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Tailoring the Optical and Catalytic Properties of Gold-Silver Nanoboxes and Nanocages by Introducing Palladium**

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Noble metal nanostructures are of great interest because of their potential applications including biomedical imaging,[1,2] surface-enhanced Raman scattering (SERS),[3] and catalysis.[4–6] Gold and silver nanostructures, in particular, have been most extensively studied because their localized surface plasmon resonance (LSPR) peaks are positioned in the visible and near-infrared regions, an attribute that allows for easy probing. Recent studies indicate that Pd-based nanostructures are also promising for photonic applications. For example, we have demonstrated that Pd-Ag alloy nanoboxes can have their LSPR peaks tuned across the visible spectrum and thus be employed as active substrates for SERS.[7] Palladium-based nanostructures are also attractive for a number of catalytic applications and have been demonstrated in a variety of reactions that include Heck coupling,[8] Suzuki coupling,[9] and hydrogenation.[10]

It has been noted by many groups that bimetallic catalysts often show enhanced performance when compared to each individual metal.[11–14] For instance, Pd-Au bimetallic systems have been shown to exhibit enhanced catalytic activity for multiple reactions including the hydrodechlorination of trichloroethene,[11–13] and Pd-Ag bimetallic catalysts have also been shown to have enhanced selectivity in the hydrogenation of hexa-1,5-diene.[14] Since the ratio between the two metals was found to be an important factor in determining the magnitude of enhancement, nanostructures with tunable compositions should provide the best candidates for bimetallic catalysts. There is also evidence that hollow structures can perform better than their solid counterparts for some reactions. While solid Pd nanoparticles used as catalysts for Suzuki coupling lost their activity after one use,[15] Pd nanoshells have been shown to retain their activity for this type of reaction for seven cycles.[16]

In this Communication, we report the synthesis of nanoboxes and nanocages (nanoboxes with porous walls) containing Pd, Au, and Ag by performing the galvanic replacement reactions in sequence. The stoichiometry of the galvanic replacement reaction provides a simple way to fine-tune the relative portion of each metal. We have investigated the optical properties of these structures as well as their use as catalysts in the decolorization of methyl red dye, and found

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that the order at which the metal salts were added during the synthesis played a vital role in determining both properties.

The galvanic replacement reaction has been shown by us and other groups to be a facile route to a variety of hollow and porous nanostructures.[17] These novel materials have been explored as SERS substrates,[7] imaging contrast agents,[18] and photothermal therapeutic agents.[19] The galvanic replacement method relies on the principle that when a metal nanostructure is in contact with the salt of another metal with a higher electrochemical potential, a replacement reaction will spontaneously occur, simultaneously dissolving the first metal into ions while converting the ions of the second metal into atoms. The metal nanostructure also serves as a template, guiding the deposition of the newly formed metal atoms. As a result, a nanostructure with a hollow interior is produced through the simultaneous dissolution of the template and plating of the new metal on the template.

This technique has been applied with great success to Ag nanocubes. By titrating a suspension of Ag nanocubes with HAuCl_4 , hollow and porous boxes of Au-Ag alloys could be routinely produced.[20] These are commonly referred to in our papers as Au nanocages. The mechanistic details of this reaction have been extensively covered in previous publications and the general scheme is sketched in Figure 1 (the first line).[20] This reaction can be divided into two distinct phases: hollowing out and dealloying. First, a pit is formed on the surface of the Ag nanocube. As the reaction proceeds, this pit turns into a hole that gradually expands to hollow out the inside of the cube. Gold is simultaneously plated on the outer surface, and interdiffusion between Au and Ag atoms causes the walls to form an alloy. At this stage, the product appears as a nanobox enclosed by smooth, nonporous walls. In the next phase of the reaction, the walls are dealloyed as the HAuCl_4 reacts with the Ag atoms selectively, generating voids that coalesce into holes in the walls of the nanobox. The final product is a cage-like structure. This progression correlates with a gradual red-shift in the LSPR peak, as observed through UV-visible spectroscopy.

The galvanic replacement reaction has also been studied with Na_2PtCl_4 and Na_2PdCl_4 , but with notable differences.[7] In the case of Pt, a uniform alloy was not formed and Pt bumps grew on the surface of the cube as the Ag nanocube was hollowed out. In the case of Pd (Fig. 1, the second line), alloy nanoboxes with smooth walls were formed and the system mimicked the reaction with HAuCl_4 until the start of the dealloying phase. Unlike the Au system, at this point Na_2PdCl_4 stopped reacting and no further morphological changes were observed. This difference suggests that the Pd and Ag quickly formed an alloy, eliminating the driving force responsible for the replacement reaction. The final morphology was a nanobox instead of a porous nanocage. For comparison, Figure 2A and B show SEM and TEM images of Au-Ag nanocages and Pd-Ag nanoboxes, respectively.

In the present work, we investigated the combination of these two systems, and found that the order in which the metal precursors were added did have an influence on the resultant morphology. For these syntheses, the galvanic replacement reactions were performed as usual except that two different salt solutions were added one after the other. Figure 1 (lines 3 and 4) shows a schematic of the reaction pathways and Figure 2C and D show SEM and TEM images of the products, with HAuCl_4 or Na_2PdCl_4 added first, respectively. In comparing these two figures, it can be seen that the resultant nanoboxes were far more porous when Na_2PdCl_4 was added first. In Figure 2C where HAuCl_4 was added first, small pits could be seen during the hollowing out phase of the reaction, but no dealloying was observed, even after large excesses of Na_2PdCl_4 had been added (e.g., 3.0 mL of a 0.5 mM solution). The only exception to this observation is when enough HAuCl_4 was added to initiate dealloying before any Na_2PdCl_4 had been introduced. This result suggests that the Na_2PdCl_4 was unable to effectively dealloy

the Au-Ag alloy walls, so once the hollowing out of the pure Ag core was complete, the reaction could not continue any further.

Figure 2D shows that if the reagents were added in the reverse order, Na_2PdCl_4 first, pores were easily formed and a cage morphology was observed. This suggests that HAuCl_4 had no problem dealloying the Pd-Ag alloy. Furthermore, this allows for the creation of a Pd-Au system with a higher surface area, which could further increase its catalytic potential since more sites are readily available for reaction.

These morphological changes correspond well with differences between the LSPR spectra of each system. In previous papers it has been noted that the LSPR peaks of Au nanocages could be continuously tuned from approximately 450 nm to 1200 nm by titrating with increasing amounts of HAuCl_4 solution.[20] This wavelength shift corresponded to the change in wall thickness as the solid nanocubes transformed into increasingly hollow boxes, cages, and finally broken pieces. Pd nanoboxes, however, could only be tuned from 450 nm to 730 nm due to the fact that the Ag in their walls could not be dealloyed. This limiting wavelength corresponded to a final morphology of hollow boxes with smooth walls. Titrating with additional Na_2PdCl_4 did not have any effect. This abrupt stop in the LSPR peak shifting corresponded to the abrupt stop in morphological changes, in particular, the thickness and porosity of the walls. [7]

The LSPR peaks of these structures were also affected by the stoichiometry of the reaction. In Figure 3A the same amounts of 0.5 mM HAuCl_4 and Na_2PdCl_4 solution were added, but the resulting LSPR peaks were separated by ~ 225 nm. Part of this difference can be attributed to the uneven stoichiometric ratios caused by the difference in oxidation state for the salt precursors. The relevant galvanic replacement reactions are:

Since three Ag atoms are required to deposit one Au atom, while only two are necessary to deposit one Pd atom, the walls of the Au nanobox will be thinner, resulting in a further red-shift for the LSPR peak.[21] It is also possible that some of this shift was caused by the difference in the percent conversion of the salt precursor to metal, as both reactions have been shown to have less than 100 % conversion.[7,20] Furthermore, the difference in dielectric function between Au and Pd should also contribute to the spectral difference.[22]

Figure 3B compares the UV-visible spectra of samples produced with different orders of precursor addition. Despite the fact that the same amount of each metal precursor was added (0.5 mL each of 0.5 mM solutions), the two peaks differed in wavelength by ~ 175 nm. The sample where Na_2PdCl_4 was added second had a shorter wavelength. This difference indicates that Na_2PdCl_4 was less effective at dealloying the Au-Ag alloy than HAuCl_4 was at dealloying the Pd-Ag alloy even before the limiting wavelength of 730 nm was reached.

Finally, the atomic compositions of these two samples were different. The HAuCl_4 followed by Na_2PdCl_4 sample was comprised of 63 % Ag, 20 % Au, and 17 % Pd. The Na_2PdCl_4 followed by HAuCl_4 sample was 55 % Ag, 17 % Au, and 28 % Pd, showing that significantly more Pd could be incorporated into the final product when Na_2PdCl_4 was added first. All of these observations support the hypothesis that HAuCl_4 could easily dealloy the Pd-Au-Ag alloy nanoboxes, but Na_2PdCl_4 had difficulty in dealloying Pd-Au-Ag nanoboxes, and could not do so at all once a certain stage in the reaction had been reached. This difference could be attributed

to the fact that $\text{AuCl}_4^-/\text{Au}$ and $\text{PdCl}_4^{2-}/\text{Pd}$ pairs have different electrochemical potentials. The electrochemical potential of the alloyed walls can increase slightly to pass the electrochemical potential for $\text{PdCl}_4^{2-}/\text{Pd}$ pair when Ag is alloyed with Pd,[23] eliminating the driving force for extracting Ag atoms from the alloyed wall by PdCl_4^{2-} .

We used methyl red as a model system to study the catalytic properties of the nanoboxes and nanocages. Many research groups have investigated the use of Pd-containing catalysts for the decolorization of azo dyes by splitting them into two amines.[24–26] The hydrogenation of the azo $\text{N}=\text{N}$ bond can be monitored by using UV-visible spectroscopy, as it results in the loss of the bright red color. Figure 4A shows a sample set of UV-visible spectra recorded at different times, and Figure 4B shows a schematic of the decolorization reaction. Note that mild decolorization was also observed even without the presence of any catalyst. The rate constants for catalyst-containing samples were divided by the number of mols of Pd in the sample to take into account small differences in concentration that may arise during washing. Table 1 lists these rate constants as well as the atomic ratios, and it can be seen that the order the two salt precursors were added had an effect on the catalytic activity. Lines 2 and 3 of Table 1 compare samples with equal amounts of HAuCl_4 and Na_2PdCl_4 added, but in different orders. The sample with Na_2PdCl_4 added first had a slightly higher rate constant than the sample where HAuCl_4 was added first, 3.1×10^7 and 2.3×10^7 , respectively. This corresponds well with the greater amount of Pd in the first sample as measured by atomic emission spectroscopy (AES). It is interesting that adding HAuCl_4 after Pd has been deposited does not prevent the Pd from acting as a catalyst. This implies that the two metals form an alloy or the Au forms an incomplete coverage over the Pd. Palladium-gold alloys have been reported, but are somewhat disfavored because of a lattice mismatch.[27] The opposite can be seen in a sample where additional HAuCl_4 was added, the last line in the table. In this case, the catalytic ability dropped to 0.4×10^7 , despite the fact that the amount of Pd was roughly equal to the sample with less HAuCl_4 added. This drop suggests that the surface was almost completely coated by Au, preventing the methyl red from accessing Pd atoms on the surface.

In summary, by performing galvanic replacement reactions sequentially with two different salt precursors, HAuCl_4 and Na_2PdCl_4 , we have prepared Pd-Au-Ag nanoboxes and nanocages with controllable optical and catalytic properties. We have also investigated how the order of precursor addition affects the morphology, composition, optical properties, and catalytic activity of these nanostructures. If Na_2PdCl_4 was added before HAuCl_4 , the product was more porous, contained more Pd, had a further red-shifted LSPR peak, and showed higher catalytic activity.

Experimental

Materials

Silver nitrate (AgNO_3 , Sigma–Aldrich, 06521AD, 100 g), sodium palladium(II) tetrachloride (Na_2PdCl_4 , Sigma–Aldrich, 01623ME, 1 g), hydrogen tetrachloroaurate(III) (HAuCl_4 , Sigma–Aldrich, 05611CC, 1 g), sodium sulfide 9-hydrate (Na_2S , JT Baker, Y51592, 500 g), ethylene glycol ($\text{OHC}_2\text{H}_4\text{OH}$, JT Baker, B25B15, 4 L) (it has been noticed that batches with low iron impurity levels work best for this synthesis), poly(vinyl pyrrolidone) ($M_w = 55000$, Sigma–Aldrich, 02313PB, 500 g), sodium chloride (NaCl , JT Baker, C51580, 500g), ethanol ($\text{C}_2\text{H}_5\text{OH}$, AAPER alcohol, 06J17QA, 1 Gal), methyl red (*p*-dimethylaminoazobenzene-*o*-carboxylic acid, JT Baker, 32001, 28.35 g), Beckman buffer (pH 4.01, Beckman Instruments), hydrogen gas (H_2 , Pacific Airgas, 99.95 %), all water used was filtered with a Millipore E-pure filtration system at $>18 \text{ M}\Omega \text{ cm}$.

Synthesis of Silver Cubes

In a typical synthesis, ethylene glycol (6 mL) was dispensed in a 24 mL vial containing a magnetic stir bar and loosely capped with a paper lined lid (VWR, 24 mL, cat. no. 66011-143) which was then heated in a 150 °C oil bath for 1 hour. After that time, Na₂S dissolved in ethylene glycol (80 µL, 3 mM) was injected with a micropipette, which was followed by a PVP solution (30 mg in 1.5 mL ethylene glycol) and a silver nitrate solution (24 mg in 0.5 mL ethylene glycol) approximately 7 minutes later. Upon addition of the silver nitrate, the solution first turned yellow, then brown, and finally became an opalescent silver color. Once this color change was complete (approximately 7–15 minutes after addition of the silver nitrate), the vials were cooled in cold water. The contents were then washed once with acetone and twice with water before being dispersed into water (4 mL).

Synthesis of Gold and Palladium Nanoboxes and Nanocages

In each reaction, the as-prepared cube solution (100 µL) was added to a PVP in water solution (5 mL, 1 mg mL⁻¹) and was preheated for 10 minutes under magnetic stirring. HAuCl₄ and/or Na₂PdCl₄ aqueous solutions (0.5 mM) were titrated using a syringe pump (KD Scientific, Single-Syringe Infusion Pump, cat no. KDS100 230) at a rate of 0.2 mL per minute, which is approximately dropwise. In reactions where both solutions were used they were titrated one after the other. After addition of the designated amount of solution, the mixture was refluxed another 10 minutes to ensure full reaction. The resulting product was washed with a concentrated NaCl solution once to remove any AgCl that formed, and then 6 times with water or a water-ethanol mixture to remove excess PVP before being dispersed in water (0.5 mL) for further analysis.

Decolorization of Methyl Red

Methyl red stock solution was prepared by dissolving solid (0.0063 g) in ethanol (25 mL), adding pH 4.01 buffer (50 mL) and then diluting to a total volume of 500 mL with water, yielding a 47 µM methyl red solution. To perform the catalysis studies, this methyl red stock solution (3 mL) was placed in a spectrophotometer cuvette. The top of the cuvette was covered with Parafilm and bubbled with hydrogen gas (supplied by a balloon) for at least 15 minutes. The spectrophotometer was set to acquire a spectrum every three minutes. Immediately after acquisition of the first spectrum, the nanocage suspension (5 µL) was injected into the hydrogen-bubbled methyl red solution and acquisitions continued at 3 minute intervals. The maximum absorbance of each scan was converted to a concentration using the measured molar absorptivity of 24123 M⁻¹ cm⁻¹. Nakaishi et al. reports the molar absorptivity of methyl red as 23360 M⁻¹ cm⁻¹ [28]. First order rate constants were calculated by finding the slope of the natural log of concentration vs. time plot for the time interval from 3 to 45 minutes.

Instrumentation

Transmission electron microscope images were captured with a Philips CM100 operated at 100 kV. Scanning electron microscope images were captured with a Sirion XL field-emission microscope (FEI, Hillsboro, OR) at an accelerating voltage of 10 kV. Energy-dispersive X-ray spectroscopy was performed with the EDAX system attached to the scanning electron microscope (EDX, Genesis 2000, Mahwah, NJ), also at 10 kV. Samples were prepared by dropping an aqueous suspension of particles onto a piece of silicon wafer (for SEM) or carbon coated copper grid (for TEM). SPR spectra were recorded using a UV-visible spectrometer (Varian, Cary 50). Concentrations of the cage suspensions and molar ratios were calculated from atomic emission spectrometry (ICP-OES, Perkin-Elmer 3300 DV with an AS93plus Autosampler).

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Figure 1.

Schematic illustration of the morphological changes produced by refluxing Na_2PdCl_4 and HAuCl_4 with a suspension of Ag nanocubes. When only Na_2PdCl_4 was added, a hollow nanobox was produced. When only HAuCl_4 was added, the reaction could continue further by dealloying the nanobox to produce a porous nanobox also known as a nanocage. By combining these systems, it was possible to create a nanobox or nanocage containing Pd, Au, and Ag. Notably, if HAuCl_4 was added before Na_2PdCl_4 , the morphology changes stopped at the box stage unless enough HAuCl_4 was added to introduce pores before adding Na_2PdCl_4 . If Na_2PdCl_4 was added before HAuCl_4 , the nanobox continued with dealloying to form a porous nanocage.

Figure 2.

SEM images (with TEM images in the insets) of four samples showing morphologies depicted in Figure 1. To each reaction was added: A) HAuCl_4 only, B) Na_2PdCl_4 only, C) HAuCl_4 followed by Na_2PdCl_4 , D) Na_2PdCl_4 followed by HAuCl_4 . The scale bar at the bottom is for the SEM images. The TEM scale bars are 40 nm.

Figure 3.

A) Comparison of the UV-visible spectra when an equal amount of HAuCl_4 or Na_2PdCl_4 was added. B) Comparison of the UV-visible spectra taken from samples when the order of solution addition was different.

Figure 4. Decolorization of methyl red by hydrogenation with Pd-Au-Ag nanoboxes acting as a catalyst. A) Gradual decrease of UV-visible peak intensity with time. Scans were taken at 3 minute intervals from top to bottom. 25 μL of the 0.5 mL HAuCl_4 + 0.5 mL Na_2PdCl_4 sample was used as the catalyst. B) The decolorization reaction.

Table 1

Comparison of rate constants and elemental ratios.

mL of 0.5 mM solution added	k mol ⁻¹ Pd	% Ag	% Au	% Pd
0.5 Na ₂ PdCl ₄	3.5×10^7	79	0	21
0.5 HAuCl ₄ + 0.5 Na ₂ PdCl ₄	2.3×10^7	63	20	17
0.5 Na ₂ PdCl ₄ + 0.5 HAuCl ₄	3.1×10^7	55	17	28
0.5 Na ₂ PdCl ₄ + 1.0 HAuCl ₄	0.4×10^7	21	64	25

^a All raw k values had the k value for the blank subtracted off and were then divided by the number of mols of palladium in the catalyst. The concentrations necessary for this calculation and the elemental ratios listed all come from AES measurements.