Cationic Polymer Coating Increases the Catalytic Activity of Gold Nanoparticles toward Anionic Substrates

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Cationic Polymer Coating Increases the Catalytic Activity of Gold Nanoparticles Toward Anionic Substrates

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Abstract
Organic coatings on catalytic metal nanoparticles (NPs) typically hinder their activity due to the blocking of active sites. Therefore, considerable effort is made to remove organic ligands when preparing supported NP catalytic materials. Here, cationic polyelectrolyte coatings are shown to
increase the catalytic activity of partially embedded gold nanoislands (Au NIs) toward transfer hydrogenation and oxidation reactions with anionic substrates compared to the activity of identical but uncoated Au NIs. Any potential steric hindrance caused by the coating is countered by a decrease in the activation energy of the reaction by half, resulting in overall enhancement. The direct comparison to identical but uncoated NPs isolates the role of the coating and provides conclusive evidence of enhancement. Our findings show that engineering the microenvironment of heterogeneous catalysts, creating hybrid materials that cooperatively interact with the reactants involved, is a viable and exciting path to improving their performance.

Keywords
gold nanoparticles, 4-nitrophenol, activation energy, kinetics, transfer hydrogenation, oxidation, polyelectrolyte

Introduction
Metal nanoparticles (NPs) are popular catalysts owing to their tunability, straightforward syntheses, high stabilities, simple separation from reaction mixtures, and the ease with which they can be designed to achieve desirable functionalities (e.g., thermo-optical). (1−5) In the field of homogeneous catalysis, activity and selectivity are typically controlled by varying the organic ligands, which alter the local environment of the metal center and interact with reactants. (6−8) This approach is rarely utilized in heterogeneous catalysis, as organic ligands are typically regarded as disadvantageous to the overall catalytic activity due to the blocking of active sites. (7−14) Since organic ligands are used in colloidal NP synthesis to control the particle size and shape (which affect the activity), (3,15−20) considerable effort is made to remove the ligands when immobilizing the NPs to make supported catalytic materials. (9,21−25)

Nevertheless, some recent studies have demonstrated beneficial effects from ligands on colloidal and immobilized NPs, though most focused on modifying the selectivity of the catalyst. (11,26−34) Specific noncovalent interactions between cinnamaldehyde and the aromatic ligand shell of a Pt/Al₂O₃ catalyst were shown to increase the selectivity of the desired product cinnamyl alcohol. (27) Increased selectivity for the hydrogenation of acetophenone using Pt NPs functionalized with l-proline compared to their unprotected counterparts was also recently demonstrated. (30) With respect to catalyst activity, positively charged Au NPs increased the rate of 4-nitrophenol reduction compared to Au NPs with a comparable but negative ligand shell. (35) While there have been examples of beneficial ligand effects on the catalyst activity, colloidal studies (6,35,36) suffer from serious limitations: (i) quantifying the absolute effect of a coating is nearly impossible, as uncoated NPs quickly aggregate; (ii) synthetizing NPs with different coatings leads to size and morphological differences in the NP core, (15) confounding the effects of the coatings themselves; and (iii) exchanging the organic ligands after synthesis often leads to a poorly characterized mixed-ligand shell, (37) or worse yet, aggregation. The proposed explanation for changes in activity and selectivity varies from molecular recognition (6,27,35,36,38) to steric effects (7,26) to ligand-induced enrichment of the electron density on the surface of the catalyst. (11) Understanding the degree and nature of the effect ligands have on catalytic reactions has major implications for the future development of highly effective catalytic materials, including responsive catalysts. (39,40) We posit that the field of heterogeneous catalysis will
gain from harnessing beneficial catalyst–ligand–reactant interactions by tuning the catalyst microenvironment. Improvements in catalyst activity enable faster transformations at lower temperatures, directly translating into reductions in the energy costs of reactions.

In this study, we show that cationic polymer coatings increase the catalytic activity of Au NPs toward anionic substrates. Au NPs are an excellent platform to investigate the catalytic properties of nanoparticles as they do not oxidize, have plasmonic absorption in the visible range, to allow for the detection of coatings, and share similar ligand binding properties with other metal NPs, making newly discovered phenomena translatable to other NP systems. To facilitate a direct study of the effect of polymer coatings, we use Au NPs supported on glass, termed nanoislands (NIs). These Au NIs, produced via a thermal annealing process, have been shown to provide near-perfect stability in a variety of solvents and are not morphologically changed when coated with ligands. (41–44) These properties enable robust comparisons between bare Au NIs and Au NI–ligand hybrid materials, a fact we have recently used to determine the absolute impact of a variety of coatings compared to bare Au. (10) We used the positive polyelectrolytes poly(allylamine hydrochloride) (PAH) and polyethyleneimine (PEI), as they are known to provide a positively charged surface after adsorption, a fact heavily utilized in the construction of electrostatic layer-by-layer assemblies. (45) Here, we intended to benefit from electrostatic interactions between the positively charged polymers and negatively charged catalytic reactants. We observe the most prominent enhancement for the transfer hydrogenation of 4-nitrophenol (4-Nip), where both the reactant (4-nitrophenolate) and the reducing agent (borohydride) carry negative charges; for the reduction of the neutral 4-nitroaniline, where only the borohydride is anionic, the effect is milder. The oxidation of the negatively charged ABTS [2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)] using hydrogen peroxide is similarly enhanced when using the Au NI–polymer hybrid, while the oxidation of the neutral substrate TMB (3,3′,5,5′-tetramethylbenzidine) is entirely unaffected. The increased activity for multiple substrates in two disparate reactions (transfer hydrogenation and oxidation) points toward the generalizability of the effect. To the best of our knowledge, it has not previously been demonstrated that polymer-coated Au NPs possess higher catalytic activity than bare Au NPs with identical morphology. The results shown in this work are an exciting step toward the utilization of organic coatings in creating highly efficient NP catalysts.

Experimental Design

Materials

VistaVision #2, 22 mm × 22 mm glass cover slips were purchased from VWR. Hydrogen tetrachloroaurate(III) trihydrate (99.99%, Alfa Aesar), trisodium citrate dihydrate (Sigma), ethanol (absolute, Supelco), methyl alcohol (anhydrous, 100.0%, Macron), nitric acid (69.8%, Macron), hydrochloric acid (37.7%, Macron), hydrogen peroxide (30%, J.T. Baker), sulfuric acid (96.4%, Macron), 3-aminopropyltrimethoxysilane (“APTMS”; 96%, TCI), 4-nitrophenol (“4-Nip”; 99%, TCI), 4-nitroaniline (“4-NA”; 99%, Acros), sodium borohydride (99%, Acros Organics), 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (“ABTS”; 98%, TCI America), 3,3′,5,5′-tetramethylbenzidine hydrochloride hydrate (“TMB”; 98%, Thermo Fisher), 2-aminoethanethiol hydrochloride (“Cysteamine”; 98%, Acros), potassium phosphate monobasic (LabChem), orthophosphoric acid (85%, VWR), poly(allylamine HCl) 79 kDa (“PAH”; Aldrich), poly(4-styrenesulfonic acid) solution 75 kDa (“PSS”;
18.4 wt. % in H₂O, Sigma-Aldrich) and polyethyleneimine ("PEI"; branched 50–100 kDa, 30% w/w, Thermo Scientific) were used as received. In all cases, water for solutions or rinsing was obtained from a Milli-Q purification unit with a resistance of 18.2 MΩ or purchased ASTM Type I/II (Ricca). Solutions containing sodium borohydride were prepared fresh as needed to avoid decomposition.

Au NI Preparation
We prepared Au NI slides according to a procedure we previously published. (10) Briefly, we cut glass coverslips (henceforth referred to as “slides”) to 8.5 mm × 22 mm and soaked them for 1 h in a fresh piranha solution (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.) followed by three rinses in Milli-Q water, three rinses in methanol, and drying with a stream of nitrogen. Afterward, we incubated the clean slides for 15 min in a 0.1% v/v aqueous solution of 3-aminopropyltrimethoxysilane (APTMS) to produce a positively charged surface, followed by three rinses in Milli-Q water and drying under nitrogen. We then incubated the slides in a 20 nM (with respect to the number of particles) solution of citrate-coated Au NPs (see synthesis details in the Supporting Information) for 2 h, followed by three rinses in Milli-Q water and nitrogen drying. We wiped NPs from the back face of the slide as well as the top corner of the front face with a cotton-tipped applicator to afford a place to hold the slide with tweezers when transferring between various solutions and containers. We also scratched identification numbers into the opposite top corner of each slide. We annealed the slides for 10 h at 600 °C with a heating rate of 5 °C/min (the 10 h duration does not include the heating stage) to yield partially embedded Au NI slides.

Au NI Functionalization
We treated Au NI slides with UV/ozone (Ossila) for 5 min, a procedure that removes surface contamination and produces a layer of gold oxide on the surface. (46) To reduce the gold oxide layer, we rinsed the slides in absolute ethanol, dried with nitrogen, and incubated the slides in a fresh 1 M aqueous solution of sodium borohydride for 1 h. Following this step, we rinsed the slides with Milli-Q water, dried them with nitrogen, and recorded their transmission spectra. Bare Au NI slides required no further treatment prior to catalysis, while ligand-modified slides were then incubated in 10 mM (with respect to the monomer for polymeric ligands) aqueous solutions of ligand (PEI was prepared in absolute ethanol) for 1 h, followed by a rinse with the appropriate solvent and nitrogen drying. Finally, we recorded the post-functionalization transmission spectra of the dried Au NI slides before their use in catalytic trials.

Transmission Spectra
We used a Jasco V-750 spectrophotometer to record transmission spectra, placing slides perpendicular to the beam inside a 4.5 mL polystyrene cuvette. For extinction measurements of Au NI slides, dry slides were placed in a cuvette, and their spectra were corrected using a baseline of a clean glass slide in an empty cuvette. Spectra were recorded in the range 400–700 nm, at 0.5 nm intervals, and using a response time of 0.06 s (an effective scan rate of 1000 nm/min).

Nitroarene Reduction
We performed kinetic trials by adding a PTFE stir bar, Milli-Q water, nitroarene, and a freshly prepared aqueous solution of sodium borohydride to a cuvette to give 2.5 mL of solution with final
concentrations of 50 μM nitroarene and 10 mM NaBH₄. The addition of the Au NI slides (to the side of the cuvette, away from the beam path) started the reaction, which was carried out for 3 h in the activation energy study and 1 h for all other catalytic data. A PAC-743 cell changer/Peltier heating and cooling attachment allowed for six simultaneous kinetic trials to be performed (two uncatalyzed controls and four catalyzed trials). We measured the extinction at 400 nm every 15 s to determine the concentration of the 4-nitrophenolate ion over the course of the reaction (as detailed in the Supporting Information). For 4-nitroaniline reduction, the absorbance at 380 nm was recorded as a function of time. The reaction was stirred at 750 rpm, and the temperature was held constant for the duration of the 3 h trial. To obtain the Arrhenius plots used to calculate activation energy, we performed time-resolved 4-Nip reduction at 10, 22, 30, 40, and 50 °C. To measure the dependence on [4-Nip]₀, 1 h kinetic trials were performed in the manner described above with starting 4-Nip concentrations of 1, 5, 10, 50, 75, 100, 125, 150, and 175 μM, while [NaBH₄]₀ remained constant at 10 mM. Pseudo-first-order kinetic traces for each trial were used to obtain apparent rate constants (kₐₚₚ) from the initial, linear reaction period.

ABTS Oxidation
We measured the rate of ABTS oxidation in a similar fashion to 4-Nip reduction. The 2.5 mL reaction solutions contained freshly prepared ABTS (2 mM) and hydrogen peroxide (111 mM) in a phosphate buffer (50 mM) at 4.35 pH. Au NI slides catalyzed the 45 min reaction, which was stirred at 750 rpm and held at 22 °C. Two controls and four catalyzed reactions were carried out in tandem for both bare and PAH-Au NI slides. The absorbance at 420 nm corresponding to the oxidized product was monitored as a function of time. Pseudo-first-order kinetic traces for each trial were used to obtain kₐₚₚ values.

TMB Oxidation
We measured the rate of TMB oxidation by adding fresh TMB (200 μM final concentration) and hydrogen peroxide (470 mM final concentration) in a phosphate-citrate buffer (50 mM) at a pH of 5 to a cuvette with a PTFE stir bar to produce a 2.5 mL solution. Two controls and four catalyzed 30 min reactions were measured for both bare and PAH-Au NI slides at 22 °C while stirring at 750 rpm. The absorbance at 652 nm corresponding to the charge-transfer complex was monitored as a function of time. Pseudo-first-order kinetic traces for each trial were used to obtain kₐₚₚ values.

TEM Imaging
We imaged colloidal Au NPs using a JEOL JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV. To prepare the samples, 100 μL of the Au NP solution was diluted with 100 μL of Milli-Q water in a glass vial, and the resulting solution was sonicated for 15 min. A 20 μL drop of the solution was then pipetted onto a Formvar/Carbon 200 mesh copper support film (Ted Pella, Inc.) and allowed to dry.

XPS Spectra
We obtained X-ray photoelectron spectra of Au NI slides using a Thermo Scientific NEXSA G2 equipped with an X-ray gun with a spot size of 400 μm and a charge compensation flood gun. Au NI slides were adhered to sample holders with copper tape. For all measurements, a survey spectrum was recorded along with spectra in the Au 4f, C 1s, N 1s, and Cl 2p regions. All signals were the average of 10 scans.
Results and Discussion

Catalyst Preparation

We fabricated Au NI slides according to our previously established procedure, detailed in the Experimental Section. (10) Optical extinction spectra showing the localized surface plasmon resonance (LSPR) band of all slides used in this study are shown in Figure S2. A representative scanning electron microscopy (SEM) image of an Au NI slide is shown in Figure 1a. Figure 1b shows the extinction spectra of a slide before and after functionalization with PAH, showing the expected redshift and increase in extinction of the LSPR peak following PAH binding. (41) A table of the average shifts of the LSPR maxima for all Au NI–organic hybrids used in this study is shown in the Supporting Information (Table S2). A photo of bare and PAH-coated catalysts, where the redshift arising from PAH adsorption is visually apparent, is shown in Figure 1c. In our previous study, a detailed evaluation of SEM and atomic force microscopy (AFM) images was conducted to determine the average dimensions of the nanoislands. (10) Au NI were fit to ellipsoidal models to give average major and minor axes of 14 ± 4 nm and 13 ± 3 nm, respectively, with an average height above the glass of 8 ± 2 nm. X-ray diffraction (XRD) measurements show the NPs have {111} texture (Section 7.2, Supporting Information), consistent with previous studies on similar structures. (47,48) To prepare them for functionalization and catalysis, slides were treated with UV–ozone, a procedure that removes organic contaminants from the surface, (46) incubated in 1 M NaBH₄ for 1 h to reduce residual oxides, and either used for catalysis as-is or functionalized with ligands (structures depicted in Scheme 1) by incubating the slide in ligand solutions (see Experimental).

Figure 1. (a) SEM image of a Au NI slide; the scale bar represents 100 nm. (b) Representative optical extinction spectra showing the shift in wavelength and increase in intensity of the LSPR peak upon adsorption of PAH (deposited from a 2 M NaCl solution) compared to a bare Au NI slide. (c) Photo of bare Au NI slide (left) and PAH-Au NI slide (right); scale bar represents 10 mm. (d) Nitrogen signal from the XPS spectrum of a thick PAH-Au NI slide. In panel d, 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 the panel (shifted from zero so it can be displayed alongside the spectrum).
Figure 1d shows the N 1s region in an X-ray photoelectron spectroscopy (XPS) scan of a PAH-coated slide. We assign the two components of the peak to the protonated (401.0 eV) and neutral (398.9 eV) amines within the polymer coating, consistent with values reported in the literature. (11,49−51) We also recorded the Au 4f spectra for bare, thin PAH-coated, and thick PAH-coated Au NI slides (Figure S4) and noticed a decrease in the amount of oxidized species in the PAH-coated Au compared to bare Au. We hypothesize this is either due to a donation of electrons from the amines of PAH to the surface Au atoms or by the passivation of edge and corner sites on the Au NI following PAH functionalization.

4-Nip Reduction Kinetics
The reduction of 4-nitrophenol (4-Nip, Scheme 2) by transfer hydrogenation serves as a common model reaction to study the activity of NPs. (7,52−57) The reactant carries a negative charge during the reaction in basic conditions, pH 10.4 (becoming 4-nitrophenolate), and so it is a good candidate for studying electrostatic effects around the catalyst. The reaction is tracked by monitoring the absorption of 4-nitrophenolate at 400 nm.

Scheme 2. Reduction of 4-Nitrophenol by Sodium Borohydride in Water at Room Temperature, Catalyzed by Au NPs; the Hydroxyl is Deprotonated at the Typical Reaction pH
Note that the NIs are slightly embedded in glass. (42)

To measure the initial rates of 4-Nip reduction catalyzed by bare and modified Au NI slides, we utilized a temperature-controlled cell-changer spectrophotometer attachment to capture parallel time-resolved kinetic trials at 22 °C. Two control reactions were performed without a catalyst for each entry, producing no reaction in every trial. Interestingly, we did not observe the commonly reported induction period at the beginning of the reaction in any of the trials. The reaction vessel (a cuvette) was stirred at 750 rpm, which may have aided the already catalytically enhanced process of dissolved oxygen removal that is responsible for the induction time. (58) The reaction was treated as pseudo-first order (53,56,57) toward 4-Nip (Section 6.1.3, Supporting Information), with borohydride in excess, using the rate law shown in eq 1.

$$\frac{d[\text{4-Nip}]}{dt} = -k[\text{NaBH}_4][\text{4-Nip}] = -k_{\text{app}}[\text{4-Nip}]$$

(1)

$$\ln[\text{4-Nip}] = \ln[\text{4-Nip}]_0 - k_{\text{app}}t$$

(2)

To find $k_{\text{app}}$, we plot the natural log of [4-Nip] vs. time (t), in accordance with eq 2, the solution for the rate law. The initial linear region was used to obtain the apparent rate constant, $k_{\text{app}}$. The results are summarized in Table 1 and discussed in detail below. All kinetic traces are shown in the Supporting Information.

Table 1. Apparent Rate Constants for 4-Nip Reduction.

<table>
<thead>
<tr>
<th>entry</th>
<th>material</th>
<th>$k_{\text{app}} \times 10^{-4}\text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>bare Au NI</td>
<td>$3.6 \pm 0.8^b$</td>
</tr>
<tr>
<td>2</td>
<td>Au NI–PAH from 2 M NaCl deposition</td>
<td>$8.2 \pm 1.7^b$</td>
</tr>
<tr>
<td>3</td>
<td>Au NI–PAH from 0 M NaCl deposition</td>
<td>$10.0 \pm 0.6$</td>
</tr>
<tr>
<td>4</td>
<td>Au NI–PAH/PSS</td>
<td>$3.64 \pm 0.08$</td>
</tr>
<tr>
<td>5</td>
<td>bare Au NI + 0.5 M NaCl</td>
<td>$3.3 \pm 0.4$</td>
</tr>
<tr>
<td>6</td>
<td>Au NI–PAH +0.5 M NaCl</td>
<td>$8.6 \pm 1.0$</td>
</tr>
<tr>
<td>7</td>
<td>Au NI–PEI</td>
<td>$8.5 \pm 0.3$</td>
</tr>
<tr>
<td>8</td>
<td>Au NI–cysteamine</td>
<td>$1.4 \pm 0.7$</td>
</tr>
</tbody>
</table>

The reaction was performed in water at 22 °C with initial concentrations of [4-Nip] = 50 μM and [NaBH$_4$] = 10 mM.

* Means and standard deviations of four replicates each, determined using the method of initial rates for pseudo-first-order kinetic traces.

b Eight replicates.

PAH More Than Doubles the Initial Reaction Rate (Entries 1 and 2; Scheme 3)

Au NI–PAH slides displayed a 128% increase in the initial rate of 4-Nip reduction compared to bare Au NI slides. The kinetic traces are displayed in Figure 2, which also shows that this is a kinetic rather than thermodynamic effect, as both bare and Au NI–PAH slides produce the same overall conversion by the end of the trial. We propose four potential enhancement mechanisms: (i) favorable interaction
between the PAH and the reactants increases the local concentration of 4-Nip and/or BH$_4^-$ near the catalytically active surface of the Au; (ii) the cationic microenvironment created by the polyelectrolyte screens the electrostatic repulsion between the reactants; (iii) the cationic amines create an image charge in the gold and generate a strong electric field between the ion and the image charge, which has been proposed to affect catalysis; (59,60) or (iv) the ligands alter the binding strength of the incoming reactants to accelerate either the substrate adsorption or product desorption steps. (61) The effect remains present even when the catalysts are reused (Table S3). Au NI–PAH slides showed no decrease in apparent rate constant for a second reaction trial compared to a 44% decrease for bare Au NI slides, an effect we suggest arises from product deposition/catalyst poisoning that is minimized by the PAH coating. The stability of the catalyst and its PAH coating under the reaction conditions was additionally verified through XPS and XRD analyses (Section 7, Supporting Information), where no changes to the structure of the Au NIs as well as the presence of the PAH layer following the reaction were observed. The LSPR spectra of bare and PAH-coated Au NI slides show no meaningful change in the intensity of the LSPR maxima. Bare Au NI slides show no change in the LSPR maximum wavelength, while PAH-Au NI slides show a slight blueshift following the reaction, indicating partial removal of the ligand.

![Figure 2](image-url)

Figure 2. Time-resolved catalytic reduction of 4-Nip by Au NI–PAH and bare Au NI slides. The traces shown are averages of eight replicate trials. Standard deviation is represented by the shaded regions around each trace.

To further probe the enhancement, we performed kinetic trials at a range of temperatures and analyzed them based on the linearized Arrhenius eq 3, where $E_a$ is the activation energy, and $A$ is the pre-exponential factor.

$$\ln k_{app} = -\frac{E_a}{RT} + \ln A$$

(3)

The resulting Arrhenius plots can be seen in Figure 3. If the enhancement results purely from local enrichment of 4-Nip at the catalyst surface (a higher effective concentration at the surface), the activation energy should remain unchanged. However, Au NI–PAH and bare Au NI slides produced vastly different activation energies of 34 ± 5 kJ/mol and 15.6 ± 0.8 kJ/mol, respectively. The massive decrease in $E_a$ is accompanied by a large decrease in the value of the pre-exponential factor, as
InA decreases from 6 ± 2 to −0.7 ± 0.3. For surface reactions, Slot et al. recently proposed that the pre-exponential factor relates to the ability of reactants to travel and collide on the surface of the catalyst. (62) In this conceptual framework, it is reasonable for the bulky polymer coating to hinder travel on the surface, and this hindrance partly offsets the gains to catalytic activity from the lower activation energy.

Figure 3. Arrhenius plot for 4-Nip reduction catalyzed by Au NI–PAH and bare Au NI slides at 10, 22, 30, 40, and 50 °C. Each data point is the average of four replicate measurements; the points for 22 °C are the average of eight measurements.

As a further test of the local enrichment hypothesis, we performed 4-Nip reduction at different initial concentrations of 4-Nip. If an increase in local concentration around the catalyst is responsible for the rate enhancement, the difference in the apparent rate constant between Au NI–PAH and bare Au NI slides should be greater at low concentrations. This was not the case—Figure 4 shows that $k_{app}$ is largely independent of the concentration of 4-Nip in the range tested (1–175 μM), for both Au NI–PAH and bare Au NI catalysts.

Figure 4. Dependence of $k_{app}$ on the concentration of 4-Nip.

PAH Layer Thickness Affects Catalysis (Entries 2 and 3)
As an additional test of the local enrichment hypothesis, we reasoned that a thinner polymer coating would act as a smaller reservoir and therefore produce weaker enhancement. The ionic strength of the
PAH deposition solution determines the thickness of the resulting polymer layer, with higher salt concentrations leading to thicker layers. (45) This is explained by the incorporation of anions (here, chlorides) into the layer, allowing the polymer to adopt a more folded conformation by screening the electrostatic repulsion between the amine groups, a concept depicted in Scheme 4. Our initial PAH coating was deposited from a 2 M NaCl solution, and so we now deposited PAH from a solution without added salt. The difference in thickness is reflected in a smaller redshift of the LSPR peak for the thinner layer (Table S2). The Jung-Campbell eq 4 can be used to estimate the thickness of the adsorbed polymers, where \( R \) is the wavelength shift of the LSPR maximum, \( m \) is the refractive index sensitivity (RIS, 38 ± 2 nm/RIU for our Au NI, see Supporting Information), \( \Delta \eta \) is the difference in the refractive index of the surrounding medium (about 0.5 for air vs organic ligand), \( d \) is the thickness of the adsorbed layer, and \( l \) is the effective decay length of the evanescent plasmon field. (41,63,64)

\[
R = -m \Delta \eta \left[ 1 - e^{-d/l} \right]
\]

(4)

Scheme 4. Representation of the PAH Layer without Added Counterions during Ligand Deposition (Left) and When 2 M NaCl Was Used during Ligand Deposition (Right); PAH Layers Not to Scale

Kedem et al. found a correlation between \( l \) and the average major axis of Au NIs. (41) Extrapolating this trend to the size of our Au NI (14 nm major axis), we estimated a value of 2 nm for the effective decay length. Using the average values for \( R \) presented in Table S2, we calculated that PAH from a 2 M NaCl deposition solution formed a 0.54 nm thick layer, while PAH from a 0 M NaCl deposition solution formed a 0.20 nm thick layer.

Perhaps surprisingly, the thin Au NI–PAH slides produced higher initial rates (entry 3) than the thicker layer; two potential explanations for this observation are that the thinner layer is more permeable to 4-Nip and that the lower counterion (chloride) concentration inside the PAH produces a more positive environment, leading to stronger electrostatic effects. The Cl 2p signals from the XPS spectra of the thick Au NI–PAH samples (those obtained from a 2 M NaCl deposition solution) contain a peak at 197.3 eV corresponding to Cl– present in the polymer coating; this component is significantly lower in area in the thin Au NI–PAH samples (Figure S6), confirming that the added salt is incorporated into the structure of the polymer coating.

Given this finding, along with the reduced activation energy and lack of dependence on 4-Nip concentration, we reject the local enrichment hypothesis as an explanation for the observed rate enhancement.
Additional Negatively Charged Polymer Layer Eliminates the Enhancement (Entry 4; Scheme 3)
PAH is commonly used to create multilayer coatings, alternating with a negatively charged polyelectrolyte such as poly(4-styrenesulfonic acid) (PSS). We hypothesized that adding a PSS layer will reduce the observed rate enhancement for two main reasons: (i) the negative charges will partially neutralize the positive charges of PAH and (ii) the PSS layer will serve as an electrostatic and a steric barrier to 4-nitrophenolate. Negatively charged ligands have been shown to inhibit 4-Nip reduction. (35) Indeed, Au NI–PAH/PSS slides produced an average initial rate identical to that of bare Au NI slides.

Ionic Strength of the Reaction Solution Does Not Affect the Enhancement (Entries 5 and 6)
To probe the possibility that the PAH layer helps screens the repulsion between 4-Nip and borohydride at the surface of the catalyst, we repeated the experiment with a high concentration (0.5 M) of sodium chloride, which should screen the interactions between 4-nitrophenolate, borohydride, and the amine-coated Au NI surface. The added salt does not meaningfully change the activity for the uncoated catalyst (entries 1 and 5), indicating that electrostatic repulsion between reactants is not rate limiting. More surprisingly, the salt does not affect the activity of the PAH-coated catalysts either (compare entries 2 and 6); this observation makes it less likely that direct attraction between amines and the reactants is the key to the acceleration effect, as the attraction would be at least partially screened by the counterions. It is possible, however, that the confined environment inside the polymer coating prevented the formation of counterion (sodium) shells around the reactants and that the reactants were able to simply displace the chlorides interacting with the ammonium groups. Determination of the exact binding mode of reactants inside the polymer coating is an extremely difficult challenge, beyond the scope of this work. However, we do not expect the added counterions to have an effect on amines directly bound to the Au surface, and these may be responsible for the change in catalytic activity. The amine-gold bonds might produce image charges in the Au and strong electric fields at the surface, affecting catalysis. (60)

PEI Also Increases 4-Nip Reduction (Entry 7)
The enhancement is not exclusive to PAH coatings. We also functionalized Au NI slides with a similar cationic polyelectrolyte, poly(ethyleneimine) (PEI), with a branched structure containing primary, secondary, and tertiary amines. We observed a similar degree of enhancement to that produced by PAH, likely through the same mechanism.

Thiolated Amine Inhibits Catalysis (Entry 8)
We coated Au NIs with the small organic molecule 2-aminoethanethiol hydrochloride (cysteamine), which binds to the Au through the thiol moiety. Cysteamine significantly inhibited the initial rate of 4-Nip reduction, in line with our previous work on small-molecule thiolated ligands. (10)

4-Nitroaniline Reduction
The reduction of 4-nitroaniline (4-NA) to p-phenylenediamine (Scheme 5) proceeds under the same conditions as 4-Nip reduction, with the only difference being a substitution of the hydroxyl group in the reactant for an amine. Unlike the negatively charged 4-Nip, 4-NA is neutral under our basic reaction
conditions (pH 10.4), and this important distinction between the two nitroarenes allows us to directly explore the role played by the electrostatic charge of the reactant. Conducting the catalytic reaction, we saw a 36% increase in the initial rate of 4-NA reduction for Au NI–PAH slides compared to their bare counterparts (Table 2). Though 4-NA is neutral, the other participant in this reaction, borohydride, is anionic, as are its various products (including hydrides), and so an electrostatic effect is still expected.

Table 2. Apparent Rate Constants for 4-NA Reduction by Au NI–PAH and Bare Au NI Slides

<table>
<thead>
<tr>
<th>entry</th>
<th>material</th>
<th>$k_{app} \times 10^{-4} \text{s}^{-1}$a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>bare Au NI</td>
<td>7.5 ± 0.4</td>
</tr>
<tr>
<td>2</td>
<td>Au NI–PAH</td>
<td>10.2 ± 0.8</td>
</tr>
</tbody>
</table>

aMeans and standard deviations of four replicates each, determined using the method of initial rates for pseudo-first-order kinetic traces. The reaction was performed in water at 22 °C with initial concentrations of [4-NA] = 50 μM and [NaBH₄] = 10 mM.

ABTS Oxidation

In order to explore this effect further and determine if it is generalizable, we studied another redox reaction using a negatively charged substrate. The catalytic activity of Au NPs is often tested with the oxidation of ABTS (Scheme 6), serving as a common probe for peroxidase-like activity. (65−70) The large size of ABTS compared to 4-Nip also tests the permeability of the PAH layer to bulkier catalytic substrates.

ABTS was oxidized by hydrogen peroxide in the presence of bare and PAH-coated Au NI catalysts for 45 min. Control reactions were performed in the absence of a catalyst. It can be seen in Table 3 that Au NI–PAH slides produced double the apparent rate constant for ABTS oxidation compared to bare Au NI slides, demonstrating that the polyelectrolyte-driven enhancement is present for two different classes of reactions: transfer hydrogenations and oxidations. A key difference between these two reactions is the charge of the products. Though both reactants, 4-nitrophenolate and ABTS, carry negative charges, 4-aminophenol is mostly neutral at the reaction pH (71) while oxABTS remains negatively charged. This
could possibly affect the ability of the products to desorb from the surface of the catalyst and diffuse out through the positively charged polymer shell. Additionally, while the reductant for 4-Nip is the anionic borohydride, for ABTS, the neutral oxidizer H2O2 is used. The enhancement observed for ABTS oxidation suggests that electrostatic interaction between PAH and borohydride is not the main reason for the enhancement seen in 4-Nip reduction. This suggestion is bolstered by the finding for 4-NA reduction (vide supra), where we only observed a mild enhancement. The high activity toward ABTS oxidation also proves that the PAH layer is sufficiently permeable for this large reactant, a somewhat surprising finding, which is highly promising for the future application of such catalyst modifications to a broad range of reactions.

Table 3. Apparent Rate Constants for the 45 min Conversion of ABTS to oxABTS, Uncatalyzed and Catalyzed by Au NI–PAH and Bare Au NI Slides

<table>
<thead>
<tr>
<th>entry</th>
<th>material</th>
<th>( \dot{k}_{\text{app}} \times 10^{-8} \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no catalyst</td>
<td>6 ± 3</td>
</tr>
<tr>
<td>2</td>
<td>bare Au NI</td>
<td>600 ± 60</td>
</tr>
<tr>
<td>3</td>
<td>Au NI–PAH</td>
<td>1200 ± 300</td>
</tr>
</tbody>
</table>

*a*Means and standard deviations of four replicates each, determined using the method of initial rates for pseudo-first-order kinetic traces. The reaction was performed in water at 22 °C with initial concentrations of [ABTS] = 2 mM and [H2O2] = 111 mM.

TMB Oxidation

Similar to the comparison between the anionic 4-Nip and the neutral 4-NA, we wanted to compare the oxidation of ABTS to that of a neutral, similarly bulky reactant. We chose the oxidation of 3,3’,5,5’-tetramethylbenzidine (TMB, Scheme 7), a neutral molecule which is known to be oxidized by hydrogen peroxide in the presence of Au NP catalysts. (72) TMB was reacted with hydrogen peroxide in the presence of Au NI–polymer hybrid and bare Au NI slides catalysts for 30 min. Control reactions were performed in the absence of a catalyst to determine a baseline rate for the reaction conditions. The results in Table 4 show no meaningful difference in the initial rate of TMB oxidation between Au NI–PAH and bare Au NI slides. In this reaction, neither the reactant (TMB) nor the reagent (H2O2) are negatively charged, and so the lack of enhancement strongly points to electrostatic interaction as central to the effect.

![Scheme 7. Oxidation of TMB to the Diimine Product by Hydrogen Peroxide in the Presence of Au NPs](image)

*The production of the charge transfer product was used for initial rate measurements.*

Table 4. Apparent Rate Constants for the 30 min Conversion of TMB to the Charge–Transfer Complex, Uncatalyzed and Catalyzed by Au NI–PAH and Bare Au NI Slides

<table>
<thead>
<tr>
<th>entry</th>
<th>material</th>
<th>( \dot{k}_{\text{app}} \times 10^{-5} \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no catalyst</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>bare Au NI</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Au NI–PAH</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions
We have demonstrated that our Au NI–polymer hybrids show increased catalytic activity for both transfer hydrogenation and oxidation reactions compared to bare Au NIs. The effect appears to depend strongly on the electrostatic charge of the reactants, as anionic substrates exhibit the strongest degree of enhancement. The rate increase results from a drastic reduction in activation energy, which is partially countered by a lowering of the pre-exponential factor in the Arrhenius relation, likely the result of hindered transport within the polymer-Au interface. The origin of the lowered activation energy requires further study but may result from enrichment of electrons or generation of a strong electric field at the Au surface; modification of the binding strength to promote reactant binding or product desorption (Sabatier principle); or electrostatic stabilization of a transition state. While previous studies probed the effect of organic coatings on selectivity, their examination of activity was limited to comparisons between ligands (which might be inhibitory to different degrees), and so was unable to establish clear evidence for the absolute enhancement of activity by a ligand. Our study suggests that engineering the microenvironment of catalysts to generate favorable interactions at the catalyst-reactant interface can play an important role in heterogeneous catalysis. The high activity observed, even for large reactants like ABTS, indicates that polymers with multiple, weakly bound attachment points still produce a highly accessible catalytic surface. This finding will guide future work on catalytic NP-polymer hybrids. Further work is required to understand the precise origins of the effect observed here and to utilize it and other potential catalyst-reactant interactions (e.g., hydrophobic, polar, π-stacking) to create superior NP-based catalytic materials for a wide range of synthetic applications. More active catalysts, requiring lower reaction temperatures, will enable significant energy savings, crucial to reducing our carbon footprint.

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.3c04087.

Description of Au NP synthesis; UV–vis spectrum of the colloidal Au NP solution; dynamic light scattering measurements and concentration calculation of Au NPs; TEM image of the Au NP solution; detailed fabrication procedure of Au NI slides; XPS measurements; LSPR peak wavelength shifts for functionalized Au NI slides; description and plot of the refractive index sensitivity of Au NI slides; and full spectra from the catalytic reactions including controls (PDF)

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Acknowledgments

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References


32. Zaera, F. Designing Sites in Heterogeneous Catalysis: Are We Reaching Selectivities Competitive With Those of Homogeneous Catalysts? *Chem. Rev.* 2022, 122, 8594–8757, DOI: 10.1021/acs.chemrev.1c00905


70. Lin, Y.; Huang, Y.; Ren, J.; Qu, X. Incorporating ATP into Biomimetic Catalysts for Realizing Exceptional Enzymatic Performance over a Broad Temperature Range. NPG Asia Mater. 2014, 6, e114 DOI: 10.1038/am.2014.42