Optical Properties of Pd–Ag and Pt–Ag Nanoboxes Synthesized via Galvanic Replacement Reactions

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ABSTRACT

Silver nanocubes dispersed in water were transformed into Pd–Ag or Pt–Ag nanoboxes by adding either Na₂PdCl₄ or Na₂PtCl₄. By controlling the amount of noble metal salt added, and therefore the molar ratio of Na₂PdCl₄ or Na₂PtCl₄ to Ag, we could tune the surface plasmon resonance peak of the nanostructures across the entire visible spectrum, from 440 to 730 nm. Replacement of Ag with Pd resulted in the formation of a nanobox composed of a Pd–Ag alloy single crystal, but the nanobox formed after replacement of Ag with Pt was instead composed of distinct Pt nanoparticles. DDA calculations suggest that both nanoboxes absorb light strongly, with Q_{abs}/Q_{sca} 5. After galvanic replacement, Pd–Ag and Pt–Ag nanostructures remain SERS active, suggesting their use as a SERS probe for studying the dependence of interfacial chemistry on composition.

The optical properties of Au and Ag nanoparticles have been under scientific scrutiny for nearly 150 years, culminating in the niche application of their surface plasmon resonance (SPR) in sensing and plasmonics.¹ In contrast, the optical properties of Pd and Pt nanoparticles remain relatively unexplored. The location of the SPR peak of Pd and Pt nanoparticles in the UV region not only gives them an uninteresting black color but it also makes their SPR characteristics much more difficult to probe because of the absorption of light at this wavelength by silica and most solvents.² However, we have demonstrated recently that the SPR peak of Pd nanocubes could be tuned to nearly the same location (∼400 nm) as that of Ag nanoparticles by increasing their sizes to ∼50 nm.³ Transformation of the Pd nanocubes into nanocages via a corrosive pitting process enabled further tuning of their SPR peak to 520 nm.⁴ This second approach, formation of hollow nanostructures, has been particularly effective for tuning the SPR peak of Au nanoshells across the visible spectrum because of the sensitivity of the SPR peak location to wall thickness.⁵ We have also shown that if Ag nanocube templates are titrated with HAuCl₄ in water, galvanic replacement of Ag with Au leads to the formation of nanoboxes and nanocages in a matter of minutes.⁶ By controlling the molar ratio of HAuCl₄ to Ag, the extinction peak of the nanostructures could be tuned from the blue (400 nm) to the near-infrared (1200 nm).⁷ Here we illustrate that galvanic replacement of Ag nanocubes with either Pd or Pt salts can also produce nanoboxes with extinction peaks tunable to the near-infrared.

Experimental details are given in ref 8. To tune the spectra of the nanostructures, we added Ag nanocubes to boiling water before titrating with the desired noble metal salt (either Na₂PdCl₄ or Na₂PtCl₄). Figure 1 illustrates the change in product morphology as Na₂PdCl₄ was added to a suspension of Ag nanocubes. At a molar ratio (Na₂PdCl₄ to Ag) of 0.14,
etch pits developed on the surfaces of the nanocubes, primarily at the corners (see Figure 1A). The atomic step edges necessarily present at the corners may present the most reactive sites for initiation of pitting at this location. Figure 1B and C shows the products at a molar ratio of Na₂PdCl₄/Ag = 0.28 and 0.42, respectively. By comparing the TEM and SEM images, we find that oxidation within the etch pits removed Ag from the interior rather than the surface of the nanocube. As Ag was dissolved from the interior, Pd accepted its electrons and plated onto the exterior of the nanocube and therefore may have helped to prevent etching of the nanocube surface. The Pd–Ag system is a well-known binary alloy, and plating of Pd will result in the formation of walls composed of a Pd–Ag alloy. Completely hollow and fully enclosed nanoboxes formed at a molar ratio of Na₂PdCl₄/Ag = 0.69 as a result of further oxidation of Ag from the interior and alloying of Pd into the exterior walls of nanocubes. If more Na₂PdCl₄ was added, then no morphological change was observed. This suggests that the Pd atoms had diffused quickly into Ag to form a homogeneous alloy, thereby eliminating the electrochemical driving force for galvanic replacement. The initial peak of the pure Ag nanocubes was located at 440 nm. This peak was red-shifted to 460 nm after formation of etch pits in the corners. Even such small etch pits have also previously caused the extinction peak to red-shift for the case of pure Pd nanocubes. As the etch pits grew in size, and the Ag nanocubes became more hollow, the extinction peak was red-shifted further to 496 and 544 nm. The red-shift stopped at 732 nm for the final Pd–Ag alloy nanoboxes. Figure 2B displays the aqueous solutions of these nanostructures tuned to the wavelengths shown in Figure 2A, indicating that the Pd–Ag nanostructures displayed bright and distinctive colors as they were tuned across the visible spectrum.

Figure 2 illustrates that the UV–visible extinction spectra of products from galvanic replacement of Ag nanocubes with Na₂PdCl₄. The amount of 0.5 mM Na₂PdCl₄ aqueous solution added to the initial Ag nanocubes is indicated on each curve. (B) Photographs of the aqueous Pd–Ag nanostructures corresponding to the curves in (A).

Figure 2. (A) UV–visible extinction spectra of products from galvanic replacement of Ag nanocubes with Na₂PdCl₄. The amount of 0.5 mM Na₂PdCl₄ aqueous solution added to the initial Ag nanocubes is indicated on each curve. (B) Photographs of the aqueous Pd–Ag nanostructures corresponding to the curves in (A).

Figure 3. (A) The predicted molar percentage of Pd in the alloyed hollow nanostructures assuming complete conversion of Na₂PdCl₄ to Pd is compared to the actual percentage of Pd as measured using AES and EDX. (B) The XRD pattern obtained from the hollow nanostructures shown in Figure 1D. The inset is the ED pattern taken from an individual nanobox by aligning the electron beam perpendicular to one of the faces. The ED lattice parameter of 4.04 ± 0.01 Å agrees with the XRD measurement.
that through controlled addition of Na$_2$PtCl$_4$, the extinction in predictable extinction peak red-shifts. Figure 4A shows crystallinity. though the nanobox walls alloyed, they retained their single pattern obtained from a single nanobox, indicating that even alloy. The inset of Figure 3B displays an electron diffraction boxes further confirms that they are composed of a Pd -pattern (Figure 3B) obtained from a sample of Pd in the alloy relative to bulk Ag. An X-ray diffraction (XRD) analysis. As Na$_2$PdCl$_4$ was added to the suspension of Ag nanocubes, the molar fraction of Pd in alloyed nanostructures increased until it reached between 33 (AES) and 49 (EDX) percent. If more Na$_2$PdCl$_4$ past this point resulted in collapse of the nanoboxes into nanoparticle aggregates. Evidently, because their outer walls were not a single-crystal alloy, Pt–Ag nanoboxes could not evolve into the porous nanocages observed for the Au–Ag system and tuning of the spectra was limited to ~700 nm for the Ag nanocubes used in the present study (~50 nm in edge length).

To enhance our understanding of the UV–visible extinction spectra exhibited by Pd–Ag and Pt–Ag alloyed nanoboxes, we performed DDA calculations on nanoboxes with dimensions and compositions approximating those of the experimental samples. Figure 5A shows the calculated extinction, absorption, and scattering coefficients from a Pd$_{0.4}$Ag$_{0.6}$ nanobox with an outer edge length of 63 nm and an inner edge length of 51 nm (wall thickness = 6 nm). The peak location of 755 nm shows a good match with that obtained from the synthesized Ag–Pd nanoboxes (732 nm). The calculated peak has a full width half-maximum (fwhm) of ~300 nm, which is significantly broader than the ~80 nm fwhm of the DDA calculated extinction peaks for Au nanoboxes of similar sizes. This result suggests that the broadening of the experimental peak as the ratio of Pd increased is due primarily to the change in composition. The calculation also suggests that Pd–Ag nanoboxes absorb much more light than they scatter; $Q_{abs}/Q_{sca}$ ≈ 5 at the peak maximum, compared with $Q_{abs}/Q_{sca}$ ≈ 1 for Au nanoboxes of similar sizes. Figure 5B shows the DDA results for a Pt$_{0.5}$–Ag$_{0.5}$ nanobox with an outer edge length of 63 nm and an inner edge length of 49 nm (wall thickness = 7 nm). Although the wall here was assumed to be an alloy rather than separate Pt and Ag layers, the calculated peak location (680 nm) is very close to that of the synthesized Pt nanoboxes (670 nm). The fwhm of ~280 nm and $Q_{abs}/Q_{sca}$ ≈ 5 are similar to that predicted for the Pd–Ag nanobox. The experimental extinction peaks for Au–Ag, Pd–Ag, and Pt–Ag alloyed nanoboxes consistently exhibit a fwhm broader than that predicted by DDA calculations. This is likely the result of small variations in wall thickness among the particles; even a 2 nm difference in wall thickness causes a 110 nm extinction peak shift. The exceptionally broad range of wavelengths across which Pd–Ag and Pt–Ag nanoboxes absorb light strongly could make them particularly useful as nanoscale photothermal heating elements.
Pd–Ag and Pt–Ag nanostructures might be particularly useful for examining the compositional dependence of oxidation, adsorption, and ligand formation with surface-enhanced Raman scattering (SERS). As an initial demonstration, we have obtained the SERS spectra of 4-mercaptopyridine on Pd$_{0.15}$Ag$_{0.85}$, Pd$_{0.30}$Ag$_{0.70}$ and Pt$_{0.15}$Ag$_{0.85}$ nanostructures. As can be seen from Figure 6, well-defined SERS spectra can still be observed using these composite nanoboxes, even for those containing as much as 30% Pd. The surface enhancement seen from these composite nanostructures is likely due to the fact they still contain a large proportion of Ag because the coupling between conduction electrons and interband electronic transitions in Pt and Pd gives these metals comparatively little SERS activity. In future work, we expect that these nanostructures will extend the capability of SERS to supply valuable information as to what surface species form in a particular reaction, and how metal composition affects this surface chemistry.

Greater understanding often comes from comparison and contrast. By extending the compositional range of nanostructures with SPR peaks in the visible region of light, we hope to illuminate the dependence of SPR characteristics on the material. We have shown that boiling Ag nanocubes in water with Na$_2$PdCl$_4$ or Na$_2$PtCl$_4$ results in the galvanic replacement of Ag with Pd or Pt and formation of well-defined nanoboxes. The extinction peaks of resultant nanostructures can be tuned continuously across the visible spectrum by titrating in controlled amounts of these noble metal salts. In the case of Pd, galvanic replacement stopped once a nanobox composed of a Pd–Ag alloy (Pd/Ag $\approx$ 0.40) was formed, suggesting that rapid formation of a homogeneous alloy eliminated the electrochemical driving force for further oxidation of silver. In contrast, Pt and Ag do not alloy at 100 °C, and the nucleation and growth of Pt particles on the Ag nanocube resulted in the formation of rough, noncrystalline nanobox walls that collapsed upon further addition of Pt salt. DDA calculations suggest that the broadness of Pd–Ag and Pt–Ag is due to their composition, and although each nanobox had a distinctive morphology, the $Q_{abs}/Q_{sca}$ ratio was $\approx$5 for both.

These composite nanoboxes represent two new systems in which SERS can be contrasted with that from either Au or Ag. In particular, the tunable surface chemistries of these nanoboxes will allow additional studies of chemical enhancement, as well as the affect of surface composition on interfacial chemistry. The specific chemical sensitivity of Pd toward hydrogen makes the Pd–Ag nanoboxes potentially useful for hydrogen storage and SPR-based sensors for hydrogen gas. The Pd–Ag and Pt–Ag nanoboxes might also find use as catalysts, photothermal heating elements, absorption contrast agents, and chemically specific optical sensors.

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References

1. See, for example, Xia, Y.; Halas, N. J. MRS Bull. 2005, 30, 338.
8. In a typical procedure, 100 μL of a dispersion of Ag nanocubes (~50 nm in edge length) was added to 5 mL of deionized water. This diluted dispersion was then refluxed for 8 min before dropwise addition of 0.5 mM Na2PdCl4 (or Na2PtCl4). After addition of the noble metal salt, the solution was refluxed until its color became stable (about 10 min). Vigorous magnetic stirring was maintained during the entire process. After the solution had been cooled to room temperature, white AgCl precipitated and settled at the bottom of the container. The AgCl was dissolved by adding a saturated solution of NaCl. The solution was then transferred into a tube and centrifuged at 10 000 rpm for 20 min. The supernatant containing the dissolved AgCl could be removed easily using a pipet. The solid was rinsed with water and centrifuged six more times before final dispersion for water for further analysis. SEM and TEM samples were prepared by drying a drop of final product on a small piece of Si wafer or a water substrate was then incubated in a 4 mM aqueous 4-mercaptopyridine solution for 1 h, rinsed with deionized water, and dried in air. SERS spectra were obtained at 785 nm laser excitation (Renishaw HP-NIR785) with 0.03 mW and a spot size of 1.6 μm at the surface using a Leica DM IRBE optical microscope equipped with a Renishaw inVia Raman system, a 1200 l/mm grating, and a thermoelectrically cooled CCD detector.
14. The extinction (Qext), absorption (Qabs), and scattering (Qscat) coefficients (Qext = Qabs + Qscat) of the nanoboxes are computed using the discrete dipole approximation (DDA) method. For the calculation, the nanobox was divided into an array of N consecutive cells, with each cell being approximated as a polarizable point electric dipole with a moment P. Under the excitation of a monochromatic optical field, these dipoles oscillate, couple with each other, and reradiate light. The complex refractive index of the alloy was obtained by a linear superposition of those of the composite metals: nAlloy = nAg + (1 − XAg) nPd, where XAg is the volume fraction of Ag. In addition, the nanobox was assumed to be surrounded and filled by water. Both absorption and scattering cross-sections could be obtained directly from P. In plotting the spectra, the cross-sections were divided by 4πn2a2 (aAg is related to the effective volume by 4πn2a2/3 = d3, where d is the outer edge length of the nanobox) to obtain the dimensionless coefficients (Q).