normalize the data by the total surface area of gold on each slide, it is important to not change the slide after the reaction by accidentally scratching the slide and removing Au NPs. The spectra were recorded again in the dry state. The slides were then annealed at 600 °C for 10 h with a heating rate of 5 °C/min (the heating stage is not included in the 10 h duration) in an air atmosphere using a Nabertherm L 3/11 furnace. The annealing process removes any organic molecules surrounding the gold and partially embeds the Au NPs into the glass to form Au NIs, as has been extensively established in the literature. 35−37 Au NPs in close proximity on the glass prior to annealing, namely, aggregates, coalesce during the annealing process to form individual, larger NIs. After cooling to room temperature in the oven, the slides’ transmission spectra were again recorded.

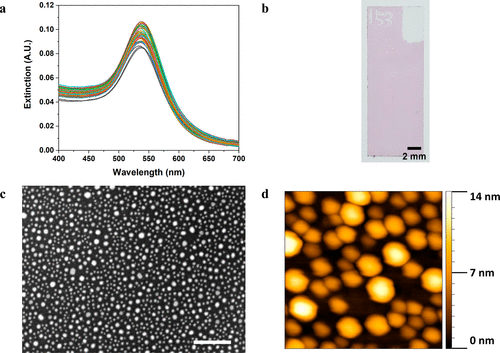


Figure 1. (a) UV/vis absorption spectra of 70 slides produced using the fabrication method described in the text. (b) Photograph of a Au NI slide after catalysis. (c) SEM image of a Au NI slide. Scale bar shown represents 100 nm. (d) AFM image of a Au NI slide, 200 × 200 nm2.

## Au NI Slide Functionalization

Au NI slides were treated in a UV/ozone cleaner (Ossila) for 5 min in order to remove potential organic contaminants adsorbed from the time the slides were fabricated; the process also oxidizes the top layer of gold atoms.50 The slides were then incubated in a 1 M NaBH4 aqueous solution for 1 h to reduce the surface oxide. The spectra were then recorded. For bare slides, there were no further incubation steps prior to catalysis. For ligand-modified slides, the slides were then placed in shell vials containing a 10 mM aqueous solution of ligand (alkanethiol ligands, 4-ABT, ALA, and MUA were prepared in ethanol). The PVP solution was prepared to 10 mM with respect to the monomer. Slides were incubated in various ligand solutions for 1 h. Following incubation, the slides were rinsed in water (ethanol for appropriate ligands), dried with nitrogen, and had their spectra recorded.

## Transmission Spectra

The transmission spectra were measured using a Jasco V-750 spectrophotometer. Slides were placed perpendicular to the beam inside a polystyrene cuvette. For postimmobilization measurements, slides were measured in water, and the measurement was corrected using a baseline of a water-filled cuvette. The spectra were recorded in the range of 400–700 nm, with a 1 nm interval, and a response time of 0.24 s (effective scan rate of 200 nm/min). For all other slide measurements, dry slides were placed in a cuvette, and the measurements were corrected using a baseline of a clean glass slide in an empty cuvette. Spectra were recorded in the range of 400–700 nm for slide measurements, a 1 nm interval, and a response time of 0.18 s (an effective scan rate of 188 nm/min).

For 4-Nip reduction trials, the solutions were measured in a polystyrene cuvette and corrected with a baseline of water in an identical cuvette. The range of wavelengths was 550–340 nm with a 0.06 s response time, 0.5 nm interval, and a 1000 nm/min scan speed. Spectra were recorded upon addition of borohydride and after 3 h. The extinction at 400 nm was used to determine the concentration of the 4-nitrophenolate ion over the course of the reaction (as detailed in the Supporting Information).

## Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to determine NI size and distribution. Slides were cut into a smaller size, immobilized onto SEM stubs with carbon tape, and partially painted with colloidal silver (Ted Pella PELCO) to improve conductivity and reduce charging during imaging. Samples were coated with 3 nm of osmium (SPI Osmium Coater) to further reduce charging. Slides were imaged using a JEOL JSM-7900FLV in high-vacuum mode, using a 15 kV accelerating voltage, a 3.9 mm working distance, and the in-lens detector. Images were analyzed using ImageJ to determine particle sizes.38 From these values, the average surface area of gold per unit area of the slide was calculated. This value was used to calculate the total surface area of gold for each slide used in the catalytic study from pictures of the individual slides (as the coated area varies slightly between slides), which is needed to determine the TONs. Detailed information regarding the area calculation is provided in the Supporting Information.

## Atomic Force Microscopy

Atomic force microscopy (AFM) was utilized to determine the average height of the Au NIs, used in the overall Au surface area calculation. Slide fragments were secured onto a large glass slide with carbon tape. Surface topography was characterized using a Bruker Dimension FastScan AFM in tapping mode.

## X-ray Diffraction

X-ray diffraction (XRD) was used to determine the crystal structure of immobilized, dry Au NPs and Au NIs using a Rigaku MiniFlex II. θ/2θ scans were run for the range of 30–90° (2θ) using a Cu Kα radiation source with a sampling interval of 2θ = 0.02° and an accelerating voltage of 30 kV.

## X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were recorded with a Thermo Scientific ESCALAB 250Xi using an Al Kα source. Slides were adhered to a sample holder with copper tape. The beam size was 500 or 900 μm in a few cases. A charge compensation electron flood gun was used since the samples are insulating. Survey spectra were obtained at a 1 eV resolution, and individual elemental spectra were obtained for C 1s, Au 4f, and S 2p. Elemental spectra were recorded at a 0.1 eV resolution, a 50 ms dwell time, and an average of 5 scans; for S 2p, 20 scans were used. Spectra were shifted so that the aliphatic C 1s peak from adventitious carbon was set to 284.8 eV to correct for sample charging. The fitting procedure is detailed in the Supporting Information.

## Catalysis

4-Nip (625 μL, 0.2 mM), Milli-Q water (1.675 mL), and sodium borohydride (200 μL, 0.125 M) were added to a 4.5 mL polystyrene cuvette fitted with a vented cap, leading to reaction concentrations of 50 μM 4-Nip and 10 mM NaBH4. Upon addition of sodium borohydride, the pH of the solution rises to 10.4 (measured using a Thermo Scientific Orion Star A211 pH meter) and the 4-Nip is converted to the 4-nitrophenolate form. A prereaction UV/vis spectrum was recorded. At *t* = 0, a Au NI slide was placed in the reaction mixture. At the 3 h mark, the slide was removed from the cuvette and the absorption spectrum of the mixture was recorded. The slide was rinsed with water, and dried under nitrogen, and its spectrum was measured. Control experiments were performed identically, except that no slide was added. The extinction of the solution at 400 nm was used to calculate the conversion of the 4-nitrophenolate ion, as is standard in the field.12,13,51,52 Beer’s law was utilized to determine the total number of 4-nitrophenolate molecules converted during the reaction, using an extinction coefficient of 18,112 M–1 cm–1, which we determined experimentally. Photographs of each slide were taken after the reaction and analyzed in ImageJ to determine the total area covered by Au NPs (the pink portion in Figure 1b). The surface area of gold per unit area of Au-coated glass was calculated from SEM and AFM images and used to determine the total surface area of gold on each slide (see details in the Supporting Information).

## Kinetic Trials

In order to obtain more information about the ligand shell during the catalytic reaction, kinetic trials were conducted. 4-Nip reduction was performed in a glass cuvette previously cleaned with piranha; this step provides a hydrophilic surface that reduces the ability of gas bubbles to adhere to the glass and interfere with the measurement beam. A bare slide and slides coated in C8SH, C12SH, and mPEG4SH were studied. Slides were placed in the cuvette away from the instrument beam path to start the reaction. Time-resolved UV/vis spectra were recorded every 90 s for the entire 3 h reaction.

# Results and Discussion

## Catalyst Preparation

Au NPs immobilized by thermal embedding on glass have been studied for sensing applications33,34 but not for catalysis. Partially embedding Au NPs into glass slides produces highly stable, ligand-free Au NIs, which enable facile functionalization with a wide range of ligands and prevent aggregation if the ligand shell is removed.35−37 In order to produce Au NIs, we synthesized colloidal citrate-coated Au NPs and deposited them on glass modified with APTMS, which provides a positive electrostatic charge to attract the negatively charged NPs.35 The Au NP synthesis produced particles with an average diameter of 11 ± 3 nm as determined by DLS measurements (Figure S1). The deposition and annealing process was optimized and is highly repeatable, as shown in Figure 1a; an example of a Au NI slide can be seen in Figure 1b.

The size of the NIs was measured using SEM, shown in Figure 1c. Analysis of six images containing a total of 2535 NIs, approximated as ellipses using ImageJ,38 yielded an average major axis of 14 ± 4 nm and an average minor axis of 13 ± 3 nm. Histograms for the major and minor axes are shown in Figure S3. AFM was utilized to determine the average height of the Au NIs, as shown in Figure 1d; analysis of six images containing a total of 272 NIs yielded an average height of 8 ± 2 nm. XRD measurements of slides before and after annealing show a single peak at 2θ = 38°, indicating a {111} facet in all cases (Figure S4).

Following cleaning and incubation in the ligand solution (see Methods), the wavelength of the localized surface plasmon resonance (LSPR) peak of most of the samples showed an increase (red shift; Figure 2). This effect arises from the change in the dielectric constant of the microenvironment around the NIs when ligands displace the air that previously occupied the area, and forms the basis for LSPR sensing.33 Therefore, longer and more densely packed molecules result in larger shifts─an effect most evident for the structurally similar alkylthiol series. We note a decrease (blueshift) in all cases, with the exception of C4SH, following the first catalytic trial, hinting at ligand removal. The slight increase following the second trial may arise from the deposition of the product, as 4-aminophenol (4-AP) contains the Au-binding amine group. This effect is clearly seen in the case of bare Au NI slides used for three consecutive trials of 4-Nip reduction (Figure S7). As there are no ligands to be removed in this case, the red shift corresponding to product adsorption is apparent after the first trial and remains present following the two subsequent trials.

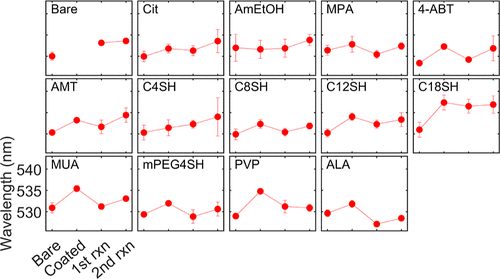


Figure 2. Average LSPR maximum wavelength for Au NI slides before and after ligand functionalization and after the first and second trial of 3 h 4-Nip reduction. Values are means of four slides each, and the error bars (at times too small to be seen) represent standard deviations.

## 4-Nip Reduction

Our main measure of catalytic activity is the conversion after 3 h, using the decrease in absorption of the 4-nitrophenolate peak at 400 nm. The 4-Nip reduction reaction is known to produce no side products (or only in negligible quantities), and the product, 4-AP, does not absorb at 400 nm. An increase of extinction at 300 nm qualitatively confirms the presence of 4-AP (Figure S11) but is not used for quantification due to absorbance from 4-AP degradation products at that wavelength.13 Allowing the reaction to proceed for hours, rather than focusing on initial rates, captures the effect of potentially slow ligand removal. As we show below, even two consecutive 3 h trials do not remove all ligands in some cases. The 3 h duration also ensures that the effect of the induction time would be negligible as the induction periods we have observed have not exceeded 35 min. Sodium borohydride is known to degrade in aqueous solutions, but we expect the rate of degradation to be consistent across all samples and not affect the observed trends. Figure 3a shows a set of typical conversion spectra for a batch of four bare gold slides compared to mPEG4SH-coated slides (Figure 3b). Control experiments (Figure S10) were performed in the absence of a catalyst to verify that no reaction occurs.

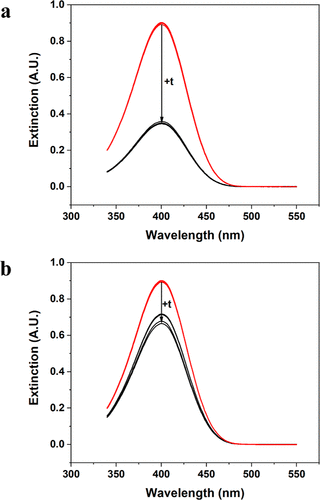


Figure 3. 4-Nip conversion over a period of 3 h catalyzed by (a) bare and (b) mPEG4SH-coated Au NI slides. Four trials are shown in each panel, with prereaction spectra in red and postreaction spectra in black.

Table 1 shows the mean TONs (molecules converted per nm2 of exposed Au) for the reduction of 4-Nip catalyzed by each set of four bare or ligand-coated Au NI slides over a period of 3 h. Removing the slide terminates the reaction (the absorption stops decreasing), demonstrating that the reaction is catalyzed by the Au NIs, rather than leached gold species in solution. For the TON calculation, we assume that all surface sites are equally likely to participate in the catalytic reaction, although it is highly likely that edge sites and other crystal defects contribute most of the activity.39,40 TON values that are significantly lower than those of the bare gold slides indicate an inhibitory effect, possibly caused by the inability of reactant molecules or borohydride anions to penetrate the ligand shell. In all cases, we observed higher TONs when the catalyst was reused for a second trial; we attribute this observation to ligand removal during the first trial. The NIs are stable and are not removed from the glass slides under the reaction conditions, making the comparison between the first and second trials valid. We verified this by comparing the extinctions at the LSPR maxima of the bare Au NI slides before and after the reaction; the average change was a decrease of 0.0005 ± 0.005 A.U., indicating no meaningful loss of gold.

### *High TONs Correlate with the Removal of Ligands*

We performed XPS measurements of slides coated with C4SH, mPEG4-SH, MPA, and C18SH (Figures 4 and S6). Prior to the reaction, the sulfur region (Figure 4a) shows two signals─the first doublet, at 162 eV, corresponds to S bound to Au; the second, at 168 eV, is attributed to oxidized S and is commonly seen in aged thiol monolayer samples (aging can occur in mere days).41 Following the catalytic trials, the peaks disappear for C4SH, mPEG4-SH, and MPA (Figures 4b and S6), indicating that the ligands were removed. Prior to the reaction, the C region for mPEG4-SH displays a strong C–O–C peak (Figure 4c), as would be expected; following the reaction, the more common contamination peak is seen, where the aliphatic signal is dominant (Figure 4d). In contrast, even after 12 h of reaction (two 6 h trials), the C18SH-coated sample displays clear S peaks and a strong aliphatic carbon peak, indicating that the ligand remains (Figure S6).

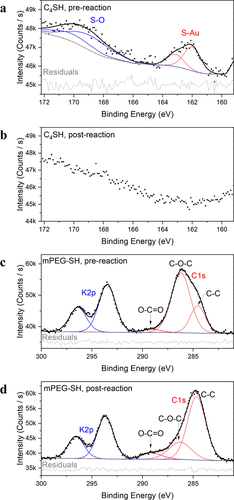


Figure 4. XPS measurements of the S 2p and C 1s regions for different samples (labeled). (a,c) Following functionalization, prior to any catalytic reaction; (b,d) following two, 3 h catalytic trials. The experimental data is shown as a scatter trace; the overall fit (envelope) is the solid black line; the individual peak components are colored solid lines; the baseline is a gray dashed line; and the fit residuals are shown as a solid gray line at the bottom of every panel (shifted from zero, so it can be displayed alongside the spectrum).

### *Weakly Bound Small-Molecule Ligands (Entries 2–3) Slightly Inhibit Catalysis but Are Removed Following the First Reaction*

Citrate and aminoethanol slightly inhibited catalysis for the first 3 h reaction period. These ligands are expected to form weak bonds with gold, and their removal is apparent following the first reaction trial, resulting in a higher turnover in the second trial, although still slightly lower than that of bare Au. This result implies that citrate-coated Au nanostructures are not a perfect comparison of catalytic activity to bare Au NPs within the first 6 h of 4-Nip reduction using similar sodium borohydride concentrations.

### *Thiolated Small-Molecule Ligands (Entries 4–6) Partially Inhibit Catalysis*

As thiolated molecules form a strong S–Au bond, we expected them to substantially, or even completely, inhibit catalysis. Surprisingly, only partial inhibition was observed, with large variation between the ligands. As XPS analysis (Figure S6) verified the near-complete removal of MPA from the surface following both reactions, the inhibition observed in the second trial indicates some residual ligand remained after the first trial, inhibiting performance at least for part of the second trial. Importantly, one outlier in the batch of MPA replicates (with TONs = 171 and 199 for first and second trials, respectively) is responsible for the large uncertainty assigned to the average TON.

### *Alkylthiol Ligands (Entries 7–10) with Increasing Chain Length Progressively Inhibit Catalysis*

We examined the impact of intermolecular interactions in the shell using a series of alkanethiol ligands of increasing length from butanethiol (“C4SH”) to octadecanethiol (“C18SH”). As the ligands increased in length, the hydrophobic interactions between the chains increased, an effect that results in denser layers.42−45 Correspondingly, we observed stronger inhibition of the catalytic activity for longer ligands, culminating in effectively no activity for C18SH for the first trial. It is interesting to note that the shorter ligands’ (C12SH, C8SH, and C4SH) hydrophobic nature does not prevent this aqueous catalytic reaction. Specifically, C4SH-coated slides yielded the highest TON of all ligand-coated cases, matching bare Au slides for both the first and the second trial. This is likely due to rapid ligand removal upon incubation in the reaction solution containing sodium borohydride. Figure 4a,b confirms the removal of C4SH (see XPS discussion above). The other alkylthiol ligand-coated slides showed an increase in TON upon reuse, once again demonstrating ligand removal. The rate of removal appears to be linked to the permeability of the ligand shell, as C12SH- and C18SH-coated slides did not reach a second trial TON comparable to that of bare Au.

### *Negatively Charged MUA (Entry 11) Displays High Activity*

MUA has a similar size to C12SH but displayed much higher activity; we attribute this observation to electrostatic repulsion between the negatively charged carboxylic acid tail groups producing a less densely packed ligand shell, which allows for more permeation of both 4-Nip and the borohydride anion compared to the tightly packed alkyl chains of C12SH.

### *Neutral, Hydrophilic Ligands mPEG4SH and PVP (Entries 12-13) Partially Inhibit the Reaction*

mPEG4SH has a similar size to C12SH but features much weaker intermolecular interactions; nevertheless, it inhibited the reaction to a similar degree. Inhibition was also shown by the neutral polymer, PVP (entry 13), an effect that has been well studied in the literature.14,20,46 Along with MPA, one outlier in the PVP replicates (with TONs = 21 and 80 for the first and second trials, respectively) skewed the uncertainty of the batch. Similar to the longer alkylthiol ligands, mPEG4SH and PVP did not increase to an activity comparable to bare Au even after reuse, showing that these ligands take longer to remove than others. These findings show that the stability of the ligand shell to borohydride depends not only (or even primarily) on the strength of the bond with the Au but also on the permeability and intermolecular interactions between the ligands.

### *Bidentate ALA (Entry 14) Partially Inhibits the Reaction*

ALA binds to the Au NI via two Au–S bonds, leading to a more strongly bound ligand shell.47 The average TON of ALA-coated slides is much lower than that of C8SH-coated slides, a ligand of similar size but monodentate and lacking the negatively charged carboxylic acid tail group. This is the opposite trend to that seen when comparing MUA to C12SH, two ligands of similar size but varying in the charge of the tail groups. While the repulsion of the ALA tail groups likely leads to a more permeable shell, the bidentate binding to the Au NI likely slows down the rate of borohydride-induced ligand desorption, leading to a lower overall turnover. Upon reuse, ALA-coated slides did not produce significantly higher TONs, supporting the notion that the bidentate binding is less susceptible to desorption.

## Kinetic Trials

To learn more about the effect of ligand removal, we performed kinetic trials according to the procedure described in the Methods section (Figure 5). Bare, C8SH-coated, C12SH-coated, and mPEG4SH-coated slides were chosen to represent four distinct levels of catalytic activity within the initial 3 h reaction timeframe. C18SH-coated Au NI slides were not used due to the complete inhibition of the reaction within the first 3 h. The induction time in this reaction is known to result from a back-reaction of an intermediate with dissolved oxygen; borohydride scavenges oxygen, primarily at the Au surface, and the reaction is seen to “turn on” once the dissolved oxygen concentration falls below a threshold value.20 Therefore, ligands blocking access to the Au will lengthen this induction period, and indeed, we observed a longer duration for coated slides (1530, 1620, and 1980 s for C8SH-, mPEG4-SH-, and C12SH-coated slides, respectively), compared to an uncoated sample (720 s). The kinetic traces demonstrate the effect of the ligand removal process─while the traces of the three coated slides initially display similar slopes, that for C8SH then accelerates, ending at much higher conversions. While the final conversion is still lower than for bare Au, this partially reflects the delay in removing the ligands and achieving the full catalytic rate. Indeed, as shown earlier (Table 1), in the second trial, C8SH-coated slides produced TONs closer to that of bare Au, indicating substantially less blocking of active sites. These results highlight the inability of the method of initial rates to capture the full effect of ligands and their removal on catalysis in reactions with labile ligands, such as those utilizing borohydride.

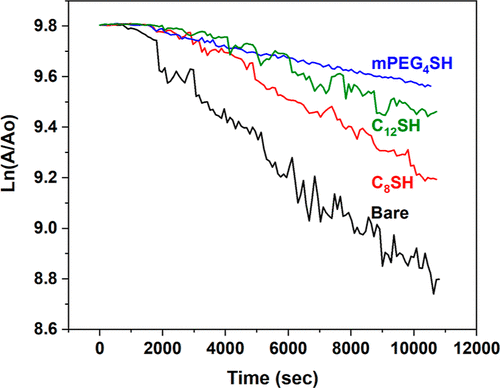


Figure 5. Kinetic trials for bare and ligand-coated Au NI slides (labeled). Noise is the result of hydrogen bubbles interfering with the optical measurement.

# Conclusions

Ligands are known to strongly affect the catalytic activity of Au NPs but have rarely been compared with one another, and differences in NP size and shape between studies (and, at times, within individual studies) limit the ability to compare their results. The reduction of 4-Nip by sodium borohydride has been widely studied as a model reaction to test the performance of Au NP catalysts, but sodium borohydride is able to remove ligands from Au NPs, introducing further complexity. In this work, Au NPs were partially embedded into glass slides for use as heterogeneous catalysts for the 4-Nip reduction reaction. The absolute impact of ligands was established by comparison to bare Au NIs, and different ligands are quantitatively compared since they coat identical, stable Au NI slides. We found that most small-molecule ligands, including strongly bound thiols, slightly inhibited the reaction for the first 3 h period but were removed by borohydride during the process, resulting in increased activity upon reuse. Citrate-coated Au NIs produced TONs slightly less than bare Au NIs, showing that they are not an appropriate comparison of catalytic activity to bare NIs within this system. Longer-chain thiolated ligands partially inhibited catalysis, with increasing inhibition correlated with longer and more hydrophobic ligands, likely due to their ability to form denser, more tightly packed shells. When the same catalysts were used for a second trial, a higher TON was observed for all systems compared to the first trial because of ligand removal, as confirmed by XPS measurements. Kinetic trials demonstrated the benefits of longer conversion studies as the common method of initial rates fails to capture the impact of slower ligand removal. The stable Au NI system used here is ideal for the quantification of ligand effects, removing the confounding factors of varying size distribution, mixed ligand shells, and colloidal instability. Our results highlight the importance of considering the stability of ligands when designing complex Au NP–ligand assemblies.

# Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c03879.

DLS measurements and concentration calculation of Au NPs; detailed fabrication procedure of Au NI slides; XRD characterization; XPS measurements; LSPR spectra of bare Au NI slides; full spectra from the catalytic reactions including controls; and TON calculation (PDF)

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# Author Information

# Notes

The authors declare no competing financial interest.

# Acknowledgments

Financial support for this work was provided by Marquette University. This work made use of the EPIC, Keck-II, and SPID facilities of Northwestern University’s NUANCE Center, which have received support from the SHyNE Resource (NSF ECCS-2025633), the IIN, and Northwestern’s MRSEC program (NSF DMR-1720139).

# References

**1** Gellé, A.; Jin, T.; de la Garza, L.; Price, G. D.; Besteiro, L. V.; Moores, A. Applications of Plasmon-Enhanced Nanocatalysis to Organic Transformations. *Chem. Rev.* **2020**, *120*, 986– 1041, DOI: 10.1021/acs.chemrev.9b00187

**2** Takei, T.; Akita, T.; Nakamura, I.; Fujitani, T.; Okumura, M.; Okazaki, K.; Huang, J.; Ishida, T.; Haruta, M. Heterogeneous Catalysis by Gold. *Adv. Catal.* **2012**, *55*, 1– 126, DOI: 10.1016/b978-0-12-385516-9.00001-6

**3** Hervés, P.; Pérez-Lorenzo, M.; Liz-Marzán, L. M.; Dzubiella, J.; Lu, Y.; Ballauff, M. Catalysis by Metallic Nanoparticles in Aqueous Solution: Model Reactions. *Chem. Soc. Rev.* **2012**, *41*, 5577– 5587

**4** Ayati, A.; Ahmadpour, A.; Bamoharram, F. F.; Tanhaei, B.; Mänttäri, M.; Sillanpää, M. A Review on Catalytic Applications of Au/TiO2 Nanoparticles in the Removal of Water Pollutant. *Chemosphere* **2014**, *107*, 163– 174, DOI: 10.1016/j.chemosphere.2014.01.040

**5** Comotti, M.; Della Pina, C.; Falletta, E.; Rossi, M. Aerobic Oxidation of Glucose with Gold Catalyst: Hydrogen Peroxide as Intermediate and Reagent. *Adv. Synth. Catal.* **2006**, *348*, 313– 316, DOI: 10.1002/adsc.200505389

**6** Carregal-Romero, S.; Pérez-Juste, J.; Hervés, P.; Liz-Marzán, L. M.; Mulvaney, P. Colloidal Gold-Catalyzed Reduction of Ferrocyanate (III) by Borohydride Ions: A Model System for Redox Catalysis. *Langmuir* **2010**, *26*, 1271– 1277, DOI: 10.1021/la902442p

**7** Islam, Md. T.; Dominguez, N.; Ahsan, Md. A.; Dominguez-Cisneros, H.; Zuniga, P.; Alvarez, P. J. J.; Noveron, J. C. Sodium Rhodizonate Induced Formation of Gold Nanoparticles Supported on Cellulose Fibers for Catalytic Reduction of 4-Nitrophenol and Organic Dyes. *J. Environ. Chem. Eng.* **2017**, *5*, 4185– 4193, DOI: 10.1016/j.jece.2017.08.017

**8** Hashmi, A. S. K. Gold-Catalyzed Organic Reactions. *Chem. Rev.* **2007**, *107*, 3180– 3211, DOI: 10.1021/cr000436x

**9** Wunder, S.; Lu, Y.; Albrecht, M.; Ballauff, M. Catalytic Activity of Faceted Gold Nanoparticles Studied by a Model Reaction: Evidence for Substrate-Induced Surface Restructuring. *ACS Catal.* **2011**, *1*, 908– 916, DOI: 10.1021/cs200208a

**10** Barbosa, E. C. M.; Fiorio, J. L.; Mou, T.; Wang, B.; Rossi, L. M.; Camargo, P. H. C. Reaction Pathway Dependence in Plasmonic Catalysis: Hydrogenation as a Model Molecular Transformation. *Chem.─Eur. J.* **2018**, *24*, 12330– 12339, DOI: 10.1002/chem.201705749

**11** Shirin, S.; Roy, S.; Rao, A.; Pillai, P. P. Accelerated Reduction of 4-Nitrophenol: Bridging Interaction Outplays Reducing Power in the Model Nanoparticle-Catalyzed Reaction. *J. Phys. Chem. C* **2020**, *124*, 19157– 19165, DOI: 10.1021/acs.jpcc.0c06237

**12** Ansar, S. M.; Kitchens, C. L. Impact of Gold Nanoparticle Stabilizing Ligands on the Colloidal Catalytic Reduction of 4-Nitrophenol. *ACS Catal.* **2016**, *6*, 5553– 5560, DOI: 10.1021/acscatal.6b00635

**13** Strachan, J.; Barnett, C.; Masters, A. F.; Maschmeyer, T. 4-Nitrophenol Reduction: Probing the Putative Mechanism of the Model Reaction. *ACS Catal.* **2020**, *10*, 5516– 5521, DOI: 10.1021/acscatal.0c00725

**14** Álvarez Cerimedo, M. S.; Baronio, L. G.; Hoppe, C. E.; Ayude, M. A. The Effect of Poly(Vinylpyrrolidone) (PVP) on the Au Catalyzed Reduction of p–Nitrophenol: The Fundamental Role of NaBH4. *ChemistrySelect* **2019**, *4*, 608– 616, DOI: 10.1002/slct.201803250

**15** Abdullah, H.; Kuo, D.-H. Utilization of Photocatalytic Hydrogen Evolved (Zn,Sn)(O,S) Nanoparticles to Reduce 4-Nitrophenol to 4-Aminophenol. *Int. J. Hydrogen Energy* **2019**, *44*, 191– 201, DOI: 10.1016/j.ijhydene.2018.04.036

**16** Grzeschik, R.; Schäfer, D.; Holtum, T.; Küpper, S.; Hoffmann, A.; Schlücker, S. On the Overlooked Critical Role of the PH Value on the Kinetics of the 4-Nitrophenol NaBH4 -Reduction Catalyzed by Noble-Metal Nanoparticles (Pt, Pd, and Au). *J. Phys. Chem. C* **2020**, *124*, 2939– 2944, DOI: 10.1021/acs.jpcc.9b07114

**17** Pradhan, N.; Pal, A.; Pal, T. Catalytic Reduction of Aromatic Nitro Compounds by Coinage Metal Nanoparticles. *Langmuir* **2001**, *17*, 1800– 1802, DOI: 10.1021/la000862d

**18** Ciganda, R.; Li, N.; Deraedt, C.; Gatard, S.; Zhao, P.; Salmon, L.; Hernández, R.; Ruiz, J.; Astruc, D. Gold Nanoparticles as Electron Reservoir Redox Catalysts for 4-Nitrophenol Reduction: A Strong Stereoelectronic Ligand Influence. *Chem. Commun.* **2014**, *50*, 10126– 10129, DOI: 10.1039/c4cc04454a

**19** Zhao, P.; Feng, X.; Huang, D.; Yang, G.; Astruc, D. Basic Concepts and Recent Advances in Nitrophenol Reduction by Gold- and Other Transition Metal Nanoparticles. *Coord. Chem. Rev.* **2015**, *287*, 114– 136, DOI: 10.1016/j.ccr.2015.01.002

**20** Neal, R. D.; Hughes, R. A.; Sapkota, P.; Ptasinska, S.; Neretina, S. Effect of Nanoparticle Ligands on 4-Nitrophenol Reduction: Reaction Rate, Induction Time, and Ligand Desorption. *ACS Catal.* **2020**, *10*, 10040– 10050, DOI: 10.1021/acscatal.0c02759

**21** Gao, M.; Yang, Y.; Guo, J. Revealing the Role of Chain Length of Ligands on Gold Nanoparticles Surface in the Process for Catalysis Reduction of 4-Nitrophenol. *Catal. Lett.* **2019**, *149*, 2110– 2118, DOI: 10.1007/s10562-019-02752-4

**22** Roy, S.; Rao, A.; Devatha, G.; Pillai, P. P. Revealing the Role of Electrostatics in Gold-Nanoparticle-Catalyzed Reduction of Charged Substrates. *ACS Catal.* **2017**, *7*, 7141– 7145, DOI: 10.1021/acscatal.7b02292

**23** Wang, C.; Salmon, L.; Li, Q.; Igartua, M. E.; Moya, S.; Ciganda, R.; Ruiz, J.; Astruc, D. From Mono to Tris-1,2,3-Triazole-Stabilized Gold Nanoparticles and Their Compared Catalytic Efficiency in 4-Nitrophenol Reduction. *Inorg. Chem.* **2016**, *55*, 6776– 6780, DOI: 10.1021/acs.inorgchem.6b01092

**24** Ansar, S. M.; Ameer, F. S.; Hu, W.; Zou, S.; Pittman, C. U.; Zhang, D. Removal of Molecular Adsorbates on Gold Nanoparticles Using Sodium Borohydride in Water. *Nano Lett.* **2013**, *13*, 1226– 1229, DOI: 10.1021/nl304703w

**25** Villarreal, E.; Li, G. G.; Zhang, Q.; Fu, X.; Wang, H. Nanoscale Surface Curvature Effects on Ligand–Nanoparticle Interactions: A Plasmon-Enhanced Spectroscopic Study of Thiolated Ligand Adsorption, Desorption, and Exchange on Gold Nanoparticles. *Nano Lett.* **2017**, *17*, 4443– 4452, DOI: 10.1021/acs.nanolett.7b01593

**26** Bastús, N. G.; Comenge, J.; Puntes, V. Kinetically Controlled Seeded Growth Synthesis of Citrate-Stabilized Gold Nanoparticles of up to 200 nm: Size Focusing versus Ostwald Ripening. *Langmuir* **2011**, *27*, 11098– 11105, DOI: 10.1021/la201938u

**27** Turkevich, J.; Stevenson, P. C.; Hillier, J. A Study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold. *Discuss. Faraday Soc.* **1951**, *11*, 55– 75, DOI: 10.1039/df9511100055

**28** Volkert, A. A.; Subramaniam, V.; Haes, A. Implications of citrate concentration during the seeded growth synthesis of gold nanoparticles. *Chem. Commun.* **2011**, *47*, 478– 480, DOI: 10.1039/c0cc02075c

**29** Al-Johani, H.; Abou-Hamad, E.; Jedidi, A.; Widdifield, C. M.; Viger-Gravel, J.; Sangaru, S. S.; Gajan, D.; Anjum, D. H.; Ould-Chikh, S.; Hedhili, M. N.; Gurinov, A.; Kelly, M. J.; El Eter, M.; Cavallo, L.; Emsley, L.; Basset, J.-M. The Structure and Binding Mode of Citrate in the Stabilization of Gold Nanoparticles. *Nat. Chem.* **2017**, *9*, 890– 895, DOI: 10.1038/nchem.2752

**30** Soliwoda, K.; Tomaszewska, E.; Tkacz-Szczesna, B.; Mackiewicz, E.; Rosowski, M.; Bald, A.; Blanck, C.; Schmutz, M.; Novák, J.; Schreiber, F.; Celichowski, G.; Grobelny, J. Effect of the Alkyl Chain Length of Secondary Amines on the Phase Transfer of Gold Nanoparticles from Water to Toluene. *Langmuir* **2014**, *30*, 6684– 6693, DOI: 10.1021/la501135q

**31** Dinkel, R.; Braunschweig, B.; Peukert, W. Fast and Slow Ligand Exchange at the Surface of Colloidal Gold Nanoparticles. *J. Phys. Chem. C* **2016**, *120*, 1673– 1682, DOI: 10.1021/acs.jpcc.5b11055

**32** Kluenker, M.; Mondeshki, M.; Nawaz Tahir, M. N.; Tremel, W. Monitoring Thiol-Ligand Exchange on Au Nanoparticle Surfaces. *Langmuir* **2018**, *34*, 1700– 1710, DOI: 10.1021/acs.langmuir.7b04015

**33** Kedem, O.; Tesler, A. B.; Vaskevich, A.; Rubinstein, I. Sensitivity and Optimization of Localized Surface Plasmon Resonance Transducers. *ACS Nano* **2011**, *5*, 748– 760, DOI: 10.1021/nn102617d

**34** Kedem, O.; Vaskevich, A.; Rubinstein, I. Improved Sensitivity of Localized Surface Plasmon Resonance Transducers Using Reflection Measurements. *J. Phys. Chem. Lett.* **2011**, *2*, 1223– 1226, DOI: 10.1021/jz200482f

**35** Karakouz, T.; Maoz, B. M.; Lando, G.; Vaskevich, A.; Rubinstein, I. Stabilization of Gold Nanoparticle Films on Glass by Thermal Embedding. *ACS Appl. Mater. Interfaces* **2011**, *3*, 978– 987, DOI: 10.1021/am100878r

**36** Karakouz, T.; Tesler, A. B.; Bendikov, T. A.; Vaskevich, A.; Rubinstein, I. Highly Stable Localized Plasmon Transducers Obtained by Thermal Embedding of Gold Island Films on Glass. *Adv. Mater.* **2008**, *20*, 3893– 3899, DOI: 10.1002/adma.200703092

**37** Karakouz, T.; Holder, D.; Goomanovsky, M.; Vaskevich, A.; Rubinstein, I. Morphology and Refractive Index Sensitivity of Gold Island Films. *Chem. Mater.* **2009**, *21*, 5875– 5885, DOI: 10.1021/cm902676d

**38** Schneider, C. A.; Rasband, W. S.; Eliceiri, K. W. NIH Image to ImageJ: 25 Years of Image Analysis. *Nat. Methods* **2012**, *9*, 671– 675, DOI: 10.1038/nmeth.2089

**39** Guczi, L.; Beck, A.; Pászti, Z. Gold Catalysis: Effect of Particle Size on Reactivity towards Various Substrates. *Catal. Today* **2012**, *181*, 26– 32, DOI: 10.1016/j.cattod.2011.08.037

**40** Mohr, C.; Hofmeister, H.; Radnik, J.; Claus, P. Identification of Active Sites in Gold-Catalyzed Hydrogenation of Acrolein. *J. Am. Chem. Soc.* **2003**, *125*, 1905– 1911, DOI: 10.1021/ja027321q

**41** Vericat, C.; Benitez, G. A.; Grumelli, D. E.; Vela, M. E.; Salvarezza, R. C. Thiol-Capped Gold: From Planar to Irregular Surfaces. *J. Phys.: Condens. Matter* **2008**, *20*, 184004, DOI: 10.1088/0953-8984/20/18/184004

**42** Brewer, N. J.; Foster, T. T.; Leggett, G. J.; Alexander, M. R.; McAlpine, E. Comparative Investigations of the Packing and Ambient Stability of Self-Assembled Monolayers of Alkanethiols on Gold and Silver by Friction Force Microscopy. *J. Phys. Chem. B* **2004**, *108*, 4723– 4728, DOI: 10.1021/jp035492r

**43** Bhadra, P.; Shajahan, M. S.; Bhattacharya, E.; Chadha, A. Studies on Varying N-Alkanethiol Chain Lengths on a Gold Coated Surface and Their Effect on Antibody-Antigen Binding Efficiency. *RCS Adv.* **2015**, *5*, 80480– 80487, DOI: 10.1039/c5ra11725a

**44** Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. Formation of Monolayer Films by the Spontaneous Assembly of Organic Thiols from Solution onto Gold. *J. Am. Chem. Soc.* **1989**, *111*, 321– 335, DOI: 10.1021/ja00183a049

**45** Pensa, E.; Cortés, E.; Corthey, G.; Carro, P.; Vericat, C.; Fonticelli, M. H.; Benítez, G.; Rubert, A. A.; Salvarezza, R. C. The Chemistry of the Sulfur–Gold Interface: In Search of a Unified Model. *Acc. Chem. Res.* **2012**, *45*, 1183– 1192, DOI: 10.1021/ar200260p

**46** Bastús, N. G.; Merkoçi, F.; Piella, J.; Puntes, V. Synthesis of Highly Monodisperse Citrate-Stabilized Silver Nanoparticles of up to 200 Nm: Kinetic Control and Catalytic Properties. *Chem. Mater.* **2014**, *26*, 2836– 2846, DOI: 10.1021/cm500316k

**47** Chinwangso, P.; Jamison, A. C.; Lee, T. R. Multidentate Adsorbates for Self-Assembled Monolayer Films. *Acc. Chem. Res.* **2011**, *44*, 511– 519, DOI: 10.1021/ar200020s

**48** Gao, Y.; Torrente-Murciano, L. Mechanistic Insights of the Reduction of Gold Salts in the Turkevich Protocol. *Nanoscale* **2020**, *12*, 2740– 2751, DOI: 10.1039/c9nr08877f

**49** Zhang, H.; Fung, K.-H.; Hartmann, J.; Chan, C. T.; Wang, D. Controlled Chainlike Agglomeration of Charged Gold Nanoparticles via a Deliberate Interaction Balance. *J. Phys. Chem. C* **2008**, *112*, 16830– 16839, DOI: 10.1021/jp806059a

**50** Ron, H.; Matlis, S.; Rubinstein, I. Self-Assembled Monolayers on Oxidized Metals. 2. Gold Surface Oxidative Pretreatment, Monolayer Properties, and Depression Formation. *Langmuir* **1998**, *14*, 1116– 1121, DOI: 10.1021/la970785v

**51** Neal, R. D.; Inoue, Y.; Hughes, R. A.; Neretina, S. Catalytic Reduction of 4-Nitrophenol by Gold Catalysts: The Influence of Borohydride Concentration on the Induction Time. *J. Phys. Chem. C* **2019**, *123*, 12894– 12901, DOI: 10.1021/acs.jpcc.9b02396

**52** Menumerov, E.; Hughes, R. A.; Neretina, S. Catalytic Reduction of 4-Nitrophenol: A Quantitative Assessment of the Role of Dissolved Oxygen in Determining the Induction Time. *Nano Lett.* **2016**, *16*, 7791– 7797, DOI: 10.1021/acs.nanolett.6b03991