Nanoporosity-Enhanced Catalysis on Subwavelength Au Nanoparticles: a Plasmon-Enhanced Spectroscopic Study

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Supporting Information

ABSTRACT: Using surface-enhanced Raman spectroscopy (SERS) to monitor catalytic reactions in real time on Au nanocatalysts has been a significant challenge because plasmon-enhanced spectroscopies require the utilization of subwavelength Au nanostructures as substrates while heterogeneous catalysis requires small Au nanoparticles in the sub-5 nm size regime. Here, we show that subwavelength Au nanoparticles with nanoscale surface porosity represent a unique bifunctional nanostructure that serves as both high-performance SERS substrates and efficient surface catalysts, allowing one to unravel the kinetics and pathways of surface-catalyzed reactions with unprecedented sensitivity and detail through time-resolved plasmon-enhanced spectroscopic measurements. The origin of the nanoporosity-enhanced catalytic activity can be interpreted as a consequence of high abundance of undercoordinated surface atoms at the edges and corners of the highly curved surfaces of Au porous nanoparticles. By measuring SERS signals from the monolayer molecules preadsorbed on the surfaces of Au porous nanoparticles, we have been able to gain quantitative new insights into the intrinsic kinetics and mechanisms of Au-catalyzed hydrogenation of aromatic nitro compounds with minimal complication introduced by the molecular diffusion, adsorption, and desorption.

INTRODUCTION

Au nanoparticles have attracted immense attention because of their intriguing size- and shape-dependent catalytic and optical properties.1−4 Distinct from Au bulk materials that are chemically inert, Au nanoparticles with diameters smaller than 5 nm exhibit remarkable catalytic activities toward a variety of oxidation and hydrogenation reactions even under mild conditions such as ambient temperature and pressure,5−11 whereas Au particles with characteristic dimensions beyond 5 nm are found to be catalytically inactive. When used for heterogeneous catalysis, the catalytically active small Au nanoparticles are typically supported on high-surface-area oxide materials.5,6,12−14 These supports can significantly enhance the synergetic catalytic performance of the hybrid materials through various mechanisms,15−18 making it extremely challenging to delineate the role of the supports and the intrinsic catalytic activities of Au. Using colloidal Au nanoparticles as free-standing, unsupported catalysts, compelling evidence on the intrinsic, size-dependent catalytic activities of Au nanoparticles has been obtained.19−21 It has become increasingly evident that the undercoordinated surface atoms located at the particle edges and corners provide a key contribution to the catalytic activities of sub-5 nm Au nanoparticles.5,22−25 Interestingly, macroscopic dealloyed nanoporous Au membranes without any support exhibit similar catalytic activities as the oxide-supported sub-5 nm Au nanoparticles even though the feature lengths of their nanopores and ligaments are far beyond 5 nm.25−31 The origin of such exceptionally high catalytic activity has been interpreted, based on high-resolution electron microscopic observations, as a result of the high fraction of undercoordinated surface atoms, comparable to that of sub-5 nm nanoparticles, present on the highly curved surfaces of the dealloyed nanoporous Au membranes.32

The development of detailed mechanistic understanding of Au-based heterogeneous catalysis requires the capabilities not only to fine-control the dimensions and surface structures of Au nanocatalysts but also to precisely monitor, in real time, the reaction kinetics and molecular transformations occurring at the reactant-catalyst interfaces. Surface-enhanced Raman spectroscopy (SERS) provides a unique approach to the in situ monitoring of molecular transformations in heterogeneous catalysis with high detection sensitivity, excellent surface selectivity, and rich molecular structural information.33−41 By measuring the SERS signals from monolayer molecules preadsorbed on the nanocatalyst surfaces, unraveling the intrinsic kinetics and mechanisms of surface-catalyzed reactions becomes possible with minimal complication introduced by the surface-capping ligands as well as the diffusion, adsorption, and desorption of reactants and products. The unique capability of SERS to resolve detailed molecular structures further enables the identification of transient intermediates along the reaction.
pathways. Using SERS to directly monitor catalytic reactions on Au nanocatalysts, however, has been challenging because SERS and catalysis require Au nanoparticles in two drastically different size regimes. SERS relies on intense plasmon-field enhancements in close proximity to the particle surfaces, which are not achievable on the catalytically active sub-5 nm Au nanoparticles. While Au nanoparticles in the subwavelength size regime exhibit strong plasmon resonances and intense local field enhancements exploitable for SERS, they are no longer catalytically active. It has been recently demonstrated that the in situ monitoring of surface-catalyzed reactions by SERS becomes possible only when catalytically active small nanoparticles of Au, Pt, or Pd and plasmonically active large Au nanoparticles are hierarchically assembled into three-dimensional multilayered complex superstructures. The structural complexity of these bifunctional hybrid particles, however, makes it challenging to directly correlate the surface structures with the catalytic activities of the nanocatalysts.

Here we study the nanoporosity-enhanced catalytic activities of subwavelength Au nanoparticles using the hydrogenation of $p$-nitrophenol by sodium borohydride as a model reaction. The introduction of nanoscale surface porosity to subwavelength Au nanoparticles dramatically enhances not only the tunability of plasmon resonance frequencies but also the near-field intensities, making the Au porous nanoparticles (PNPs) ideal substrates for single-particle SERS. In addition, Au PNPs possess highly curved surfaces rich of undercoordinated atoms at the surface steps and kinks, well-mimicking the surfaces of the sub-5 nm nanoparticles and dealloyed nanoporous Au membranes. Therefore, Au PNPs exhibit drastically enhanced catalytic activities compared to the Au quasi-spherical nanoparticles (QSNPs) of the same sizes. Furthermore, the monometallic Au PNPs are compositionally simpler than the dealloyed nanoporous Au membranes containing residual less-noble elements, such as Ag, that cannot be completely removed through the dealloying process. The catalytic activity of the dealloyed nanoporous Au membranes strongly depends on the amount and spatial distribution of the residual Ag, though the exact roles of the residual Ag still remain unclear. The compositional simplicity of free-standing Au PNPs allows us to build direct correlations between the surface structures and the intrinsic catalytic activities without the complication due to the effects of oxide supports and residual less-noble elements. As demonstrated in this work, the unique dual functionality of Au PNPs as both substrates for plasmon-enhanced spectroscopy and efficient surface catalysts enables detailed, quantitative spectroscopic study of the intrinsic kinetics and mechanisms of surface reactions on Au nanocatalysts.

**RESULTS AND DISCUSSION**

Subwavelength Au PNPs were fabricated using a versatile, room-temperature, seed-mediated growth method we recently developed. This approach allows for the selective fabrication of various Au nanostructures, such as QSNPs, PNPs, and
trisoctahedral (TOH) nanoparticles, through deliberate control over the particle growth kinetics. As demonstrated in detail in our previous publication, fast nanoparticle growth resulted in the selective formation of single-crystalline TOH nanoparticles enclosed by high index \{221\} facets, whereas slow nanoparticle growth favored the formation of multi-twinned QSNPs enclosed by thermodynamically stable low index \{111\} and \{100\} facets. The Au PNPs were found to be a unique structure resulting from the intermediate particle growth kinetics that fell between the kinetically favored regime and the thermodynamically controlled regime. As schematically illustrated in Figure 1A, we started with colloidal Au seeds prepared by reducing chloroauric acid (HAuCl₄) with sodium borohydride (NaBH₄) in the presence of cetyltrimethylammonium chloride (CTAC). As shown in Figure S1 in the Supporting Information, the as-prepared Au seed particles were 2 ± 0.2 nm in diameter and no plasmon resonance peak was observed in the optical extinction spectrum due to the small particle sizes. The growth of the Au PNPs was initiated by injecting various volumes of diluted Au seeds into the particle growth solution, which contained HAuCl₄, CTAC, and appropriate amount of L-ascorbic acid (AA). Addition of HCl into the growth solution significantly slowed down the growth of the nanoparticles, leading to the formation of Au QSNPs. The average sizes of the PNPs and QSNPs can be both fine-controlled in the range from ~50 nm to ~250 nm by simply adjusting the amount of Au seeds added into the growth solution. Figures 2B–E show the scanning electron microscopy (SEM) and bright-field transmission electron microscopy (TEM) images of the Au PNPs and QSNPs with the same average overall particle size around 125 nm. While the QSNPs exhibited relatively smooth, multifaceted surfaces, the surfaces of the PNPs were porous and highly curved with pore diameters in the range from 5 to 30 nm. In this study, we used the PNPs and QSNPs of the same overall size (125 nm) to systematically investigate the effects of the nanoscale surface porosity on the catalytic activities of the subwavelength Au particles.

The catalytic hydrogenation of p-nitrophenol by NaBH₄ was used as a model reaction to quantitatively evaluate the catalytic activities of subwavelength Au PNPs, QSNPs, and 2 nm Au seeds. In a basic environment, p-nitrophenolate ions gradually decreased as the catalytic reduction reaction proceeded in the presence of NaBH₄ and Au nanocatalysts (Figure 2A). Meanwhile, a new absorption band emerged at ~315 nm and became progressively more intense, indicating the formation of the product, p-aminophenol. The intensities of the absorption peak at 400 nm were used to quantify the concentration of p-nitrophenol as a function of reaction time, based on which the reaction kinetics was analyzed. In Figure 2B, we directly compare the kinetics of the reactions catalyzed by the Au seeds, PNPs, and QSNPs with the same particle concentration at 3.0 × 10⁸ particles mL⁻¹. For all these experiments, the initial concentrations of p-nitrophenol and NaBH₄ were kept at 66.7 μM and 16.7 mM, respectively. In the absence of Au nanoparticles, no reaction was observed over extended time periods up to a few days. At the same nanocatalyst concentration, the Au PNPs exhibited much higher catalytic activity than the Au QSNPs. The 2 nm Au seeds, which were expected to be highly active as catalysts, also showed much slower reaction kinetics than the Au PNPs because of the much smaller total surface areas available for catalysis. Interestingly, an induction time in which no reduction took place, was observed regardless of the sizes and morphologies of the Au nanocatalysts. This induction time was previously observed in the p-nitrophenol reduction catalyzed by other Au nanostructures as well, which was hypothetically ascribed to the time required for p-nitrophenol to diffuse and adsorb onto the Au surfaces or the molecular
adsorption-induced surface restructuring of the Au nanocatalysts before the reaction could be initiated. We also adjusted the particle concentrations to compare the reaction kinetics in the presence of nominally the same total surface area of the nanocatalysts. As shown in Figure 2C, with the same total surface area, Au seeds exhibited the highest catalytic activity, and the Au PNP were still catalytically much more active than the Au QSNP. Therefore, the nanoporosity-enhanced catalysis observed on the subwavelength Au nanoparticles should be interpreted as a result of not only the much larger surface areas per particle but also, more essentially, the higher reactivity of the highly curved nanoporous surfaces of Au PNP.

To gain further insight into the nanoporosity-enhanced catalytic activity, we used high-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) to resolve the atomic-level surface structures of Au PNP. The central panel of Figure 3 shows a HAADF-STEM image of one individual Au PNP, which exhibited porous and highly curved surface structures. Each Au PNP consisted of several monocrystalline domains packed together to form a twinned crystalline structure. HAADF-STEM images from four different monocrystalline regions labeled as i, ii, iii, and iv in the central panel, respectively, are shown with higher magnification in Figure 3. The crystalline domains in these four regions were all imaged with the electron beam projected along the [110] zone axis, and the fast Fourier transform (FFT) patterns further confirmed the orientation and single-crystalline nature of each domain. Exposed facets with Miller indices of {100} and {111} were observed on relatively flat local regions, whereas at surfaces with convex or concave curvatures, a series of high-index facets with high densities of atomic steps and kinks were observed. The orientation of the high-index facets appeared to be highly localized and essentially defined by the local surface curvature. Although the overall characteristic dimensions of the nanopores and protrusions on the surfaces of the Au PNP were much larger than 5 nm, the surface atomic steps and kinks well-mimicked the local surface structures of the catalytically active sub-5 nm Au nanoparticles. The Au PNP also exhibited similar density of undercoordinated surface atoms on their surfaces in comparison to the dealloyed porous Au membranes. It has been reported that the residual Ag plays a key role in stabilizing the stepped and kinked surfaces of the dealloyed porous Au membranes. In contrast, the Au PNP were monometallic in nature with no residual Ag present on their surfaces. Therefore, the high stability of the atomic steps and kinks on the surfaces of Au PNP can be interpreted most likely as the consequence of the structural integrity of the particles and the surface stabilization by the capping ligand, CTAC.

The Au PNP exhibited extraordinarily robust catalytic activity toward the hydrogenation of 4-nitrophenol by NaBH₄. As shown in Figure 4A, the Au PNP could be recycled after the completion of the hydrogenation reaction and their
The catalytic hydrogenation of \( p \)-nitrophenol is a model reaction that has been widely used for the evaluation of catalytic activities of noble metal nanoparticles. It is known that the catalytic hydrogenation of \( p \)-nitrophenol by borohydride is a multistep process. Borohydride ions first interact with the metallic nanoparticle surfaces and transfer an active hydrogen species to the particle surface to form metal hydrides. Once \( p \)-nitrophenol molecules are adsorbed onto the surface of the nanoparticles, reduction of \( p \)-nitrophenol is induced by the surface hydrogen species. The final step of the catalytic cycle is desorption of the product, \( p \)-aminophenol, from the nanoparticle surfaces. It is worth mentioning that the overall reaction kinetics measured by solution-phase UV–vis absorption spectroscopy strongly depends on the structures and surface properties of the nanocatalysts. Esumi et al. investigated the catalytic activity of bulky dendrimer-stabilized metal nanoparticles and concluded that the reaction was diffusion controlled, whereas Ballau and co-workers showed that the surface reaction became the rate limiting step when polymer-supported small Au nanoparticles were used as the catalysts.

Assuming that the diffusion of the reactants to the nanocatalysts and all the adsorption/desorption steps are much faster than the surface catalyzed reaction step, the catalytic hydrogenation reaction is expected to obey pseudo-first order reaction kinetics in the presence of excess borohydride and the analysis of the kinetic data can be done using the Langmuir–Hinshelwood (LH) model. As shown in Figure 5A, the hydrogenation of \( p \)-nitrophenol started after a certain period of induction time and followed a first-order rate law at the early stage of the reaction in the presence of excessive borohydride. An apparent initial rate constant was obtained through least-squares fitting of the linear part of the curves using the following equation

\[
\ln\left(\frac{A}{A_0}\right) = k_0 \times (t - t_0)
\]

where \( A \) is absorption intensity at 400 nm at particular time spots during the reaction, \( A_0 \) is absorption intensity at 400 nm before the reaction started, \( t \) is the reaction time, \( t_0 \) is the induction time, and \( k_0 \) is apparent initial rate constant.

It is interesting that at later stages of the reaction, significant deviation from the first order rate law was observed, and the apparent rate constant became larger as the concentration of \( p \)-nitrophenol further went down. We hypothesized that the reaction might follow altered pathways at the later stages of the reaction when the coverage of \( p \)-nitrophenol on the surfaces of the Au PNP's became low. The UV–vis spectroscopy results shown in Figure 5A, unfortunately, did not provide further mechanistic insights into the possible reaction pathways.

The reaction kinetics was also found to be sensitively dependent on the concentration of Au PNP's when fixed amounts of \( p \)-nitrophenol and borohydride were introduced. As shown in panels B and C in Figure 5, the rate constant increased with a concomitant decrease in the induction time as the concentration of Au PNP's increased. The acceleration of the reaction at high Au PNP concentrations can be interpreted as a result of increased total surface areas available for catalysis. If we assume that the overall kinetics measured by UV–vis spectroscopy truly reflects the intrinsic kinetics of the surface reactions, the rate constant is expected to be proportional to the total surface area or the concentration of Au PNP's on the basis of the following equation

\[
\frac{dC(t)}{dt} = k_0 C(t) = k^* S C(t)
\]

where \( C(t) \) is the concentration of \( p \)-nitrophenol at time \( t \), \( k_0 \) is the initial rate constant, \( S \) is the total surface area of Au PNP's.
monolayers (SAMs) of 4-nitrothiophenol (4-NTP) molecules adsorbed on colloidal Au PNP s than on the Au QSNPs (see Figure S4B in the Supporting Information). We have previously demonstrated both experimentally and theoretically that the Raman enhancements of 4-aminothiophenol (4-ATP) adsorbed on individual subwavelength Au PNP s are more than 2 orders of magnitude higher than those on Au QSNPs of the same overall particle sizes, approaching enhancement factors on the order of $10^6$ when the plasmon is on resonance with the excitation laser. $^{45}$ Previously published results of finite-difference time-domain (FDTD) calculations $^{45}$ showed that the near-field “hot-spots” for SERS were located precisely at the catalytically active, highly curved particle surfaces of the Au PNP s, providing a unique platform for the monitoring of surface-catalyzed molecular transformations by SERS.

To monitor the kinetics of the hydrogenation reaction using SERS, we immobilized a saturated SAM of 4-NTP (the hydroxyl group of $p$-nitrophenol was substituted with a thiol group) onto the surfaces of Au PNP s through Au-thiol interactions. A confocal Raman microscope was used for the SERS measurements with the laser beam focused into a small volume ($\sim 100$ pL) of the colloidal suspensions of 4-NTP-coated Au PNP s. In this confocal mode, each freely diffusing Au NP was exposed to the excitation laser for a short time period (within the diffusion time), effectively eliminating possible photoreactions of 4-NTP $^{54}$ and photoinduced damage of the samples (see the results of control experiments in the absence of NaBH$_4$ in Figures S5 in the Supporting Information). As shown in Figure 6A, 4-NTP had three characteristic vibrational bands in the SERS spectrum at 1080, 1338, and 1571 cm$^{-1}$, corresponding to C–S stretching ($v_{\text{CS}}$), O–N–O stretching ($v_{\text{NO}}$), and the phenol-ring modes, respectively. $^{37,39,54}$ Upon exposure to 30 mM NaBH$_4$, there was an induction time of $\sim 100$ s during which the SERS features of 4-NTP remained unchanged. Because the 4-NTP molecules were immobilized on the surfaces of Au PNP s, this induction time was apparently not related to the diffusion and adsorption of the 4-NTP and was thus most likely due to the interactions of borohydride ions with the Au surfaces through which active surface hydrogen species were generated. Only when the concentration of the surface hydrogen species was built up to a certain threshold value could the catalytic hydrogenation of the surface-adsorbed 4-NTP be initiated. Once the hydrogenation reaction started, the intensities of both 1338 and 1571 cm$^{-1}$ Raman bands were decreased progressively with the concomitant emergence of a new band corresponding to the phenol-ring modes ($v_{\text{CC}}$) of 4-ATP at 1590 cm$^{-1}$. $^{39,55}$ Raman bands were not related to the diffusion and adsorption of the 4-NTP and was thus most likely due to the interactions of borohydride ions with the Au surfaces through which active surface hydrogen species were generated. Only when the concentration of the surface hydrogen species was built up to a certain threshold value could the catalytic hydrogenation of the surface-adsorbed 4-NTP be initiated. Once the hydrogenation reaction started, the intensities of both 1338 and 1571 cm$^{-1}$ Raman bands were decreased progressively with the concomitant emergence of a new band corresponding to the phenol-ring modes ($v_{\text{CC}}$) of 4-ATP at 1590 cm$^{-1}$.

All the vibrational modes observed in SERS correlate well with the bands in normal Raman spectra of 4-NTP and 4-ATP. $^{57}$ Interestingly, at the intermediate stages of the reaction, Raman modes at 1140, 1388, and 1438 cm$^{-1}$, which could be assigned to the characteristic vibrational modes of 4,4′-dimercaptoazobenzene (DMAB), $^{56,58}$ were clearly resolved, allowing us to identify DMAB as the intermediate along the reaction pathway. We also found that while the SAMs of 4-NTP and DMAB were stable on the surfaces of Au PNP s, the final product, 4-ATP, dissociated from the Au PNP surfaces in the presence of excessive NaBH$_4$ as the characteristic peaks of the $v_{\text{CC}}$ (1080 cm$^{-1}$) and $v_{\text{CS}}$ (1590 cm$^{-1}$) modes of 4-ATP both gradually decreased in intensity upon the completion of the hydrogenation reaction. It has been recently reported that NaBH$_4$ induces desorption of small organothiol molecules from Au nanoparticle surfaces predominantly through organothiol...
displacement by hydride.\textsuperscript{59,60} The SAMs of 4-NTP and DMAB appeared to be more robust against NaBH\textsubscript{4}-induced desorption than those of 4-ATP most likely due to the fact that 4-NTP and DMAB have delocalized electrons distributed over larger conjugation systems than 4-ATP, which may optimize the charge distribution and thus enhance the stability of the surface-adsorbed molecules.\textsuperscript{60} The evolution of the peak intensities of the $v_{\text{NO}}$ mode (1338 cm\textsuperscript{−1}) of 4-NTP, the $v_{\text{NN}} + v_{\text{CC}} + \beta_{\text{CH}}$ mode (1432 cm\textsuperscript{−1}) mode of DMAB, the $v_{\text{CC}}$ mode (1590 cm\textsuperscript{−1}) of 4-ATP, and the $v_{\text{CS}}$ mode (1080 cm\textsuperscript{−1}) as a function of reaction time is shown in Figure 6B. Based on the SERS results, a possible reaction mechanism was proposed and schematically illustrated in Figure 6C. The entire catalytic hydrogenation reaction may involve four key steps: (1) generation of surface-hydrogen species through interactions between borohydride ions and metal surfaces, which gave rise to the induction time; (2) reduction of surface-adsorbed 4-NTP by the surface-hydrogen species to form the intermediate, DMAB; (3) further reduction of DMAB into the final product, 4-ATP; and (4) desorption of 4-ATP from the metallic surfaces.

To further confirm the NaBH\textsubscript{4}-induced desorption of 4-ATP from the surfaces of Au PNP\textsubscript{s}, we first saturated the surfaces of Au PNP\textsubscript{s} with 4-ATP SAMs and then exposed the 4-ATP-coated PNP\textsubscript{s} to 20 mM NaBH\textsubscript{4}. The NaBH\textsubscript{4}-induced 4-ATP desorption could be monitored in real time using SERS, as shown in Figure 7A. The stability of the 4-ATP was found to be highly dependent on the surface curvature of the Au nanoparticles. 4-ATP SAMs formed on Au trisoctahedral (TOH) and elongated tetrahexahedral (ETHH) nanoparticles were much more stable than those on the Au PNP\textsubscript{s} with almost no detectable desorption when exposed to 20 mM NaBH\textsubscript{4} (Figure 7B). Although both Au TOH and ETHH nanoparticles were also enclosed by catalytically active high index facets ({221} for TOH\textsuperscript{61} and {730} for ETHH particles\textsuperscript{62}), their surfaces were relatively flat in comparison to the highly curved surfaces of Au PNP\textsubscript{s} (see Figure S6 in the Supporting Information). The nanoscale curvature of the Au PNP surfaces may decrease the stability of the 4-ATP SAMs, which makes the surface-adsorbed 4-ATP more vulnerable to NaBH\textsubscript{4}. This is in line with previous observation that SAMs of organothiols were more stable on the surfaces of larger Au nanoparticles than on smaller Au nanoparticles.\textsuperscript{60} As shown in Figure 7C, the kinetics of the 4-ATP desorption was also dependent on the concentration of NaBH\textsubscript{4}. Higher NaBH\textsubscript{4} concentration resulted in faster desorption kinetics. Similar to the catalytic hydrogenation reaction, an induction time was also observed during the NaBH\textsubscript{4}-induced 4-ATP desorption, which became shorter as the concentration of NaBH\textsubscript{4} increased.

We chose the O−N=O stretching ($v_{\text{NO}}$) mode of 4-NTP at 1338 cm\textsuperscript{−1} to quantify the fraction of reactant at various reaction times, based on which the kinetics of the reactant consumption was analyzed (Figures 8A). In our SERS measurements, NaBH\textsubscript{4} was in excess and its concentration remained constant throughout the entire reaction process.
Therefore, this surface reaction obeyed pseudo-first-order kinetics and the rate constants could be determined by performing least-squares curve fitting to the reaction trajectories shown in Figure 8A using the following rate equation

$$-\ln\left(\frac{I}{I_0}\right) = k_{app}(t - t_0)$$

where $I$ is intensity of $\nu_{NO}$ mode at particular time spots during the reaction, $I_0$ is intensity of $\nu_{NO}$ mode before the reaction started, $t$ is the reaction time, $t_0$ is the induction time, and $k_{app}$ is apparent first-order rate constant.

The kinetic curves obtained through SERS measurements (Figure 8A) exhibited two remarkable features that were strikingly different from the solution-phase UV–vis spectroscopy results shown in Figure 5. First, the reactions obeyed the first-order rate law throughout the entire reaction process until the complete conversion of 4-NTP to 4-ATP. Second, both the apparent rate constant and the induction time were independent of the concentration of Au PNPs (Figure 8B, C). These features strongly indicate that performing SERS measurements on surface-immobilized reactants allows one to resolve the intrinsic kinetics of the surface-catalyzed reactions with minimal interference from the diffusion, adsorption, and desorption of the reactants and products.

Assuming that the surface-catalyzed hydrogenation is an elementary reaction between the surface-adsorbed BH$_4^-$ and 4-NTP, the apparent rate constant can be described as

$$k_{app} = kS\theta_{4\text{-}\text{NTP}}\theta_{BH_4^-} = a\theta_{BH_4^-}$$

where $\theta_{4\text{-}\text{NTP}}$ and $\theta_{BH_4^-}$ are the relatively degree of surface coverage by 4-NTP and BH$_4^-$, respectively, $k$ is the molar rate constant per unit surface area, $S$ is the surface area of the Au PNPs, and $a$ is a fractional constant. Because a saturated SAM of 4-NTP was preadsorbed on the surfaces of Au PNPs, $\theta_{4\text{-}\text{NTP}}$ was a constant and $k_{app}$ became proportional to $\theta_{BH_4^-}$. In Figure 9A, we show the kinetic curves obtained from time-resolved SERS measurements in the presence of various concentrations of NaBH$_4$. The $k_{app}$ and $t_0$ values as a function of NaBH$_4$ concentrations ($C_{\text{NaBH}_4}$) were plotted in panels B and C in Figure 9, respectively. The $k_{app}$ progressively increased while $t_0$ decreased as $C_{\text{NaBH}_4}$ increased until reaching a plateau at $C_{\text{NaBH}_4}$ above 120 mM. We performed least-squares curve fitting using the Langmuir adsorption isotherm (eq 5) and Hill equation (eq 6), respectively.

$$k_{app} = a\theta_{BH_4^-} = \frac{aC_{\text{NaBH}_4}}{1 + aC_{\text{NaBH}_4}}$$

$$k_{app} = a\theta_{BH_4^-} = \frac{C_{\text{NaBH}_4}^n}{K_a + C_{\text{NaBH}_4}^n}$$
where $\alpha$ and $K_a$ are two constants describing the binding affinities between the molecules and substrates and $n$ is the Hill coefficient rated to the adsorption cooperativity. The major difference between these two models is that Hill equation includes the cooperativity of molecular adsorption whereas the Langmuir monolayer adsorption model does not consider the adsorption cooperativity. The best fitting results obtained using these two models were shown as solid and dash curves in Figure 9B. It is apparent that the Hill equation gave us much better fit to the experimental results than the Langmuir adsorption isotherm. Previous studies showed that the adsorption of NaBH$_4$ onto the polymer-supported $\sim$2 nm Au nanoparticles followed the Langmuir adsorption isotherm. However, our results strongly indicate that the adsorption of NaBH$_4$ onto the surfaces of Au PNP was highly cooperative because the least-squares curve fitting gave a Hill coefficient ($n$) of $2.35 \pm 0.23$, which was much larger than 1. The surface structures of the Au PNP were fundamentally different from the sub-5 nm Au nanoparticles. Although each sub-5 nm Au nanoparticle only has limited surface areas accessible to adsorbate molecules, the total surface area of each subwave-length PNP is much larger and may thus accommodate much larger numbers of molecules. The local curvature of the PNP surfaces may also facilitate the cooperative binding of adsorbate molecules onto the Au surfaces. Although the origin of such adsorption cooperativity still remains unclear, our results clearly indicate that BH$_4^-$ adsorbs onto the nanoporous Au surfaces in a highly cooperative manner.

We have further performed SERS measurements to study the effects of 4-NTP surface coverage on the reaction kinetics. The surface coverage of 4-NTP could be fine-controlled by adjusting the concentration of 4-NTP incubated with Au PNP (Figure 10A and Figure S7 in the Supporting Information). Interestingly, the adsorption of 4-NTP on the surfaces of Au

Figure 9. Effects of NaBH$_4$ concentrations on the kinetics of hydrogenation of 4-NTP adsorbed on Au PNP. (A) Natural logarithms of Raman intensity at 1334 cm$^{-1}$ (normalized against the initial point) as a function of time upon exposure to various concentrations of NaBH$_4$ as labeled in the figure. The error bars represent the standard deviations obtained from five experimental runs. (B) The apparent rate constant ($k_{app}$) and (C) induction time ($t_0$) as a function of NaBH$_4$ concentration ($C_{NaBH_4}$). The least-squares curve fitting results using the Langmuir adsorption isotherm and the Hill equation were shown as dash and solid curves in B, respectively.

Figure 10. Effects of surface-coverage of 4-NTP ($\theta_{4\text{-NTP}}$) on the hydrogenation kinetics. (A) 4-NTP coverages ($\theta_{4\text{-NTP}}$) as a function of 4-NTP concentration ($C_{4\text{-NTP}}$). The least-squares curve fitting results using the Langmuir adsorption isotherm and the Hill equation were shown as dash and solid curves, respectively. (B) SERS spectra collected from 4-NTP absorbed on the surfaces of Au PNP (incubated with 2 $\mu$M 4-NTP, $\theta_{4\text{-NTP}} = 0.47$) at different reaction times of 0, 50, 100, 200, 300, 400, 500, and 600 s upon exposure to 10 mM NaBH$_4$. (C) Natural logarithms of Raman intensity at 1334 cm$^{-1}$ (normalized against the initial point) as a function of time upon exposure to 10 mM NaBH$_4$ for different $\theta_{4\text{-NTP}}$ as labeled in the figure. The error bars represent the standard deviations obtained from five experimental runs. (D) Apparent rate constant ($k_{app}$) and (E) induction time ($t_0$) as a function of $\theta_{4\text{-NTP}}$. 

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PNPs was also found to be cooperative and followed the Hill equation very well with a Hill coefficient of 2.31 ± 0.32, which was extremely similar to that of NaBH₄. Although the cooperative adsorption on the Au PNP surfaces appeared to be general for various adsorbate molecules, whether the cooperative adsorption is a unique feature of the nanoporous surface structures still remains an open question at this stage. In Figure 10B, we show the spectral evolution of 4-NTP adsorbed on Au PNP at a nominal θ₄-NTP of 47% during the catalytic hydrogenation reaction. At this unsaturated 4-NTP coverage, the surface-adsorbed 4-NTP molecules were more separated from each other in comparison to the saturated coverage, and thus the formation of DMAB, which required two 4-NTP molecules in close proximity to each other, was suppressed. No spectroscopic features of DMAB were observed in the SERS spectra during the reaction (Figure 10B), indicating that the hydrogenation reaction might have switched to an alternative reaction pathway. At low 4-NTP coverages, the catalytic hydrogenation reaction may undergo a direct transformation from 4-NTP to 4-ATP or an altered pathway involving extremely short-lived transient intermediates that are not resolvable by the time-resolved SERS measurements. As shown in Figure 10C–E, as the surface coverage of 4-NTP decreased, the rate constant became significantly larger and the induction time became shorter. This can be interpreted as a consequence of larger surface areas available for NaBH₄ adsorption when 4-NTP coverage became lower. The SERS results presented here provide quantitative insights into the 4-NTP coverage-dependent reaction kinetics, which can be used to interpret the deviation from the pseudo-first-order kinetics at late stages of the reactions observed by UV–vis spectroscopy (see Figure 5).

■ CONCLUSIONS

In summary, subwavelength Au PNP possess highly curved, porous surfaces with high abundance of uncoordinated atoms at the surface steps and kinks, well-mimicking the catalytically active surfaces of oxide-supported sub-5 nm Au nanoparticles and deallloyed nanoporous Au membranes. The catalytically active surface structures of the Au PNP were highly robust and the catalytic activity of Au PNP was well-preserved over multiple cycles of catalytic hydrogenation reactions. The Au PNP also provide a compositionally simple, free-standing nanocatalyst system that enables direct correlation of catalytic activities with surface structures without complication introduced by the oxide supports and residual less-noble elements. Meanwhile, the nanoscale surface porosity dramatically enhances the tunability of localized plasmon resonances and optimizes the near-field enhancements of the subwavelength particles for single-particle SERS under near-infrared excitations. Using catalytic hydrogenation of 4-NTP as a model reaction, we have demonstrated that the dual functionality of Au PNP opens up unique opportunities for us to develop detailed, quantitative understanding of the intrinsic kinetics and mechanisms of surface-catalyzed reactions through noninvasive in situ SERS measurements. The knowledge gained through this work provides significant new insights on the structure–property relationship of Au nanocatalysts and sheds light on the kinetics and mechanisms of the interfacial molecular transformations catalyzed by nanoarchitectured Au surfaces.

■ METHODS

Materials. Gold(III) chloride trihydrate (HAuCl₄·3H₂O, ACS grade) was obtained from J.T. Baker. Sodium borohydride (NaBH₄, 99%), hydrochloric acid (HCl, 37%), L-ascorbic acid (AA, 99.5%), and 4-nitrophenol (C₆H₄NO₃, 4-NP, 99%) were obtained from Sigma-Aldrich. Silver nitrate (AgNO₃, 99.995% metals basis), (1-hexadecyl)-trimethylammonium chloride (CTAC, 96%), 4-aminophenol (C₆H₄NO₂, 4-ATP, 97%), and 4-nitrophenol (C₆H₄NO₃S, 4-NTP, 80%) were obtained from Alfa Aesar. (1-Hexadecyl)trimethylammonium bromide (CTAB, > 98%) and sodium oleate (NaOL, >97%) were purchased from TCI America. Ethanol (200 proof) was purchased from Fisher Scientific. All reagents were used as received without further purification. Ultrapure water (18.2 MΩ resistivity, Barnstead EasyPure II 7138) was used for all experiments.

Synthesis of Au PNP and QSNPs. Au PNP and QSNP were prepared following a recently published protocol based on seed-mediated growth in aqueous solution. To prepare colloidal Au seeds about 2 nm in diameter, 0.30 mL of ice-cold, freshly prepared NaBH₄ (10 mM) were quickly injected into a solution containing CTAC (10.00 mL, 0.10 M) and HCl (0.25 mL, 10 mM) under magnetic stirring (1200 rpm). The seed solution was stirred for 1 min, then left undisturbed for 2 h, and finally diluted 1000-fold with CTAC (0.10 M). The particle growth solution was prepared by sequentially adding HAuCl₄ (0.50 mL, 10 mM) and AA (0.10 mL, 0.10 M) into a CTAC (10.00 mL, 0.10 M) solution. To prepare Au PNP with average diameter of ~125 nm, 50 μL of the diluted Au seed solution was added into the growth solution. The reaction solution was gently mixed for 30 s and then left undisturbed at room temperature for 4 h. The obtained Au PNP were washed with water three times through centrifugation/redispersion cycles, and finally dispersed in 4.0 mL of water. The QSNP were fabricated following a similar protocol for the Au PNP except for the addition of HCl. The growth solution was prepared by sequentially adding HAuCl₄ (0.50 mL, 10 mM), HCl (0.20 mL, 1.0 M) and AA (0.10 mL, 0.10 M) into a CTAC (10.00 mL, 0.10 M) solution. After gently mixing the reactants for 30 s, the growth of Au QSNP was initiated by adding 40 μL of the diluted Au seed solution, and then left undisturbed at room temperature for 4 h. The obtained Au QSNP were washed with water three times, and finally dispersed in 4.0 mL of water.

Synthesis of Au TOH and ETNH Nanoparticles. Au TOH nanoparticles were fabricated following a similar protocol for the Au PNP except for the increased amount of AA. The growth solution was prepared by sequentially adding HAuCl₄ (0.50 mL, 10 mM) and AA (1.0 mL, 0.10 M) into a CTAC (10.00 mL, 0.10 M) solution. After gently mixing the growth solution for 30 s, the growth of Au TOH nanoparticles was initiated by adding 15 μL of the diluted Au seed solution, and then left undisturbed at room temperature for 4 h. The obtained Au TOH nanoparticles were washed with water three times, and finally dispersed in 4.0 mL of water.

Au ETHH nanoparticles were prepared following a previously published protocol. Colloidal Au seeds were prepared by the reducing HAuCl₄ with NaBH₄ in the presence of CTAB. First, 5.0 mL of 0.5 mM HAuCl₄ was mixed with 5 mL of 0.2 M CTAB solution. Then, 1.0 mL of ice-cold, freshly prepared 6 mM NaBH₄ was quickly injected into the mixture under magnetic stirring (1200 rpm). The seed solution was stirred for 2 min and then left undisturbed for 30 min before use. To prepare the Au ETHH nanoparticle growth solution, we dissolved 7.0 g of CTAB and 1.23 g of NaOL in 250 mL of water at 60 °C. The solution was cooled to 30 °C and then 24 mL of 4 mM AgNO₃ was added. The mixture was kept undisturbed at 30 °C for 15 min, followed by the addition of 250 mL of 1 mM HAuCl₄. The solution became colorless after 90 min of stirring at 700 rpm and 2.1 mL of HCl (37 wt % in water, 12.1 M) was then introduced into the mixture. After another 15 min of slow magnetic stirring at 400 rpm, 1.25 mL of 64 mM ascorbic acid was added; 0.8 mL of seed solution was injected into the growth solution and the mixture solution was vigorously stirred for another 30 s and then left undisturbed at 30 °C for 12 h for particle growth. The resulting Au ETHH nanoparticles
were collected by centrifugation and finally redispersed in 30 mL of 0.1 M CTAC.

Characterizations. The morphologies and structures of the nanoparticles were characterized by bright-field TEM using a Hitachi H-8000 transmission electron microscope operated at an accelerating voltage of 200 kV. All samples for TEM measurements were dispersed in water and drop-dried on 300 mesh Formvar/carbon-coated Cu grids. The structures of the nanoparticles were also characterized by SEM using a Zeiss Ultraplus thermal field-emission scanning electron microscope. The samples for SEM measurements were dispersed in water and drop-dried on silicon wafers. The atomic level structures of the nanoparticles were resolved by high-resolution HAADF-STEM microscopy equipped with a CEOS CS corrector for the illumination system. The samples for HAADF-STEM measurements were dispersed in water and drop-dried on 400 mesh Cu grids with ultrathin carbon support film. The samples for HAADF-STEM measurements were dispersed in water and drop-dried on silicon wafers. The atomic level structures of the nanoparticles were resolved by high-resolution HAADF-STEM microscopy equipped with a CEOS CS corrector for the illumination system. The samples for HAADF-STEM measurements were dispersed in water and drop-dried on 400 mesh Cu grids with ultrathin carbon support film.

UV–Vis Spectroscopic Measurements of Catalytic Reaction Kinetics. We used the hydrogenation of 4-nitrophenol by NaBH4 at room temperature as a model reaction to evaluate the catalytic activities of Au PNPs, QSNPs, and Au seeds. In a typical procedure, 0.2 mL of 1.0 mM 4-nitrophenol and 0.1 mL of 0.5 M NaBH4 (freshly prepared, ice-cold) were sequentially added to 2.6 mL of ultrapure water in a cuvette and mixed thoroughly. Then, 100 μL of Au NP solution were injected into the system. After thoroughly mixed for 5 s, UV–Vis extinction spectra were collected in real time to monitor the catalytic reaction process. We compared the catalytic activities of Au PNPs, QSNPs, and Au seeds at the same particle concentration (3.0 × 108 particles/mL) and nominally the same surface area (the nanoparticles were resolved by high-resolution HAADF-STEM microscopy equipped with a CEOS CS corrector for the illumination system. The samples for HAADF-STEM measurements were dispersed in water and drop-dried on 400 mesh Cu grids with ultrathin carbon support film (Electron Microscopy Science Inc.). The optical extinction spectra of the nanoparticles were measured on aqueous colloidal suspensions at room temperature, using a Beckman Coulter Du 640 spectrophotometer.

Monitoring Reaction Kinetics by Time-Resolved SERS. To use SERS to monitor the catalytic reactions, we first preadsorbed SAMs of 4-NT onto the surfaces of Au PNPs. In a typical procedure, 500 μL colloidal suspension of Au PNPs with (~1 × 1010 particles mL−1) were incubated with 500 μL ethanol solution of 50.0 μM 4-NT overnight to form saturated SAMs of 4-NT on the nanoparticle surfaces. Then, the 4-NT-coated Au PNPs were centrifuged (3000 rpm, 3 min) and redispersed in ultrapure water. The desorption occurred at room temperature upon the addition of 50 μL of Au nanoparticles, 30 μL of ultrapure water, and 20 μL of 100 mM NaBH4 in a 0.5 mL Eppendorf centrifuge tube. The desorption kinetics was measured in real time using time-resolved SERS. We compared the desorption rates of 4-ATP from Au PNPs, Au TOH, and Au ETHH nanoparticles under same particle concentration (7.5 × 108 particles mL−1) and same NaBH4 concentration (20 mM). We also investigated the desorption rates of 4-ATP from Au PNPs in the presence of various NaBH4 concentrations (10, 20, 30, and 40 mM).

ASSOCIATED CONTENT

Supporting Information

Extinction spectrum and TEM image of ~2 nm Au seeds, HAADF-STEM images of Au PNPs after three cycles of catalytic reactions, extinction spectra of Au PNPs before and after multiple cycles of catalytic reactions, extinction and SERS spectra of Au PNPs and Au QSNPs, SERS spectra of 4-NTP SAMs adsorbed on the Au PNPs in the absence of NaBH4, TEM images and extinction spectra of Au ETHH and TOH nanoparticles, and SERS spectra of 4-NTP adsorbed on Au PNPs at different surface coverages. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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