Surface-Limited Galvanic Replacement Reactions of Pd, Pt, and Au onto Ag Core Nanoparticles through Redox Potential Tuning

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Supporting Information Placeholder

ABSTRACT: Galvanic replacement reactions (GRR) have served as a powerful synthetic strategy to obtain hollow and morphologically-complex bimetallic nanostructures. Extensive work has been done in the literature to vary the synthetic parameters of GRR, but achieving a surface self-limiting galvanic exchange remains challenging. In this work, we tune the extent of GRR between Ag⁰ nanoparticles and Pd, Pt, and Au ions through tailored complexation of metal cations with organic amine and phosphine ligands. Increasing the number of bound organic ligands systematically lowers the reduction potential of the metal ion and therefore the driving force towards GRR with Ag⁰. In each case, we are able to obtain an oxidized metal-ligand complex with sufficiently low GRR driving force to restrict metal deposition to the surface of the Ag core. This synthetic method serves as a general strategy to synthesize bimetallic Ag@AgM or Ag@M (M = Pd, Pt, Au) core-shell nanoparticles and may be extendable to other galvanic replacement reactions of base metal cores with noble metal complexes. By depositing the Pt and Pd atoms only at the surface of the nanoparticle, these materials exhibit good mass-activity in the electrocatalytic hydrogen evolution reaction.

Introduction

Galvanic replacement reactions (GRR) between reduced metal templates and oxidized metal complexes are a synthetically useful strategy to obtain bimetallic nanomaterials of varying composition and morphology.^{1,2} Silver, as the least expensive member of the noble metal family, has been studied extensively as the template metal for depositing Au, Pt, and Pd. Numerous nanostructured morphologies of Ag-Pd, Ag-Pt, and Ag-Au have been synthesized via galvanic replacement, most of which feature hollow or cage-like structures due to etching of the Ag core during GRR.³⁻⁸ For catalytic applications, arresting the galvanic replacement of the catalytically active precious metal to generate a single surface monolayer of metal or metal alloy would be advantageous toward maximizing catalytic utilization and efficiency of the precious metal component.⁹⁻¹¹ However, achieving a surface-limited galvanic replacement reaction remains a significant challenge.

Morphological control in GRR, a particular focus in previous literature examples, has been achieved through the variation of a range of synthetic parameters including metal precursor identity and speciation, size and shape of the template nanoparticle, relative concentrations of metal precursor and template nanoparticle, pH and composition of solvent, time and temperature of exchange, and the addition of coordinating or redox-active species.^{5,12-15} In particular, the identity and oxidation state of the metal halide species has been studied in the GRR of Ag and Pd core nanoparticles in the presence of AuX_n and PtX_n (X = Cl, Br, I) precursors. In work by Gao et al., the galvanic exchange process between Ag cores and Au³⁺ precursors was completely inhibited by moving from AuCl₄⁻ to AuI₄⁻, which shifted the reduction potential of the Au precursor negatively by 0.37 V.^{16,17} In another example by Zhang et al., switching from Cl⁻ to Br⁻ ligands in the Pt precursor enhanced the galvanic replacement process with Pd nanocubes by asymmetrically shifting the redox potentials of both the oxidation and reduction half reactions.¹⁸ Besides the variation of halide precursors, however, relatively little work has been done to more finely tune the driving force for GRR through the use of metal-ligand coordination complexes as the oxidizing agents.

Scheme 1. Comparison of bimetallic morphologies resulting from galvanic replacement of Ag⁰ nanoparticles with Pd, Pt, and Au using (a) conventional halide precursors and (b) metalligand complexes with tunable redox potential.



Based on the phase diagrams for the Ag-Pd, Ag-Pt, and Ag-Au alloys, divergent bimetallic morphologies are anticipated in these three systems (**Scheme 1a**). Ag and Pd are miscible at all compositions, and the Ag-Pd solid solution is more stable than the monometallic structures, which typically results in the formation of hollow Ag-Pd alloy nanoparticles after GRR.^{7,13,19} Ag-Pt, in contrast, is poorly miscible and tends to phase segregate across the majority of compositions, resulting in a variety of phase-segregated morphologies including core-shell nanoparticles, Janus-type nanostructures, and secondary nucleated Pt particles.^{7,20-24} Ag-Au shows intermediate behavior between complete alloying and complete phase segregation. While Ag and Au are miscible across the entire range of compositions, resulting in alloying at moderate Au concentration followed by dealloying at higher Au concentration.²⁵⁻²⁹ Despite

these differences in bimetallic miscibility, we aim to develop a general method to achieve surface-limited galvanic replacement for all three systems through precursor ligand chemistry. We use organic amine and phosphine ligands to modify the redox potential of Pd, Pt, and Au precursor complexes and in doing so, fine-tune the driving force for GRR with the Ag core to selectively generate coreshell structures (Scheme 1b).

Synthetic Strategy

We will first describe the design and synthesis of Pd precursor complexes for the surface-limited Ag GRR, and both the Pt and Au complexes will follow a similar design. Typical galvanic exchange reactions in the literature between Pd²⁺ complexes and metallic Ag take place in aqueous solution with PdCl4²⁻ salts that form a mixture of PdCl_x(OH₂)_y precursors in situ.¹² The standard reduction potential for Pd(OH₂)_{4²⁺} and PdCl4²⁻ complexes are 0.91 V and 0.62 V vs. SHE, respectively (Eq. 1-2), both of which provide a large driving force towards oxidizing Ag⁰ to AgCl or Ag₂O (Eq. 4-5, 7-8).³⁰ As a result, galvanic replacement reactions between these aqueous Pd complexes and Ag⁰ nanoparticles typically proceed until all Pd precursors are consumed or a bulk ~Ag₆₀Pd₄₀ alloy is formed, at which point, the Ag is no longer oxidizable by the Pd²⁺ precursor.^{7,31}

Reduction Half Reactions

$Pd(OH_2)_4^{2+} + 2e^- \rightarrow Pd^0 + 4H_2O$	$E^0 = +0.91$ V vs. SHE (1)
$PdCl_4^{2-} + 2 e^- \rightarrow Pd^0 + 4 Cl^-$	$E^0 = +0.62$ V vs. SHE (2)
$Pd(NH_3)_4^{2+} + 2 e^- \rightarrow Pd^0 + 4 NH_3$	$E^0 = +0.00 V vs. SHE (3)$
Oxidation Half Reactions	
$Ag^0 + Cl^- \rightarrow AgCl + e^-$	$E^0 = -0.22$ V vs. SHE (4)
$2 Ag^{0} + 2 OH^{-} \rightarrow Ag_{2}O + H_{2}O + 2 e^{-}$	$E^0 = -0.34$ V vs. SHE (5)

Full Reactions

$[Pd(OH_2)_4]Cl_2 + 2Ag \rightarrow Pd^0 + 2AgCl + 4H_2O$	$E_{cell} = +0.69 V (7)$
$PdCl_4^{2-} + 2Ag \rightarrow Pd^0 + 2AgCl + 2Cl^-$	$E_{cell} = +0.37 V(8)$
$[Pd(NH_3)_4]Cl_2 + 2Ag \rightarrow Pd^0 + 2AgCl + 4NH_3$	$E_{cell} = -0.22 V (9)$

Switching the Cl⁻ to a stronger binding NH₃ ligand reduces the standard reduction potential for the complex to 0.00 V vs. SHE, which falls below the potential required to oxidize Ag to Ag⁺ (Eq. 3, 6, 9).³² Based on this principle, we will vary the reduction potential of the Pd precursor over a ~600 mV window by systematically exchanging Cl⁻ ligands for oleylamine to form the mixed Pd(OAm)_xCl_y (x = 0–4) complexes in organic solvent.

To prepare the Pd-oleylamine complexes, we first phase-transfer an aqueous K₂PdCl₄ complex into toluene using tetraoctylammonium bromide (TOAB) as the phase-transfer agent. We then add 0– 4 equiv. of oleylamine to the (TOA)₂PdCl₄ complex in toluene and allow the ligand-exchange reaction to proceed for 12 hours. UV-Vis absorption spectra of these in-situ generated Pd-OAm complexes show consumption of the features associated with PdCl₄^{2–} and a blue shift in the d–d transition peak, as anticipated for Pd– amine bond formation (**Figure S1**). All subsequent reactions are carried out in non-coordinating organic solvents in order to ensure that the Pd(OAm)_xCl_y complexes do not further evolve through solvent exchange.

We utilize cyclic voltammetry (CV) and differential pulse voltammetry (DPV) to ascertain the reduction potentials for the benchmark $PdCl_{4^{2-}}$ and $Pd(NH_3)_{4^{2+}}$ complexes in aqueous electrolyte as

well as the Pd(OAm)_xCl_y complexes in THF. Reduction potentials for the benchmark complexes measured by CV in aqueous solution correspond well to the known values from the literature (Figure 1, S2a). Voltammograms in THF solvent were measured with 0.1 M TBAClO₄ electrolyte and an internal ferrocene/ferrocenium (Fc/Fc⁺) reference. Reduction potentials were then converted to the standard hydrogen electrode (SHE) based on literature standards.^{33,34} For the series of Pd(OAm)_xCl_y compounds in THF, complexes with 0 and 1 equiv. OAm were unstable under electrochemical conditions, and the reduction potentials could not be reliably obtained. The complexes with 2-4 equiv. of OAm exhibited reduction potentials between +0.2 V and -0.2 V vs. SHE, shifting systematically to more negative values as the number of bound oleylamine ligands increased (Figure 1, S2b-c). These potentials match closely to the measured and calculated values for the analogous series of $Pd(NH_3)x^{2+}$ complexes. Overall, the reduction potentials of the organic-soluble $Pd(OAm)_xCl_y$ complexes with x = 0-4 span a ~700 mV potential range. While the total GRR driving force between these complexes and Ag⁰ could not be determined because the potential for the oxidation half reaction also shifts in the presence of oleylamine ligands in organic solvent, comparison to the aqueous standard reduction potentials suggests that the GRR reaction would become near thermoneutral at 2-3 equiv. of OAm and unfavorable at 4 equiv. of OAm. The solubility of the resulting AgCl(OAm) complex in toluene may also play a role in the extent of galvanic replacement.5



Figure 1. Measured reduction potentials for $Pd(NH_3)_xCl_y$ and $Pd(OAm)_xCl_y$ complexes in aqueous and THF electrolyte, respectively, and calculated reduction potentials for $Pd(NH_3)_xCl_y$ based on literature stability constants.

The Ag core nanoparticles utilized for all galvanic replacement reactions are ~12 nm in diameter, capped with oleylamine ligands, and highly colloidal in nonpolar solvents such as hexanes and toluene (**Figure S3**).³⁵ To affect the galvanic exchange, we add 0.5 equiv. of each Pd(OAm)_xCl_y (x = 0–3) complex to a 10 mM solution of Ag@OAm nanoparticles in toluene (by nominal Ag at.%) and allow the mixture to stir for 24 hours. At the end of the reaction, we clean away all excess Pd precursor complex through repeated cycles of precipitation and centrifugation in toluene and ethanol.

The galvanic replacement of Pt and Au complexes are carried out in a similar fashion to the Pd example described above. Because the Pt-aquo, Pt-halide, and Pt-ammine complexes show the same trend in standard reduction potential as Pd, varying equivalents of oleylamine are also utilized to tune the redox potential of Pt(OAm)_xBr_y complexes (Eq. S1-S2). In contrast, amine ligands bind much more weakly to Au, so we instead synthesize the phosphine-bound Au(PPh₃)Cl complex, which should exhibit a significantly lower standard reduction potential compared to the halideonly HAuCl₄ or HAuCl₂ complexes due to the strong gold-phosphorus bond (Eq. S3-S4).³⁶⁻³⁹

Structural Characterization

To determine the bimetallic structure of the Ag-Pd, Ag-Pt, and Ag-Au nanoparticles after surface-limited GRR in the presence of metal-ammine and metal-phosphine precursors, we perform a range of structural characterization including elemental mapping, electron microscopy, and X-ray spectroscopy.



Figure 2. (a-d) TEM images of Ag-Pd nanoparticles resulting from 24 h GRR between Ag^0 cores and $Pd(OAm)_xCl_y$ complexes (x = 0–3), (e) Ag and Pd elemental ratios as a function of oleylamine equivalents obtained by ICP-OES and XPS.

Beginning with the Ag-Pd system, low-resolution transmission electron microscopy (TEM) reveals dramatic differences in particle morphology as a function of the number of oleylamine ligands bound to the $Pd(OAm)_xCl_y$ (x = 0–3) precursor. In the absence of oleylamine, hollow nanoparticles with irregular shape are formed at the end of the 24-hour galvanic exchange reaction (**Figure 2a**). Inductively-coupled plasma–optical emission spectroscopy (ICP-OES) of the digested particles indicate a 27:73 ratio of Pd:Ag in the overall sample (**Figure 2e**). Due to the excellent miscibility of Ag and Pd as well as the strong Ag–Pd bond in the bimetallic structure, these hollow nanoparticles are likely to be Ag-Pd solid solutions with a gradient of compositions.

Upon binding of a single oleylamine ligand to the Pd complex, the fraction of hollow and irregularly shaped nanoparticles decreases significantly (**Figure 2b**). On average, only 16% Pd relative to Ag is exchanged into the sample after 24 hours. At 2 and 3 equiv. OAm relative to Pd, the hollowing of the Ag nanoparticles is completely suppressed, and the percentage of Pd exchanged into the sample drops even further to 5% and 3% based on ICP-OES, respectively (**Figure 2c-d**). The overall nanoparticle size distribution in the 3 equiv. OAm sample is similar to that of the original Ag cores, which is indicative of surface-limited galvanic replacement (**Figure S4**). At 4 equiv. OAm, no Pd is detected in the sample, as anticipated based on the very weak oxidation ability of the Pd(OAm)4²⁺ complex (**Figure S5**).

Interestingly, we find that the extent of galvanic replacement using the Pd(OAm)_xCl_y complexes is unaffected by both the amount of Pd precursor as well as the time of reaction, two of the key parameters used in previous studies to tune GRR. Using 2 equiv. of Pd precursor with respect to nominal Ag at.%, four times the concentration in the standard method, an identical quantity of Pd is deposited on the Ag core by the end of 24 h of GRR (**Figure S6**). Reducing the reaction time from 24 h to 1 h likewise does not alter the nanoparticle morphology or amount of Pd deposited during GRR (**Figure S7**). These data suggest that the thermodynamic driving force for the redox reaction is indeed the dominant factor dictating the product composition after GRR, and reactions are selflimiting under these conditions.

In order to characterize the spatial distribution of Ag and Pd within a single nanoparticle, we obtained high-resolution STEM imaging coupled to EDS elemental analysis (Figure 3, S8-S9). In the 1 equiv. OAm sample, which shows a heterogeneous distribution of intact and hollow nanoparticles, we find that Pd loading at the single nanoparticle level is correspondingly heterogeneous. Intriguingly, the morphology of the nanoparticle is directly correlated to the amount of Pd exchanged into the nanoparticle, which provides us with snapshots of the nanoparticle at differing stages of the galvanic replacement reaction (Figure 3a). Initially, Pd complexes exchange with surface Ag atoms to form a Ag-Pd alloy shell with an intact Ag core. These intact spherical nanoparticles are able to accommodate up to ~7% Pd wrt to Ag. As galvanic replacement proceeds, Ag begins to be removed from the core of the nanoparticle, resulting in pitting as >10% Pd is incorporated into the subsurface layers of the nanoparticle. These pits continue to grow until completely hollow nanostructures with Ag-Pd walls are generated at ~20% Pd. Finally, the hollow nanoparticles are further broken to form small, irregular Ag-Pd crescent nanoparticles as the Pd quantity in the particle exceeds 20%.



Figure 3. STEM images and elemental ratios for Ag-Pd nanoparticles resulting from GRR using Pd(OAm)_xCl_y precursors. (a) 1 equiv. OAm, (b) 2 equiv. OAm.

After Pd GRR using 2 and 3 equiv. OAm, the average Pd content in both samples remain below 7% Pd, which is consistent with the compositions of intact particles in the snapshots above. High-resolution EDS mapping of the 2 equiv. OAm sample shows that the Ag cores remain intact, and Pd is deposited uniformly on each nanoparticle (**Figure 3b**). However, the surface Pd layer is too thin at these Pd loadings to observe a distinct shell structure by EDS mapping. To determine whether Pd species remain on the surface or migrate further into the core of the Ag nanoparticle, we also obtained X-ray photoelectron spectroscopy. Due to the relatively short inelastic mean free path of photoelectrons in a solid, XPS interrogates the structure of the top ~10–20 Å of the sample.⁴⁰ Thus, the difference between the bulk composition obtained by ICP-OES and the surface composition by XPS provides important information about the distribution of Pd in the GRR samples.

For all Ag-Pd samples, XPS spectra show a much higher Pd composition than ICP-OES, which indicates a significant surface enrichment of Pd in the exchanged nanoparticles (**Figure 2e**). Intriguingly, while the bulk Pd composition drops steadily with increasing OAm content, the surface composition of Pd remains relatively constant at 50-60% Pd up to 2 equiv. of OAm. This ~50:50 ratio of Pd-Ag solid solutions. These data clearly indicate that the Pd₅₀Ag₅₀ alloy is preferentially formed at the surface in all of the galvanic replacement reactions even when the core remains primar-

ily Ag. In the surface-limiting condition at 2 equiv. OAm, we anticipate that the top few monolayers have been fully exchanged to the AgPd alloy but the core remains pure Ag. At 3 equiv. of OAm, the surface Pd composition drops significantly to $Pd_{13}Ag_{87}$, indicating that the reduced driving force of the $Pd(OAm)_3Cl$ precursor results in a more Ag-rich alloy at the surface.



Figure 4. High-resolution XPS spectra of the **(a)** Ag 3d region with arrows indicating FWHM and **(b)** Pd 3d region with overlaid peak fittings.

High-resolution XPS spectra of the Ag 3d and Pd 3d regions were also obtained to assess the electronic properties of metal atoms in the galvanically-exchanged samples. In the Ag 3d region, the most notable change in the spectrum with increasing oleylamine ligands and decreasing Pd incorporation is a systematic narrowing of the Ag 3d peaks (Figure 4a). The fully-exchanged alloy surfaces in the 0 and 1 equiv. OAm samples show broad Ag features with full-width half-maximum (FWHM) values of 1.22 eV compared to 0.95 in the original Ag@OAm nanoparticles (Figure S10). In Ag-Pd alloys, the Ag 3d states have been observed to shift to lower binding energies relative to monometallic Ag due to charge transfer from Ag to neighboring Pd atoms.⁴¹ The observation of broadened peaks in our exchanged nanoparticles corroborate the formation of a Ag-Pd solid solution in the surface layers, leading to a distribution of core-level shifts due to a non-uniform local coordination environment for Ag atoms. The large proportion of Ag atoms exposed at the surface of the hollow Ag-Pd nanoparticles formed at 0 and 1 equiv. OAm may also contribute to peak broadening in the XPS.⁴²

In the 2 and 3 equiv. OAm samples, the Ag 3d peaks narrow substantially as the exchanged Pd atoms become confined to the surface, thereby leaving the Ag core intact.

In the Pd 3d region, galvanically-exchanged samples up to 2 equiv. OAm show only Pd⁰ peaks, indicating successful galvanic replacement of Pd atoms onto the Ag core and full removal of unreacted Pd precursor (**Figure 4b**). However, at 3 equiv. OAm, in which only 3% Pd is exchanged into the sample, 40% of the Pd remains oxidized. The observed binding energy for the oxidized species (337.9 eV) most likely represents unreacted Pd(OAm)₃Cl precursor that is adsorbed to the nanoparticle surface even after repeated cleaning steps, based on comparison to the known $[Pd(NH_3)4]^{2+}$ complex (338.5 eV) and PdO phase (336.4 eV).^{43,44}

Finally, electrocatalytic activity for the hydrogen evolution reaction (HER) in 0.1 M HClO4 corroborates the presence of a uniform AgPd alloy surface regardless of the bulk concentration of Pd in the sample. Prior to catalysis, oleylamine ligands are chemically stripped from the nanoparticle in order to expose metal surface atoms. All Pd-exchanged samples show similar HER geometric current densities, which are significantly higher than the activity over Ag alone (Figure 5a). When normalized by the mass of Pd obtained by ICP-OES, the 2 and 3 equiv. OAm samples show much higher mass-activity for HER because the majority of deposited Pd atoms remain at the surface of the Ag nanoparticle (Figure 5b). The plasmon resonance of the Ag core also broadens and dampens as the AgPd alloy forms (Figure 5c). The 2 and 3 equiv. OAm samples show the greatest retention of the Ag plasmon due to surface-limited AgPd alloy formation while the 1 and 0 equiv. OAm samples dampen the plasmon completely due to bulk AgPd alloy formation.¹³ Together, these data provide clear evidence that the redox potential of Pd precursor complexes can be tuned through amine ligand chemistry to achieve surface-limited galvanic replacement of Pd atoms onto Ag cores.

To assess the generality of our surface-limited galvanic exchange reaction, we also performed GRR of Pt and Au precursor complexes with colloidal Ag@OAm nanoparticles. The similarity in precursor chemistry between Pd and Pt enables us to use the analogous series of oleylamine-coordinated Pt(OAm)_xBr_y complexes (x = 0-4) to achieve surface-limited GRR (**Figure S12**). At 0 equiv. OAm, GRR between (TOA)₂PtBr₄ and Ag⁰ in toluene generates secondary-nucleated Pt particles as the Ag core is consumed, resulting in an extremely heterogeneous mixture of heavily-etched Ag-Pt and pure Pt nanostructures (**Figure 6a**). All of the PtBr₄^{2–} precursor (0.5 equiv. wrt Ag) in solution is completely consumed, resulting in 49% Pt in the final sample (**Figure 6d**).







Upon addition of oleylamine to the Pt precursor complex, the driving force for galvanic exchange drops considerably. Using the Pt complex treated with 1 eq. OAm, 18% Pt relative to Ag is deposited after 24 h of GRR (**Figure 6b**). Within this morphologically heterogeneous mixture, particles that remain spherical typically comprise <5% Pt (**Figure 7a**). As the galvanic replacement proceeds, small Pt nanoparticles supported on the Ag-rich core are observed at $\sim6-10\%$ Pt, and major etching and distortion to the original nanoparticle morphology are present at >15% Pt. XPS elemental analysis of this sample shows lower Pt percentage (6%) relative to the bulk composition obtained using ICP (18%), likely due to its morphological and compositional heterogeneity (**Figure 6d**)

At 2 eq. OAm, the exchanged nanoparticles now retain their spherical morphology, and no secondary nucleation of Pt is observed (**Figure 6c**). On average, only ~1% Pt is present in the bulk sample based on ICP-OES, and individual particles mapped using STEM-EDS all comprise \leq 1% Pt (**Figure 7b, S14**). XPS characterization of the surface composition reveals a ~4-fold higher Pt elemental ratio compared to the bulk, consistent with deposition of a Pt shell on the Ag core rather than secondary nucleation of pure Pt particles (**Figure 6d**). High-resolution STEM-EDS mapping corroborates the preferential deposition of Pt on the surface of the Ag spheres (**Figure 7b**). At such a low concentration of Pt, the Pt shell appears incomplete, consisting of few-layer Pt islands supported on the Ag nanoparticles. XPS of the Ag 3d region corroborates the

relative immiscibility of Ag and Pt in the galvanically-exchanged nanocrystals (**Figure 6e**). Minimal peak broadening is observed at 1 and 2 equiv. of OAm because the majority of Ag and Pt atoms remain phase-segregated rather than alloyed in a solid solution (**Figure S15**). Due to secondary nucleation of Pt nanoparticles, the geometric HER activity is highest when the GRR is carried out with pure PtBr4²⁻, but the mass-normalized activity remains highest for the 2 equiv. OAm sample because of the preferential exposure of exchanged Pt atoms on the surface of the Ag cores (**Figure S16**).





The galvanic exchange of Au precursors onto Ag@OAm nanoparticles proved analogously tunable using triphenylphosphine (PPh₃) as the organic ligand. In the absence of PPh₃, GRR of HAuCl4 with Ag⁰ nanoparticles in a toluene and oleylamine solution results in complete consumption of Au precursors to yield bimetallic nanoparticles containing 52% Au (Figure 8a, c). This fully-exchanged sample exhibits a morphologically heterogeneous mixture of distorted, hollow, and crescent-shaped AgAu nanoparticles of varying composition. Analogous to the Pt and Pd examples above, the morphology of the exchanged nanocrystals provides an indication of the extent of galvanic replacement. Intact spherical particles exhibit the lowest percentages of Au (<10%) with Au atoms concentrated at the surface of the nanoparticle (Figure 9a). At higher degrees of Au GRR, Au deposits become less uniform with the observation of Au-rich protrusions atop hollow or crescent nanostructures.

When HAuCl₄ is treated with 2 equiv. PPh₃, we obtain the Au(PPh₃)Cl complex, which has substantially lower reduction potential than HAuCl₄ or HAuCl based on computed stability constants from the literature.³⁹ Using this complex, the amount of Au present in the sample after 24 hour GRR drops to 3% relative to Ag, and the nanoparticles retain the size and shape of the original Ag@OAm nanoparticles (Figure 8b). The XPS shows ~4-fold higher percentage of Au compared to the bulk percentage, indicating surface enrichment of the deposited Au (Figure 8c). EDS mapping of individual nanoparticles shows intact Ag spheres with thin Au islands deposited on the surface, each of which contain approximately 1% Au (Figure 9b, S18). Broadening of the Ag 3d XPS peaks corroborates AgAu alloy formation in the absence of PPh3 and retention of the Ag core when using Au(PPh₃)Cl as the precursor for GRR (Figure 8d, S19). The plasmon resonance of the Ag core is likewise completely retained after the surface-limited GRR (Figure S20).

Conclusion

In conclusion, we have developed a general method to achieve surface-limited galvanic replacement reactions of oxidized Pd, Pt, and Au complexes onto Ag⁰ cores through the tuning of metal precursor redox potentials. Varying the number and binding strength of organic ligands coordinated to the precursor complex enables systematic variation of the reduction potential and subsequent driving force for galvanic replacement with Ag⁰. By reducing the thermodynamic driving force for GRR, even in the presence of large excesses of oxidized precursor, hollowing of the metallic core is completely inhibited, and deposition of the second metal occurs exclusively on the surface of the nanoparticle. In this fashion, we are able to selectively synthesize bimetallic core-shell structures comprising Ag cores with thin AgM alloy or pure M shell layers simply through modulation of the precursor structure. We anticipate that the surface-limited galvanic exchange method developed herein will enable the synthesis of a broad range of core-shell structures with base metal cores and thin precious metal shells for use in thermal and electrochemical catalysis.

Methods

Synthesis of (TOA)Pd(OAm)_xCl_y and (TOA)Pt(OAm)_xBr_y complexes. K₂PdCl₄ (32.6 mg, 0.1 mmol) was dissolved in 2.2 mL of 1 M aqueous HCl in a 20 mL scintillation vial. In another 20 mL vial, TOAB (109 mg, 0.2 mmol) was dissolved in 5 mL toluene. The colorless TOAB solution was layered on top of the deep orange K₂PdCl₄ solution. The biphasic solution was shaken until the aqueous layer became colorless and the non-polar layer turned red, indicating phase transfer and formation of the (TOA)₂PdCl₄ complex.⁴⁵ The toluene layer was then transferred to a clean vial and diluted with additional toluene to generate a 5 mM solution of (TOA)₂PdCl₄ in toluene. Varying amounts of oleylamine (6.6–19.8 uL, 0.02–0.06 mmol) were stirred with 4 mL aliquots of the (TOA)₂PdCl₄ solution (0.02 mmol) for 12 h to obtain Pd(OAm)_xCl_y (x = 0–3).

An analogous biphasic exchange process was carried out using K_2PtBr_4 , KBr and TOAB to generate the (TOA)₂PtBr₄ complex dissolved in toluene. The (TOA)₂PtBr₄ complex was then stirred with the appropriate quantities of oleylamine for 12 h.

Galvanic replacement between metal complexes and Ag@OAm nanoparticles. Ag@OAm nanoparticles were synthesized based on a literature method and diluted to a nominal concentration of 10 mM by Ag at.% in toluene.³⁵ To this 10 mM solution of Ag@OAm (1 mL, 10 μ mol), 1 mL of the 5 mM metal precursor solution (5 μ mol, 0.5 equiv.) was added, and the reaction mixture was stirred for 24 h at room temperature. The exchanged nanoparticles were precipitated out of solution using 2 mL of ethanol. The solid obtained upon centrifugation was then redissolved in 1 mL of toluene to generate a nominal 10 mM solution of AgM nanoparticles.

Electrochemical Methods. Electrochemical measurements to determine the redox potentials of Pd precursor complexes were carried out in a three-electrode setup using a Pine WaveDriver 20 Bipotentiostat. The working electrode was a polished glassy carbon disk.

Cyclic voltammograms (CVs) for aqueous Pd complexes, K_2PdCl_4 and Pd(NH₃)₄Cl₂, were obtained at 50 mV/s scan rate in an aqueous electrolyte containing 50 mM Pd complex, 0.1 M NaClO₄ and 0.1 M NaCl under N₂ atmosphere. Only the 1st CV scan is utilized for calculating reduction potentials due to irreversible reduction of the Pd complexes during the CV. The counter electrode was a Pt wire. Potentials were measured against a Ag/AgCl reference (3 M NaCl) and converted to the real hydrogen electrode (RHE) reference scale using:

E(vs RHE) = E(vs Ag/AgCl) + 0.210 V + 0.0591 V * pH

Differential pulse voltammograms (DPVs) for organic-soluble (TOA)Pd(OAm)_xCl_y complexes were obtained in THF solution containing 25 mM Pd complex, 0.1 M TBAClO₄ and 0.1 M TBACl under N₂ atmosphere. DPV scans were collected with 100 mV amplitude, 20 mV increment, and 100 ms period. The counter electrode was a graphite rod. Potentials were measured against a platinum wire pseudo-reference and internally referenced to the ferrocene/ferrocenium redox couple. These potentials were converted to the standard hydrogen electrode (SHE) reference scale using the following relationships, obtained from the literature.³³

$$E_{Fc/Fc^+} = 0.53 \text{ V vs. SCE}$$

E (vs SHE) = 0.24 V + E (vs SCE)

Hydrogen evolution reactivity measurements were conducted on a rotating disk electrode (RDE) setup with a Pine WaveDriver 20 Bipotentiostat in 0.1 M HClO₄ purged with N₂. To prepare the working electrode, 10 μ L of a 10 mM colloidal nanoparticle solution was drop-cast on a polished glassy carbon disk. To remove oleylamine ligands from the colloidal nanoparticle surface, the electrode was rotated at 100 rpm in an ethanol solution containing 0.1 M TBACl and activated carbon for 30 min. Finally, the electrode was rinsed with ethanol and air-dried. The counter electrode was a graphite rod. Potentials were measured against a Ag/AgCl reference (3 M NaCl) and converted to the real hydrogen electrode (RHE) reference scale using:

E(vs RHE) = E(vs Ag/AgCl) + 0.210 V + 0.0591 V * pH

Linear scan voltammetry (LSV) was performed for all samples between 0.27 V and -0.33 V vs. RHE at 20 mV s⁻¹ scan rate and 1600 rpm rotation rate. No IR compensation was applied. The geometric current density for HER is assessed in the 1st scan and the mass of Pd/Pt on electrode is determined by ICP-OES to obtain mass activity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Materials, additional experimental methods, and additional electrochemical and physical characterization. (PDF)

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