Structural and Optical Properties of Discrete
Dendritic Pt Nanoparticles on Colloidal Au
Nanoprisms

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ABSTRACT

Catalytic and optical properties can be coupled by combining different metals into nanoscale architectures where both the shape and composition provide fine-tuning of functionality. Here, discrete, small Pt nanoparticles (diameter = 3 - 6 nm) were grown in linear arrays on Au nanoprisms, and the resulting structures are shown to retain strong localized surface plasmon resonances. Multi-dimensional electron microscopy and spectroscopy techniques (energy dispersive X-ray spectroscopy, electron tomography and electron energy-loss spectroscopy) were used to unravel their local composition, 3D morphology, growth patterns, and optical properties. The composition and tomographic analyses disclose otherwise ambiguous details of the Pt-decorated Au nanoprisms, revealing that both pseudospherical protrusions and dendritic Pt nanoparticles grow on all faces of the nanoprisms (the faceted or occasionally twisted morphologies of which are also revealed), and shed light on the alignment of Pt nanoparticles. The electron energy-loss spectroscopy investigations show that the Au nanoprisms sustain multiple localized surface plasmon resonances despite the presence of pendant Pt nanoparticles. The plasmonic fields at the surface of the nanoprisms indeed extend into the Pt nanoparticles, opening possibilities for combined optical and catalytic applications. These insights pave the way towards comprehensive nano-engineering of multi-functional bimetallic nanostructures, with potential application in plasmon-enhanced catalysis and in-situ monitoring of chemical processes via surface-enhanced spectroscopy.
1. INTRODUCTION

Metallic nanostructures comprised of more than one component have attracted much attention because of their vast potential for multi-functionality.\(^1\)\(^-\)\(^3\) In the best cases, such architectures provide function beyond the sum of their parts, enabling useful or unique combinations such as plasmon-enhanced catalysis,\(^4\)\(^-\)\(^7\) magnetically addressable drug delivery systems and catalysts,\(^2\)\(^,\)\(^8\)\(^-\)\(^10\) or combined contrast agents and hyperthermal cancer treatment.\(^11\)\(^-\)\(^15\)

The combination of a plasmonic and a catalytic material is particularly interesting, as plasmonic materials can interact with light in unique ways. For example, the emergence of localized surface plasmon resonances (LSPRs), which are light-driven, coherent oscillations of the conduction electrons in metallic particles smaller than the wavelength of light. LSPRs create enhanced local electric fields that can increase signal intensity in optical spectroscopies, giving rise to techniques such as localized refractive index sensing,\(^16\)\(^-\)\(^18\) surface-enhanced Raman,\(^19\) fluorescence,\(^20\) and infrared absorption spectroscopies.\(^21\) These approaches are exceptionally sensitive to subtle changes in surface chemistry, sometimes down to the single particle level,\(^22\)\(^,\)\(^23\) and can provide feedback on chemical reactions as they occur.\(^7\)\(^,\)\(^19\)\(^,\)\(^24\)\(^-\)\(^26\) The decay of the LSPR can also be useful, and may lead to either localized heat\(^27\)\(^,\)\(^28\) or hot electrons\(^5\)\(^,\)\(^6\) that can speed up or enable new chemical reactions.\(^4\)\(^,\)\(^6\)\(^,\)\(^29\)\(^,\)\(^30\)

Combining materials in controllable ways is a prerequisite for the creation of multi-functional optical and catalytic nanostructures. This is especially so for the class of multi-functional materials that seek to combine catalytic and plasmonic materials. These combinations are particularly interesting in cases where catalytic metals such as Pt and Pd do not sustain strong plasmon resonances (due to significant losses in the visible range\(^31\)\(^-\)\(^33\)), and where more
traditional plasmonic metal nanoparticles such as Au and Ag may not be well-suited as catalysts for a target chemical reaction. Several studies have now shown LSPR activity both numerically and experimentally in core-shell bimetallic architectures containing both plasmonic and catalytic materials.\textsuperscript{34-37} Here, the morphology and optical properties of triangular Au nanoprisms decorated with Pt nanoparticles (NPs) of sizes relevant for catalysis (~3-6 nm) are reported. The alignment and structure of particles on both the side and large \{111\} Au facets are disclosed, as are the different LSPRs sustained by these bimetallic architectures.

2. EXPERIMENTAL DETAILS

\textbf{Nanoparticle Synthesis.} Hexadecyltrimethylammonium bromide (CTAB, 99%), chloroplatinic acid (H\textsubscript{2}PtCl\textsubscript{6}, 8 wt. % in H\textsubscript{2}O) hydrogen tetrachloroaurate trihydrate (HAuCl\textsubscript{4}\textcdot3H\textsubscript{2}O, 99.999%), L-ascorbic acid (99%), sodium borohydride (NaBH\textsubscript{4}, 99.99%), sodium hydroxide (99.99%), sodium iodide (NaI, 99.999%), and trisodium citrate (99%) were obtained from Sigma Aldrich and used as received. NANOpure\textsuperscript{TM} water (Thermo Scientific, > 18.2 M\(\Omega\cdot\text{cm}\)) was used for all washing, synthesis, and purification protocols as well as in the preparation of all solutions. All stock solutions were aqueous and prepared fresh before each reaction, unless otherwise noted. All glassware was washed with aqua regia (3:1 ratio of concentrated HCl and HNO\textsubscript{3} by volume) and rinsed thoroughly with water. \textit{Caution: aqua regia is highly toxic and corrosive and requires personal protective equipment. Aqua regia should be handled in a fume hood only.}

Au nanoprisms were synthesized according to literature protocols.\textsuperscript{38,39} Two hours after Au nanoparticle seeds were added to the nanoprism growth solution, the reaction mixture was heated in a H\textsubscript{2}O bath to 37 °C for 1 minute to dissolve any CTAB that may have recrystallized during
the growth period (this crystallized CTAB can interfere with nanoprism purification by centrifugation). To separate the nanoprisms from pseudospherical nanoparticle reaction byproducts, 90 mL of the reaction mixture was divided into 15 mL conical tubes and centrifuged at 820 relative centrifugal force (rcf) for 15 minutes (Eppendorf centrifuge 5804 with swing bucket rotor A-4-44). The supernatant and pellet were both extracted and the nanoprism thin film was resuspended in 1.0 mL of H$_2$O by vortexing for 5 seconds. To remove additional CTAB and excess reagents, this mixture was transferred to 1.5 mL centrifuge tubes, and the prisms were then centrifuged using a Spectrum mini-centrifuge (SC1006-R) for approximately 5 minutes. After centrifugation, the supernatant was removed and the prisms were resuspended in 1.0 mL of H$_2$O and subsequently combined in a 15 mL conical tube. The concentration of the purified nanoprisms in the nanoprism stock solution was then adjusted by diluting with H$_2$O to an optical density (O.D.) of 1.0 a.u. at the maximum absorption wavelength ($\lambda_{\text{max}}$, approximately 1300 nm) by ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy.

Pt was deposited on the Au nanoprisms using the purified Au nanoprism product (synthesis described above). Briefly, 0.5 mL of the prism stock solution (O.D. at $\lambda_{\text{max}}$ = 1.0 a.u.) was added to a 1.5 mL centrifuge tube and diluted with 0.5 mL of water. To this mixture, 20 µL of 20 mM ascorbic acid was added (for a final H$_2$PtCl$_6$:ascorbic acid molar ratio of 1:10), and the solution was briefly mixed by vortexing. Then, 4 µL of 10 mM H$_2$PtCl$_6$ was added (pH = 1.8), and the solution was mixed by vortexing again. After allowing one hour for completion of nanoparticle growth, the reaction mixture was purified from excess reagents by centrifugation (5 minutes at 2200 rcf using a Spectrum mini-centrifuge (SC1006-R)). After removal of the supernatant, the particles were resuspended in 1.0 mL of H$_2$O by brief sonication (~10 s). The undecorated and decorated Pt nanoprisms studied were from the same synthesis batch.
**UV-vis-NIR Spectroscopy.** The extinction spectra of the resulting colloid was measured by ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy using a Cary 5000 spectrophotometer (Agilent, Inc.). Spectra were baseline corrected with respect to the spectrum of water for optical density measurements.

**Electron Microscopy.** Particles were drop cast from solution onto Si₃N₄ membrane windows (EELS, TEMWindows Inc.) or thin carbon film supports (tomography and energy dispersive X-ray spectroscopy (EDS), Agar Scientific) immediately prior to analysis. Electron energy-loss spectroscopy (EELS) data of decorated Au prisms were obtained on a monochromated, Cₐ and Cₐ corrected FEI Titan G4 PICO (Forschungszentrum Jülich) equipped with a Gatan Quantum ERS electron spectrometer. EELS data of bare Au nanoprisms, precursor to the decorated nanoprisms, were obtained on a monochromated, Cₐ corrected FEI Titan Themis (Rice University) equipped with a Gatan Quantum ERS electron spectrometer. The pixel dwell time was set to 40-50 µs and 0.02 s on the PICO and Themis, respectively. The beam energy was set to 80kV in both instruments to optimize the width of the zero-loss peak (ZLP, ~0.08 eV on the PICO and ~0.13 eV on the Themis), and maximize the plasmon interaction cross-section. EELS spectrum images were obtained for six decorated Au/Pt nanoprisms and five undecorated Au nanoprisms, from which three representative examples of each are shown in the manuscript and Supporting Information. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) tilt series images for tomography was acquired on a Cₐ corrected FEI Titan G2 ChemiSTEM equipped with a Bruker Super-X quad EDS detector and operated at 80 kV. An EDS spectrum image was acquired with 1024 x 1024 pixels and 4096 energy channels (0.01 keV dispersion) on the same FEI Titan G2 ChemiSTEM instrument. EDS data analysis was performed in HYPERSPY (an open source software, available at hyperspy.org) on a 4x spatially
binned spectrum image (256 x 256 pixels and 4096 energy channels for improved intensity statistics). X-ray intensities reported are background subtracted, integrated over an appropriate window centered around the Pt and Au L\textsubscript{\alpha} and L\textsubscript{\beta1} lines; the M lines for these elements were not used as they present a high degree of overlap.

HAADF-STEM tilt series images for electron tomography were acquired manually, with tilt increments of 2 or 5\degree and angular ranges of ca. \pm 65\degree, and were aligned using a combination of cross-correlation (FEI Inspect3D) and landmark based alignment\textsuperscript{40} (TomoJ). The tilt series images were background subtracted and normalized such that all images in each tilt series had the same integrated intensity; these steps reduced the impact of carbonaceous contamination and diffraction contrast. Tomographic reconstruction of the background-subtracted tilt series was carried out via a compressed sensing approach,\textsuperscript{41} using the ASTRA toolbox\textsuperscript{42,43} (available at: https://sourceforge.net/projects/astra-toolbox/) in conjunction with a 3D implementation of TVAL3 (reference 44 available at: http://www.caam.rice.edu/~optimization/L1/TVAL3/) for total variation minimization. Thorough description of total variation minimization and its implementation in electron tomographic reconstruction can be found in references\textsuperscript{41,42,44,45}.

Volume rendering and isosurface visualizations of the 3D reconstructions were generated using ParaView (available at http://www.paraview.org/). The z-direction labeled on the reconstructions is parallel to the optic axis (the “missing wedge” direction; Supporting Information), the y-direction is parallel to the tilt axis and the x-direction perpendicular to these.

STEM-EELS data analysis was performed in HYPERSPY. A 200 x 200 pixel x 2048 energy channel (0.01 eV dispersion) spectrum image was acquired for the particle shown in Figures 6 and 7; the spectrum was cropped to 0.25-5.0 eV for analysis. A blind source separation approach based on non-negative factorization (as described previously\textsuperscript{34,46,47}) was used to decompose the
spectrum image into a set of \( n \) spectral components (or “factors”), which are then used to reconstruct the EEL spectra at each pixel. Because the whole data set is fitted at once, information about both the spectral and spatial distribution of LSPRs is obtained. The same \( n \) components are used to fit each spectrum; their relative intensity is varied at each point. The amount by which each component is multiplied for each point is called a loading; mapping this loading provides information about the spatial distribution of the probability of exciting this particular component. Note that components are not restrained to specific lineshapes.

3. RESULTS AND DISCUSSION

**Structure and Composition.** The reduction of \( \text{H}_2\text{PtCl}_6 \) on large (100-300 nm edge length) colloidal Au nanoprisms yielded an array of small Pt NPs decorating the Au \{111\} facets (Figure 1). In addition to triangular structures, the reaction mixture contained a small number of various truncated nanoprisms, hexagonal plates, and some elongated, ribbon-like morphologies (Figure S1). All particle shapes are thin plates (typically ca. 7 nm thick), display broad \{111\} facets, and also support the deposition of Pt NPs.

The composition of the decorated nanoprisms was confirmed to be Au and Pt by EDS. Figures 1(d, e) show elemental maps for Pt and Au (obtained from the background subtracted integrated intensities for both \( \text{L}_\alpha \) and \( \text{L}_{\beta 1} \) emission, located at 9.71 and 11.44 keV for Au, and 9.44 and 11.07 keV for Pt; full spectrum and additional maps available in Figure S2). The EDS map for Au is generally homogeneous, as expected for a prismatic nanoparticle. The EDS map for Pt is not homogeneous. The regions of higher X-ray intensity correlate well with the regions of higher HAADF-STEM intensity, as shown by red ellipses in Figures 1(c, d). Thicker regions of material
or higher atomic number \((Z)\) material give rise to stronger scattering and thus higher HAADF-STEM intensity. In this case, \(Z\) of Au and Pt are nearly identical and the HAADF contrast is mainly due to thickness effects. The correlation between the Pt EDS map and the HAADF-STEM image indicates that the thicker regions are where Pt NPs have grown. Analogously, the regions where fewer Pt NPs are present, contained in yellow ellipses in Figure 1(c, d), generate weaker X-ray emission in the Pt map. Finally, the EDS signal from the NPs located at the edges of the nanoprisms more clearly verifies their chemical identity, containing almost exclusively Pt signals, as shown by the difference map in (Figure S2(e)).

**Electron Tomography.** Traditional (electron or other) transmission microscopy techniques provide an image that represents an integral “projection” through an object, meaning that information pertaining to three-dimensional (3D) structure may be hidden. In the case of a very thin nanoprism decorated on both sides, this makes discerning the shape, size, and distribution of the Pt NPs on each respective side difficult, if not impossible. Previous reports used scanning electron microscopy, an essentially surface-sensitive technique, to observe the alignment of the Pt NPs, bypassing the projection obstacle by observing strictly one side of the structure at a time.\(^{38}\) However, that approach does not readily allow analysis of both sides of a given nanopris, nor of the full 3D structure. Here, tilt series (from large negative to large positive sample tilt angles) of HAADF-STEM images were obtained and used to study the 3D structure of the Pt-decorated Au nanoprism via tomographic reconstruction (Figure 2 and Supporting Information). This approach is successful because, as noted above, to a sufficient approximation (Supporting Information) the HAADF-STEM signal varies according the thickness of the specimen (i.e., the thicker the region of the sample, the stronger the high-angle scattering and the
higher the image intensity). This enables tomographic reconstruction of a 3D structure involving “back-projection” of the tilt series images.

From Figure 2 it can be seen that Pt NPs form in abundance over all faces of the nanoprisms (further visualization is provided in the Supporting Information). In addition to enabling more clear analysis of the growth of Pt NPs on each of the large Au \{111\} surfaces (Figure 2 and *vide infra*), the 3D reconstructions reveal information about the shape of the underlying Au nanopism. Interestingly, in addition to the planar morphology expected (Figures 2(a-c)), one of the nanoprisms is considerably bent (Figure 2(d)). This bending is consistent with the occasional observation of strong diffraction contrast in TEM and dark field TEM imaging – a consequence of local bending of the crystal structure. The bent morphology is only fully revealed, however, by electron tomographic reconstruction. The vast majority of nanoprisms analyzed though exhibit an overall planar morphology dictated by their face-centered cubic crystallography. Figure 2(c), for example, shows an orthoslice perpendicular to the large \{111\} facets, revealing a convex edge structure of the nanopism, consistent with the presence of slow-growing \{111\} facets and predicted theoretically from modified Wulff constructions.\textsuperscript{48,49} These nanoprisms are confirmed here for the first time to be very thin truncated bitetrahedra with eight \{111\} facets and, as previously known from electron diffraction, containing a central \{111\} twin plane.\textsuperscript{50}

**Pt NP morphology.** The electron tomography reconstructions also enable detailed analysis of the Pt NP morphologies, as shown in Figures 3 and 4 (further visualization is also provided in the Supporting Information). In Figure 3, orthoslices (2D “slices” through the 3D tomogram) are shown at different heights, intersecting the NPs on the extended faces of the Au nanopism at different vertical positions, as well as providing cross-sections of the NPs on the nanopism side faces. Projection images (such as conventional 2D HAADF-STEM images) mix the signal from
NPs on the top and bottom of the nanoprism, but the 3D tomogram and orthoslices enable separate analysis.

The pendant Pt NPs grow epitaxially and exhibit a dendrite-like morphology, which is a growth mode observed in several systems involving Pt overgrowth. However, the orthoslices (Figure 3) and 3D isosurface renderings (Figure 4) reveal several distinct motifs. One motif is a “mushroom-like” morphology where Pt NPs exhibit a narrow “trunk” region that is directly appended to the nanoprism surface, and is “capped” by a more broad Pt feature; examples are highlighted in the enlarged region of Figure 3(d) and in Figure 4(b). As highlighted in the enlarged region of Figure 3(g) and in Figure 4(c), there are also NPs that develop an irregularly branched morphology (dendritic-type), as well as particles that are not branched at all. In the case of extensive Pt NP growth (Figure 2(c); see also volume renderings and orthoslices in the Supporting Information), the NPs form a dense array in which many of the particle branches are irregularly shaped, and in which many Pt NPs are no longer discrete, as their branches are fused to those of neighboring NPs.

**Pt NP Growth Patterns.** Pt NPs deposit on both the broad triangular facets and the side facets of the Au nanoprisms, and tend to align in parallel to one of the nanoprism edges. This alignment results in the formation of discrete lines of Pt NPs, although these may migrate and/or fuse over time (Figure 2(c)). The decorated triangular nanoprisms either exhibit Pt NP rows oriented with respect to a single edge of the nanoprism, or there may be 2 or 3 different row directions; each of which is oriented parallel with respect to a different nanoprism edge.

The separable analysis of top and bottom Pt NPs made possible by the 3D tomograms is useful to understand whether there is a relationship between the alignment of the Pt NPs on the top and
bottom surfaces. Registration could indicate cooperative alignment across the high curvature nanoprism side facets. To explore this possibility, the alignment of NPs was analyzed using a series of orthoslices parallel to the main \{111\} facets; each orthoslice enables analysis of the Pt NPs on either the top or the bottom, without any contribution from the other side. Lines were drawn as shown in Figure 5, and the alignment was observed through a stack of orthoslices ranging from the NP “roots” to their “caps”. Conservatively, lines not obvious in the entire half-volume were rejected. Although there is some similarity in line directions, this appears related more to growth mediated by the edges of the nanoprisms. The superposition of the top and bottom sets of lines (Figure 5(d, h)) does not show explicitly consistent coupling of patterns for the top/bottom Pt NPs lines. This result indicates that there is no or minimal cooperative effects between growth on the top and bottom facets.

Alignment is increased when the nanoprism symmetry is lowered to 2-fold, as seen in parallelograms (Supporting Information), and when the size of the nanoprism is increased. Conversely, NPs tend to align less on small nanoprisms; the particle shown in Figure 2(c), with less alignment of Pt NPs, is smaller than those in Figure 2(a) and (b). It is also worth making brief remark that the Pt NP growth sometimes result in distinct circular patterns (e.g. Figure S4(c)), as well as localized patches of lower NP density or lower NP growth, as revealed clearly by the orthoslices. Note also that many of these regions of lesser NP growth are not mirrored on top and bottom surfaces suggesting NP growth (and/or migration over time) without top/bottom coupling.

**Localized Surface Plasmon Resonances (LSPRs).** Pt is an excellent catalyst, but a poor plasmonic material.\(^{31-33}\) Use of Pt in the form of small, high surface area discrete NPs on a plasmonic material such as Au offers an opportunity for plasmon-driven catalysis and in-situ
monitoring of catalytic processes via surface-enhanced spectroscopies. Using STEM-EELS performed in a monochromated FEI Titan, we confirmed that the presence of discrete Pt NPs did not prevent enhanced fields at the surface of the Au nanoprisms.

Electrons passing near the surface of a plasmonic nanostructure can excite LSPRs and lose the amount of energy associated with this resonance; such electrons are dispersed by an electron spectrometer and imaged on a charge coupled device (CCD), yielding information about the spatial distribution of LSPRs. Spectra at different positions of an ~190 nm side length Pt-decorated Au nanoprism, binned from areas 5 pixels (9.3 nm) wide, are shown in Figure 6. When the electron beam is near the nanoprism corners, a distinct peak is visible at ~1 eV, indicating that many electrons lose ~1 eV of energy. Similarly, when the beam passes near the center of an edge, electrons are likely to lose ~1.3 eV. These peaks suggest that the nanoprisms may sustain LSPRs with different energy and spatial distribution.

To unravel spatial and spectral information about LSPR excitation on Pt-decorated Au nanoprisms, STEM-EELS spectrum images were analyzed using non-negative matrix factorization (NMF) (see Experimental Details). This approach enables the extraction of both spectral component energy and spatial localization, and has been applied to several systems, including bimetallics. Figure 7 shows the results of this decomposition applied to the spectrum image of the nanoprism shown in Figure 6. Four components were used, as this number was found sufficient to explain the full spectrum image. Systematic analysis ($n_{\text{components}} = 4-7$) for the particle presented in Figures 6 and 7, and other particles, are reported in the Supporting Information.
The overall greatest contribution to the spectrum image of Figure 7 is the tail of the ZLP, i.e. the energy distribution of the incoming electrons. As a result of absorption and scattering, this spectral contribution is weakest inside the particle; it is constant outside the particle as the underlying Si$_3$N$_4$ film thickness is reasonably uniform. The second contribution to the spectrum image is a broad component with an onset at \( \sim 1 \) eV; this represents the interband transitions (IBTs) in both Au and Pt. Indeed, that Pt contributes to this energy loss can be seen by the considerable intensity of the component in regions exactly corresponding to NPs, i.e. at the edges of the nanoprisms. The next component, represented by a blue line in Figure 7(a), is the edge LSPR. Its spectrum is centered at \( \sim 1.25 \) eV, with a full-width half-maximum (FWHM) of \( \sim 0.7 \) eV. The spatial distribution of the edge LSPR is akin to that observed in undecorated Au nanoprisms.\(^{54,55}\) The other component unraveled by NMF is the corner LSPR, which localizes the electric field at the tips of the nanoprisms.\(^{54,55}\) This component is centered at \( \sim 0.9 \) eV, and is sharper, with a FWHM of \( \sim 0.4 \) eV. Both LSPRs extend into the Pt NPs, which, combined with studies of far-field optical coupling, may open possibilities for multi-functional nanostructures.

STEM-EELS experiments and NMF data analysis performed on undecorated Au nanoprisms from the same synthesis batch used for producing the decorated nanoprisms (Supporting Information), as well as previous studies on similar bare structures,\(^{54,55}\) reveal nearly identical corner and edge resonances. All undecorated and decorated nanoprisms studied here by STEM-EELS (five and six of each, respectively) showed similar behavior. However, a direct comparison of the plasmon energy before and after Pt decoration is not feasible with STEM-EELS due to impracticality of locating the same nanoprism(s) before and after decoration, as well as the potentially perturbing effects of a substrate on solution-phase growth. Here, a bulk measurement, UV-Vis-NIR spectroscopy, provides additional information about the effects of Pt
on the LSPR and complements STEM-EELS by providing statistical, ensemble-averaged behavior. UV-Vis-NIR spectra show a slight red-shift and dampening of the plasmon (Supporting Information), consistent with previous studies on core-shell nanorods and nanospheres.\textsuperscript{37,56} This spectral broadening effect is primarily due to the poor plasmonic activity of Pt caused by interband transitions.\textsuperscript{31-33} Combined, these analyses strongly corroborate the notion that plasmonic activity is only minimally impeded by the presence of Pt.

4. CONCLUSIONS

Reduction of Pt salts can be used to produce discrete dendritic Pt nanoparticles at sizes relevant for catalysis across all surfaces of colloidal Au nanoprisms, with distinct nanoparticle morphologies ranging from pseudospherical to dendritic, and spatial distributions that appear to be strongly dictated by the nanop prism geometry. Pt-decorated Au nanoprisms can sustain localized surface plasmon resonances, which extend into the Pt NPs. Given the well-known catalytic properties of Pt and the burgeoning field of plasmon-enhanced catalysis, these insights provide a step towards, and motivation for, precise tailoring of bimetallic nanoparticles that couple catalytic and optical properties to provide versatile multi-functional systems.
**Figure 1.** Pt-decorated Au nanoprisms. (a, b) HAADF-STEM images of Au nanoprisms before and after Pt decoration, (c) HAADF-STEM and (d, e) STEM-EDS maps of Pt and Au. The red and yellow ellipses highlight areas of high and low Pt concentration, respectively. Scale bars, 50 nm.
**Figure 2.** Volume rendering visualizations of the four Pt-decorated Au nanoprisms studied by electron tomography. (a, b) Planar ~7 nm thick Au nanoprisms with lower and higher amounts of Pt NP growth, respectively (total thickness ~15 nm). (c) Smaller (edge length ~110 nm) but thicker (~14 nm) Au nanoprism with extensive Pt NP growth (combined thickness ~25 nm). The
inset orthoslice reveals well-defined convex \{111\} facets of the Au nanoprism. (d) Pt-Au nanoprism with twisted morphology. Further volume rendering visualizations are available in Supporting Figures 3-6 and Movies 9-12.

**Figure 3.** Sequential orthogonal slices (a-g) through the electron tomographic reconstruction of a Pt decorated Au nanoprism (corresponding to that shown in Figure 2(a)). Orthoslices are labeled according to the regions of the Pt NPs on the extended faces of the Au nanoprism that they dominantly intersect; roots, trunks or caps, as labeled on the inset enlarged view of a side-face NP in (d). Orthoslices for all nanoprisms studied by electron tomography are available in Supporting Figures 3-6 and Movies 5-8.
**Figure 4.** Isosurface renderings of the electron tomographic reconstructions, showing the Pt NP morphologies. (a) Overview of NPs on main and side faces. (b, c) Specific morphologies: (b) distinctive root, trunk and “mushroom-like” caps; (c) irregularly branched (“dendritic-type” cap), and NPs without caps and greater (uncapped trunk) and lesser (stump) height.

**Figure 5.** Alignment of the Pt NPs on Au nanoprisms. (a, e) HAADF-STEM images, which comprise a projection through both top and bottom surfaces. (b, c) and (f, g) Orthoslices of the tomographic reconstructions for the top and bottom surfaces, respectively, taken at heights
corresponding approximately to the “trunks” of the Pt NPs. (d, h) Schematic of top and bottom NP growth lines. Scale bars, 50 nm.

**Figure 6.** Raw (color-coded diamonds, binned 5 x 5 pixels equivalent to 9.3 x 9.3 nm) and fitted (linear combination of NMF-extracted components, black lines) EELS spectra obtained from a Pt-decorated Au nanoprism, at the positions indicated by color-coded squares in the HAADF-
STEM image (square sizes exaggerated by a factor of 3 for clarity). Spectra are vertically offset for clarity. The solid and dotted black arrows show the approximate position of the corner and edge LSPRs, respectively. Scale bar, 50 nm.

Figure 7. LSPRs and other contributions to EELS spectrum imaging of the Pt-decorated Au nanoprism shown in Figure 6. (a) NMF-extracted spectral components and fit of the raw data, for the EELS response of a 5 x 5 pixel region (9.3 x 9.3 nm) at the position in the inset (purple square size exaggerated by a factor of 3 for clarity). (b) Spatial loadings of each of the
components across the full spectrum image; ZLP, IBTs, edge LSPR, corner LSPR. Scale bars, 50 nm.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

Additional STEM images, EDS spectra and maps, EELS spectra and maps for decorated and undecorated nanoprisms, tomography results and UV-Vis-NIR extinction spectra (PDF)

Movies of electron tomography tilt series and reconstructions (AVI)

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Notes

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