Mask-Assisted Seeded Growth of Segmented Metallic Heteronanostructures

Cameron C. Crane,[†] Jing Tao,[‡] Feng Wang,[†] Yimei Zhu,[‡] Jingyi Chen^{†,*}

[†]Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701

[‡]Condensed Matter Physics and Materials Science Department, Brookhaven National
Laboratory, Upton, NY 11973

*Corresponding author: chenj@uark.edu (+1 479-575-6203)

ABSTRACT: Controlling the deposition of exotic metals in the seeded growth of multi-metal nanostructures is challenging. This work describes a seeded growth method assisted by a mask for synthesis of segmented binary or ternary metal nanostructures. Silica is used as a mask to partially block the surface of a seed and a second metal is subsequently deposited on the exposed area, forming a bimetallic heterodimer. The initial demonstration was carried out on a Au seed, followed by deposition of Pd or Pt on the seed. It was found that Pd tends to spread out laterally on the seed while Pt inclines to grow vertically into branched topology on Au. Without removal of the SiO₂ mask, Pt could be further deposited on the unblocked Pd of the Pd-Au dimer to form a Pt-Pd-Au trimer. The mask-assisted seeded growth provides a general strategy to construct segmented metallic nanoarchitectures.

KEYWORDS: Solid-State Chemistry, Nobel Metal Nanoparticles, Silica, Sol-Gel, Microemulsion.

INTRODUCTION

Heterostructures of two or more metals with interfaces at the nanoscale is of particular significance because they exhibit unique properties and multi-functions distinctly different from the individual components.¹⁻⁴ The diverse surface chemistry of these heteronanostructures enables new applications that are not possible with each component alone. For example, multi-segmented metal nanorods have been demonstrated for applications in synergistic heterogeneous catalysis,⁵⁻⁶ self-electrophoretic nanomotors/ nanobatteries,⁷⁻⁸ multifunctional biomedicine,⁹⁻¹⁰ and multiplexed detections.¹¹⁻¹² To fabricate the heteronanostructures, sequential electrochemical deposition of metal ions into templates is the most common method since the 1990s.¹³⁻¹⁴ In this approach, commercially-available alumina or polycarbonate membranes with uniform pores are often used as templates, yielding segmented metal rods.¹⁵ This method could be further extended to selective growth of additional metals within the templates in solution after the initial electrochemical deposition of rod-shaped seeds.¹⁶⁻¹⁷ To generate heterostructures with other configurations, it is usually required to involve cost-intensive and time-consuming lithography techniques.¹⁸ In this work, a site-selective seeded growth method, termed mask-assisted seeded growth (MASG), is developed to expand the library of metal heterostructures with complex nanoarchitectures.

Seeded growth has emerged as a compelling method to create a wide variety of novel metal nanostructures.¹⁹⁻²⁴ Conditions that yield heteronanostructures depend on a number of factors such as the structural characteristics of constituent components, the reduction kinetics of metal precursors, and the capping agents. For example, a high degree of lattice mismatch between the seed and the second metal prevents conformal growth of core@shell structures and yields heteronanostructures of Au on CoPt₃,²⁵ Au rods on Pt cubes,²¹ and Cu on Au.²⁴ Controlling the

reduction kinetics can selectively direct the nucleation and subsequent growth of the second metal on the seed to form dimers of Au on Pd²⁶ or other non-conformal structures such as Ag/Au on Pd cubes²⁷⁻²⁸ and Ag on Au nanorods.²⁹ On the other hand, blocking specific facets of the seeds by capping agents could lead to the growth of Rh on Pd heterostructures.³⁰ Despite these advances, optimization of the growth conditions is largely material specific and it is beneficial to develop a general approach for the synthesis of multi-component heteronanostructures.

In this work, the MASG method uses SiO₂ as a mask in seeded growth to partially block the surface of the seed and thus direct the deposition of exotic metals on the exposed surface of the seed, forming heteronanostructures. The asymmetric coating of SiO₂ was demonstrated in the classical Stöber synthesis by using a polymeric ligand to partially block the diffusion of the sol-gel precursor to reach the surface of the nanoparticle.³¹ However, this method is only suitable for water-soluble nanoparticles. To overcome this limitation, the water-in-oil (W/O) microemulsion method is used to form the SiO₂ mask. Unlike the classical Stöber synthesis of SiO₂ coating,³¹⁻³⁴ the W/O microemulsion confines the sol-gel condensation within the water droplets in bulk oil, particularly useful for the formation of SiO₂ coating on nanoparticles suspended in hydrophobic solvents.³⁵ By reducing the concentration of sol-gel precursor in the W/O microemulsion, phase separation between the surface ligand and hydrolyzed precursor is created on the particle surface, leading to partial condensation of SiO₂ on individual Au nanospheres to yield Au-SiO₂ dumbbell structures. Sequential reduction of Pd and Pt precursors on these dumbbell structures generates heterodimers of Pd-Au and Pt-Au, and more complex Pt-Pd-Au heterotrimers. The reaction mechanisms of the microemulsion for preparation of Au-SiO₂ dumbbells and their subsequent use for synthesis of heteronanostructures are elucidated. These heteronanostructures exhibit tunable optical properties in the visible markedly different from the individual components.

EXPERIMENTAL SECTION

Chemicals. Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99%), potassium tetrachloroplatinate (K_2PtCl_4 , 99.9%), potassium tetrachloropalladate (K_2PdCl_4 , 99.9%), and ammonium hydroxide (28-30% $\text{NH}_3 \cdot \text{H}_2\text{O}$) were purchased from Alfa Aesar. Tetradecylamine (TDA, >95%) was purchased from TCI. Tetraethoxysilane (TEOS, 98%), poly(oxyethylene) nonylphenyl ether (Igepal CO-520), and polyvinylpyrrolidone (PVP, M.W. = 55,000) were purchased from Sigma-Aldrich. Cyclohexane (ACS grade) was purchased from EMD. All chemicals were used as received unless specified otherwise.

Synthesis of Au-SiO₂ Dumbbells. The Au-SiO₂ dumbbells were synthesized by controlling the hydrolysis and condensation of the SiO₂ precursor during the coating process using W/O microemulsions. Initially, 10-nm Au nanoparticles were prepared by reducing $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (19.7 mg, 0.05 mmol) in 5 g of TDA at 160 °C for 20 min under argon. After the reaction, the product was cooled to 100 °C and purified with toluene and ethanol to remove unreacted precursor and excess TDA. The Au nanoparticles were then dispersed in cyclohexane for silica coating in W/O microemulsions. In a typical procedure, 1 mL of 200 nM Au nanoparticles was added to the mixture of 0.14 M Igepal CO-520 in 40 mL cyclohexane in a round-bottom flask equipped with a magnetic stirring bar. Various amounts of TEOS (20-200 μL) were added to the reaction mixture and allowed to mix for 30 min before the addition of 0.280 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$. The Au-SiO₂ dumbbell structures were formed when less than 50 μL of TEOS was used. The reaction was allowed to proceed for 48 h and stopped by adding ethanol to interrupt the emulsion. The product was washed by ethanol and dispersed in 18 M Ω H₂O for future use.

Synthesis of Pd-Au Dimers. The Pd-Au dimers were synthesized by reducing the Pd precursor in the presence of Au-SiO₂ dumbbells using ascorbic acid. In a typical procedure, 8

mL of K_2PdCl_4 was added, at a rate of 0.1 mL/min, to a 5 ml aqueous solution containing Au- SiO_2 dumbbells (~ 15 pmol) and PVP (1 mg/mL) at room temperature. Final concentrations of K_2PdCl_4 (0.06, 0.2, and 0.35 mM) in the reactions were used to yield Pd depositions with different thickness of ~ 4 , ~ 7 , and ~ 10 nm, respectively. The molar ratio of ascorbic acid to K_2PdCl_4 was kept at 10 to 1 for all three reactions. The product was washed by ethanol and dispersed in 18 M Ω H_2O . The SiO_2 component was then dissolved by mixing the Pd-Au- SiO_2 particles overnight in an aqueous solution containing excess NaOH and PVP (10 mg/mL). The product was washed with water and dispersed in 18 M Ω H_2O .

The thickness (x_{Pd}) of Pd deposition was estimated using a crude model which approximates the Pd layer is a semi-spherical shell interfacing with a spherical Au core. The radius of the semi-shell (r_{Pd}) can be derived from the average volume of Pd (nm^3 per particle):

$$V_{Pd} = \frac{1}{2} \left(\frac{4}{3} \pi r_{Pd}^3 - \frac{4}{3} \pi r_{Au}^3 \right), \text{ where } r_{Au} \text{ is the radius of the Au core that can be measured from the}$$

transmission electron microscopy (TEM) image. The V_{Pd} was obtained from $\frac{V_{Pd}}{V_{Au}} = \frac{C_{Pd} a_{Pd}^3}{C_{Au} a_{Au}^3}$,

where V_{Au} is the average volume of Au (nm^3 per particle) assuming spherical shape ($V_{Au} = \frac{4}{3} \pi r_{Au}^3$);

C_{Pd} and C_{Au} are the concentration of Pd and Au (mol/L), respectively, which can be measured from the bulk sample; a_{Pd} and a_{Au} are the lattice constant of Pd and Au (nm), respectively. The difference of the r_{Pd} and r_{Au} gives the thickness of the Pd semi-shell: $x_{Pd} = r_{Pd} - r_{Au}$.

Synthesis of Pt-Au Dimers. The procedure for Pt-Au dimers was the same as that for Pd-Au dimers described above, with the exception that K_2PtCl_4 was used as the Pt precursor and final concentration of Pt in the reaction solution is 2.4mM.

Synthesis of Pt-Pd-Au Trimers. The Pt-Pd-Au trimers were synthesized using a similar procedure as that for Pt-Au dimers except that the Au-SiO₂ was replaced by the pre-synthesized Pd-Au-SiO₂ described above.

RESULTS

The MASG method has been demonstrated to synthesize bimetallic and trimetallic heteronanostructures. **Figure 1A** illustrates the general strategy of the MASG method using a Au seed and a second metal Pd as an example to create heterodimers. This method involves SiO₂ to mask one side of a spherical nanoparticle and expose the other side for deposition of successive metals. After deposition, the SiO₂ mask can be removed to yield heterodimers, trimers, or oligomers depending on the number of repeating depositions performed during the seeded growth. As an initial demonstration, Au and Pd were used as the seed and the second metal, respectively. The Au seeds prepared by reducing chloroauric acid in tetradecylamine were spherical nanoparticles with diameter of 9.7±1.3 nm (**Fig. 1B**). High resolution TEM (HRTEM) analysis shows that the Au seeds adopted decahedral geometry consisting of five tetrahedral subunits (**Fig. S1**). The subunits were bounded by {111} crystal faces, arranging along a five-fold rotation axis along the [110] zone.³⁶ Silica was subsequently condensed on these seeds using a modified W/O microemulsion method to form Au-SiO₂ dumbbells (**Fig. 1C**). The yield of dumbbells was close to 90% with half of the seed surface covered by SiO₂. These SiO₂-masked seeds were used for the deposition of Pd. Upon reducing Pd precursors with ascorbic acid, Pd was selectively deposited on the unblocked Au surface of these dumbbells to generate heterostructures of Pd-Au-SiO₂ (**Fig. 1D**). Removal of the SiO₂ mask yielded Pd-Au heterodimers (**Fig. 1E**).

Figure 1. (A) Schematic illustration of the MASG method for synthesis of metallic heteronanostructures. TEM characterization of products from each step in the process using Pd-Au as a demonstration: (B) Au spherical nanoparticles with a mean diameter of 9.7 ± 1.3 nm; (C) Au-SiO₂ dumbbell nanoparticles; (D) Pd-Au-SiO₂ nanoparticles; and (E) Pd-Au heterodimers. TEM characterization of an individual Pd-Au heterodimer: (F) HRTEM image and (G) HAADF-STEM image and EDX elemental mapping.

The Pd-Au dimers were further characterized by HRTEM, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDX). The HRTEM image of individual Pd-Au dimers clearly shows that the two components were assembled into heterostructures (**Fig. 1F**). The Z-contrast HAADF-STEM image and EDX mapping indicate that the dimers adopted a mushroom configuration with a Au spherical stem and a Pd cap (**Fig. 1G**). Further analysis of the HRTEM image shows the continuation of lattice fringes from Au to Pd. The lattice spacing was measured to be 0.236 and 0.228 nm corresponding to the spacing of {111} planes of Au and Pd, respectively. This result suggests an

epitaxial growth of Pd on the {111} facets of decahedral five-fold twinned Au nanoparticles, in agreed with the previous *in situ* TEM observations.³⁷ Without the SiO₂ mask, no Au-Pd dumbbells were found in the product under identical conditions (**Fig. S2**).

The growth of Pd on Au-SiO₂ dumbbells could be manipulated by varying the amount of Pd precursor introduced during the deposition onto the Au-SiO₂ seeds. The amount of Au-SiO₂ seeds was kept constant and the concentration of Au-SiO₂ was estimated using the extinction coefficient at 520 nm ($\epsilon_{Au} = (1.55 \pm 0.01) \times 10^8 \text{ M}^{-1} \cdot \text{cm}^{-1}$, **Fig. S3**). To maintain the same reaction volume, different concentrations of K₂PdCl₄ were added to the reaction containing 15 μmol of Au-SiO₂ at a rate of 0.1 mL/min. Because the underpotential deposition of Pd on Au favors heterogeneous nucleation of Pd on Au over Pd on Pd,³⁸⁻³⁹ Pd preferentially nucleates laterally on the Au surface to cover the entire area of the exposed Au prior to the growth on newly-deposited Pd. Increased concentration of K₂PdCl₄ from 0.06, to 0.20 and 0.35 mM resulted in thicker deposition of Pd, as shown in **Figure 2A, 1D, and 2B**, respectively. A crude model was established to calculate the deposition thickness of Pd by approximating the Pd layer as a semi-spherical shell interfacing with a spherical core of Au as described in the experimental section. The deposition thickness of Pd was estimated to be 4, 7, 10 nm for the three samples, denoted as *s*Pd-Au-SiO₂, *m*Pd-Au-SiO₂, *l*Pd-Au-SiO₂, respectively.

Careful control of the reduction rate of the second metal is important to ensure heterogeneous nucleation and subsequent growth. A mild reduction of Pd was maintained for the deposition of Pd on Au using ascorbic acid as a reducing agent. The correlation between the amount of Pd formed and the amount of Pd precursor added was plotted in **Figure 2C**. In this study, the amount of ascorbic acid was in excess, 10:1 equivalent to the Pd precursor. The amount of deposited Pd on Au was linearly proportional to the amount of Pd precursor added to the reaction

in the range of molar ratios of Pd to Au less than 10. The slope of the linear fitting curve was 0.90 ± 0.04 , suggesting that nearly all the Pd precursor was reduced under these reaction conditions. The XRD results also show an increase of the Pd-to-Au ratio from *s*Pd-Au-SiO₂, to *m*Pd-Au-SiO₂ and *l*Pd-Au-SiO₂ by comparing the ratio of (111) peaks of Pd to Au in **Figure 2D**. Diffusion between the two metals at the interface may occur,⁴⁰ however, the rate could be rather slow at room temperature.⁴¹⁻⁴²

Figure 2. TEM characterization of Pd-Au-SiO₂ heteronanostructures with different thickness of Pd deposition: (A) 4; and (B) 10 nm. The insets show the corresponding TEM images of Pd-Au heterodimers after the removal of silica. (C) Plot of the relative quantities of Pd in the dimers versus that in the precursor. (D) XRD patterns of the Au-SiO₂ dumbbell nanoparticles (Au-SiO₂) and Pd-Au-SiO₂ heteronanostructures with Pd deposition thickness of 4, 7, and 10 nm, denoted as *s*Pd-Au-SiO₂, *m*Pd-Au-SiO₂, *l*Pd-Au-SiO₂, respectively.

The deposition of Pd on Au could be monitored by the change of the optical properties of the resultant heteronanostructures. **Figure 3A** shows the UV-Vis spectra of *s*Pd-Au-SiO₂, *m*Pd-Au-SiO₂ and *l*Pd-Au-SiO₂. Due to the damping effects of Pd on the surface plasmon resonance of

Au,⁴³ the extinction peak of Au nanoparticles at 520 nm was gradually flattened out as the deposition volume of Pd increased. The optical spectra were further simulated using the discrete dipole approximation (DDA) method,⁴⁴ based on our crudely modelled geometry shown in the insets of **Figure 3, B-D**. Due to small size of the particles, light absorption dominated over scattering for their surface plasmon resonances. The simulated spectra matched well with the empirical extinction spectra, showing a decrease in extinction efficiency of Au at 520 nm after deposition of Pd, from 0.652 (**Fig. S4**) to 0.420 (**Fig. 3B**), by about one third. As the size of Pd increases from a x_{Pd} of 4 nm to 7 nm and 10 nm, the extinction efficiency at 520 nm slightly increases from 0.420, to 0.470 and 0.550, respectively. The corresponding extinction cross sections of individual dimers increase from 0.75×10^{-16} , to 1.40×10^{-16} and $2.50 \times 10^{-16} \text{ m}^2$. The optical spectra of another possible model of the Au-Pd dimer containing the same amount of Au and Pd by volume were also calculated. In this second model, the Au sphere is covered by a partial ellipsoid, as shown in **Figure S5**. The calculated spectra of the second model are very similar to the semi-spherical Pd shell model, suggesting that the optical spectra of the Au-Pd dimer are insensitive to certain details of the configuration such as the flat cutoff of a half-shell versus the curvature of an ellipsoid. By observing the change in the spectral shapes and intensity at 520 nm, the colorimetric method provides a simple and convenient means to track the deposition thickness of Pd *in situ*.

Figure 3. UV-Vis spectra of the Pd-Au-SiO₂ heteronanostructures with a Pd deposition thickness of 4, 7, and 10 nm on Au nanoparticles with a diameter of 9.7 ± 1.3 nm, denoted as sPd-Au-SiO₂, mPd-Au-SiO₂, and lPd-Au-SiO₂, respectively. DDA simulation of the optical spectra of Pd-Au heterodimers with a Pd thick deposition of 4, 7, and 10 nm on a Au nanosphere with a diameter of 10 nm, denoted as sPd-Au (B), mPd-Au (C), lPd-Au (D), respectively. The insets show the geometries of the Pd-Au heterodimers used for the simulation.

To further evaluate the versatility of the MASG method, Pt was examined as a second metal for deposition on the Au-SiO₂ dumbbells. Interestingly, Pt was deposited on Au as a dendritic configuration branching out vertically as opposed to the lateral growth of Pd on Au (**Fig. 4**). Further analysis of HRTEM images shows the lattice spacing was measured to be 0.236 and 0.228 nm corresponding to the spacing of {111} planes of Au and Pt, respectively. It is suggested that Pt clusters could be deposited on Au seeds through either direct reduction or oriented attachment on the {111} facets of decahedral five-fold twinned Au nanoparticles.⁴⁵⁻⁴⁶ After the initial epitaxial growth of Pt on Au, growth of Pt on Pt is more favorable than that on Au possibly due to the overpotential of Pt deposition on the Au surface. The slow reduction

kinetics promotes the growth of Pt along the $\langle 111 \rangle$ direction into branched structures.⁴⁷ The HAADF-STEM image and EDX elemental mapping verified the composition of Au and Pt heterodimer structures.

Figure 4. TEM characterization of Pt-Au-SiO₂ heterostructures: (A) overview image; (B, C) HRTEM of individual particles; and (D) HAADF-STEM image and EDX elemental mapping.

The MASG method can be further extended to grow an additional component at a designated site of the heterodimers using the SiO₂ masking strategy. As a demonstration, Pt was added with ascorbic acid to the suspension of Pd-Au-SiO₂ heterostructures with Au protected by the SiO₂ coating. Dendritic Pt caps were formed on the Pd side of the Pd-Au dimers as shown in **Figure 5**, in contrast to equal deposition on both Pd and Au, which was observed on the unprotected dimers (**Fig. S6**). It is hard to differentiate Pd and Pt by comparing the lattice spacing of $\{111\}$ facets because their lattice constant are almost identical (0.389 nm for Pd versus 0.392 for Pt).⁴⁸ However, the vertical growth pattern of Pt is distinctly different from the lateral one of Pd. From

the HRTEM analysis, it was found that epitaxial growth was extended from Pd on Au {111} faces to Pt on Pd {111} faces of Pd-Au. The composition of Au, Pd, and Pt of individual heterotrimers was further confirmed by the HAADF-STEM image and EDX elemental mapping.

Figure 5. TEM characterization of Pt-Pd-Au-SiO₂ heteronanostructures: (A) overview image; (B) HRTEM of an individual particle; (C) HAADF-STEM image and EDX elemental mapping.

DISCUSSION

The formation of metal-SiO₂ dumbbell nanoparticles is the key to the success of the MASG method. A high yield of Au-SiO₂ dumbbells was accomplished by a modified W/O microemulsion method. In a typical W/O microemulsion, the silica coating on a nanoparticle is formed by hydrolysis and condensation of TEOS within a micrometer- or nanometer-sized droplet that is generated in a homogeneous mixture of water, organic solvent (oil), and surfactant. The conventional method often results in core@shell structures with minimal inhomogeneity in the coating.³⁵ The modified W/O microemulsion was carried out by hydrolysis and condensation of TEOS on TDA-coated Au nanoparticles using ammonia in the presence of surfactant (Igepal CO-520) and organic solvent (cyclohexane). To increase the yield of Au-SiO₂

dumbbells, the concentration of TEOS was reduced to create phase separation between TDA and hydrolyzed TEOS on the surface of Au nanoparticles.

Figure 6. (A) Schematic illustration of the mechanism of silica coating via a micro-emulsion process. TEM characterization of the corresponding samples in the proposed mechanism using two different concentrations of TEOS under identical reaction conditions: (B) at low concentration (3.4 mM); and (C) at high concentration (22.4 mM).

The mechanism based on phase separation in the W/O microemulsion was illustrated in **Figure 6A**. Initially, TDA ligands on the nanoparticles were partially replaced by the hydrolyzed TEOS, resulting in phase segregation of hydrophobic oleylamine and hydrophilic TEOS.⁴⁹ Further condensation of TEOS was limited to the hydrophilic portion of the particle surface, yielding dumbbell structures of Au-SiO₂ (**Fig. 6B**). As the concentration of TEOS increases, more TDA ligands are substituted by the hydrolyzed TEOS, leading to a gradual expansion of TEOS to encompass the entire surface of the Au nanoparticles and thus further condensation to form complete SiO₂ shell (**Fig. 6C**). The resultant SiO₂ is porous, allowing small molecules to

diffuse in and out more easily as compared to crystalline materials. For example, water can diffuse through the pores of SiO₂ to reach the surface of Au nanoparticles, resulting in a SiO₂ shell filled with water. Assuming that a simple mathematic average can be used to estimate the dielectric constant of a two-component mixture, the refractive index of porous SiO₂ surrounding Au nanoparticles can be shown to be very similar to that of toluene. This was confirmed by measuring the extinction spectra of Au nanoparticles in toluene and Au-SiO₂ in water. The spectra are very similar and consistent with our approximation (**Fig. S7**). Despite of its porous nature, the SiO₂ mask can act as a protecting group and effectively reduce the surface accessibility of reactant molecules in a chemical reaction. To verify the protecting function of SiO₂, the reactivity of Au in the dumbbells and the core@shell structures was compared using two model reactions: an etching experiment using excess KCN and the reduction of *p*-nitrophenol by excess NaBH₄.

The reactivity of the Au cores in the dumbbells is markedly different from that of core-shell structures because SiO₂ coating largely blocks the diffusion of reactants. The etching of Au involves the use of KCN in aqueous solution as follows: $4\text{Au} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4[\text{Au}(\text{CN})_2]^- + 4\text{OH}^-$. The rate of the reaction is mainly limited by the diffusion of CN⁻ through the pores of SiO₂ because the dissolved O₂ and water molecules have covered the surface of Au. As the size of Au nanoparticles decreases during the etching process, the extinction efficiency reduces linearly while cross-section decreases exponentially (**Fig. S6**). The dissolution of Au could then be monitored by the diminished rate of extinction at 520 nm (**Fig. 7A**). It was found that the etching rate of Au in the dumbbell particles was faster than that in the core@shell structures. In the case of core@shell structures, the etching rate was further slowed down after 10 min, possibly because the slower diffusion rate of the larger [Au(CN)₂]⁻ anions further slows

down the etching rate of Au. After dissolution of Au, the dumbbell particles yielded half shells of silica while complete silica shells were found as the product for core@shell particles (**Fig. 7, B and C**). The slight change of SiO₂ morphology after etching could be possibly due to the structure reconstruction in the basic solution during etching process.⁵⁰

Figure 7. Etching process of Au nanoparticles: (A) Plot of extinction at 520 nm as a function of etching time; TEM images of Au@SiO₂ core@shell structures (B) and Au-SiO₂ dimers (C) after etching. Kinetic study of 4-nitrophenol reduction on Au-SiO₂ nanostructures: (D) plot of normalized absorbance (I/I_0) of *p*-nitrophenolate ion at 400 nm as a function of time for different catalysts; and (E) plot of $-\ln(I/I_0)$ as a function of time for different catalysts. The solid lines are the linear fits of the data and the slope gives k_{app} of the reaction.

The accessibility of SiO₂-masked surface is much more difficult for the deposition of additional metals because the reduction typically involves two reactants: a relatively-large anion of transition metal complex and ascorbic acid. The assumption was examined by a model reaction involving two reactants, the reduction of *p*-nitrophenol by excess NaBH₄. The same amounts of dumbbell particles and core@shell particles were used to catalyze the *p*-nitrophenol

reduction. The reaction was monitored by decreased intensity of absorbance at 400 nm corresponding to the disappearance of *p*-nitrophenol (**Fig. 7D**). The reduction could be treated as a pseudo first order reaction when NaBH₄ was in large excess.⁵¹ The data were then plotted as first order with respect to *p*-nitrophenol (**Fig. 7E**). The rate constant of *p*-nitrophenol reduction on the dumbbell particles was found to be $(4.64 \pm 0.01) \times 10^{-3} \text{ s}^{-1}$, more than 10 fold faster compare to the core@shell structures $(4.11 \pm 0.32) \times 10^{-4} \text{ s}^{-1}$). In fact, the *p*-nitrophenol reduction on the core@shell particles deviates from the first order kinetics, suggesting that the concentration of NaBH₄ is insufficient to assume pseudo first order reaction. This result, in turn, implies that the diffusion rates of reactants are significantly reduced. Both the etching reaction of Au and the *p*-nitrophenol reduction have demonstrated that the SiO₂ coating indeed serve as a mask to block chemical reactions.

CONCLUSION

The MASG method has been developed using SiO₂ as a mask to partially protect the surface of seeds from further reaction and subsequently applied to synthesize Pd-Au and Pt-Au heterodimers and Pt-Pd-Au heterotrimers. The initial Au-SiO₂ dumbbell structures could be readily synthesized by a modified W/O microemulsion due to the phase separation of hydrophobic surface ligands and hydrophilic hydrolyzed TEOS. Further epitaxial growth of Pd and Pt on Au was observed. Interestingly, Pd is apt to laterally grow on Au by capping the unblocked Au surface while Pt prefers to grow vertically into branched structures after initial deposition on Au. Replacing the noble metal with a 3d transition metal as the second metal, the active metal could subsequently be oxidized or sulfurized to oxide or sulfide.⁵²⁻⁵³ Therefore, the MASG method is potentially a versatile strategy to generate hybrid heteronanostructures with

multi-components for improving the existing applications and finding new uses in many areas related to energy conversion and human health.

Supporting Information

Experimental details, TEM characterization of Au nanoparticles and Pt-Pd-Au heteronanostructures synthesized without protection of SiO₂, UV-Vis spectra of Au nanoparticles and Au-SiO₂ dumbbells, as well as DDA simulation of optical spectra of individual Au nanospheres with different diameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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