Structural characterization of Au nano bipyramids: reshaping under thermal annealing, the capping agent effect and surface decoration with Pt

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Abstract
Anisotropic gold nanoparticles offer potential applications due to their functionalities and shape-dependent properties. Reshaping noble metal nanoparticles is an interesting field with optical, surface-enhanced Raman spectroscopy, catalytic applications and potential application as a photothermic therapy. This work comprises a structural study on gold nano bipyramids (Au NBPs) and nanodumbbells, and the evolution of Au NBPs capped with cetyltrimethylammonium bromide and dodecanethiol through an in situ and ex situ heating process in high vacuum. Also, we study the reshaping of Au NBPs by the addition of Pt to study the surface modification and the strain generated on a single particle by geometric phase analysis.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction
Metal nanostructures are an interesting group of materials whose properties are determined by their sizes and shapes. The considerable interest in studying gold nanostructures to be used in a variety of applications arises from the fact that gold has high electrical conductivity and reflectivity, and it constitutes a relatively inert material, which provides stability and resistance to corrosion and oxidation in these nanomaterials [1]. Also, nanostructured materials offer the opportunity to enhance their unique properties. For example, noble metal nanoparticles (NPs), in particular Au NPs, possess strong plasmonic properties with potential applications. Localized surface plasmon resonance (LSPR) is an optical phenomenon generated by the collective oscillation of the electron gas in some metal nanostructures surrounded by a dielectric. In Au NPs, LSPR appears as a response to the absorption and scattering at specific resonant wavelengths when a gold NP is irradiated with light, and depends on the morphology and dielectric environment of the NP [2–4].
At present a wide variety of gold nanostructures with different shapes and sizes can be obtained by colloid chemistry, such as spherical NPs [5–7], hollow NPs [8] and elongated structures as nanorods [9–11], nano bipyramids (NBPs) [10–12] and nanowires [13, 14]. Nanorods and Au NBPs exceed the spherical structures regarding the range of light absorption, since in the case of spherical structures the maximum absorption due to LSPR can occur between 500–600 nm, while the elongated structures can have absorption peaks in the near-infrared (NIR) region [2]. This is important because of the so-called ‘biological transmission window’ of 650–950 nm, where tissues become transparent to electromagnetic radiation by applying NIR laser radiation for the excitation of the NP LSPR in photothermal cancer therapeutics [2, 15].

Notably, Au NBPs are gaining attention in the fields of sensing [16–19] and catalysis [20]. Also, the morphology of Au NBPs presents sharp tips and edges and, in agreement with theoretical calculations, an essential local field enhancement is expected in those parts (hot spots) [16–21]. This makes them suitable candidates for surface-enhanced Raman spectroscopy (SERS) [22]. The synthetic methodologies to obtain Au NBPs are mainly based on the gold seed-mediated growth, kinetically assisted by the underpotential deposition of silver atoms [11]. Afterwards, the bipyramids can be regrown under different experimental conditions, mostly by varying the relative amounts of surfactants, and the quantity of added silver, to obtain a different type of Au NBP-based nanostructure, such as larger bipyramids and dumbbells [12]. The reshaping of the ends and size of these structures generates a fine tuning of the LSPR band in the visible and NIR region [12].

There is plenty of work devoted to tailoring surface properties of Au nanostructures by attaching different types of organic molecules (known as ‘organic capping’) and covering the surface with other metals or metal oxides [23–28].

Capping molecules are usually surfactants or other organic molecules that are attached to the Au surface and assist during the synthesis, keeping the NPs stable and allowing their redispersion in different solvents, according to their polarity and nature. Commonly, Au NBPs are capped with cetyltrimethylammonium bromide (CTAB) molecules [11, 12]. As some of the potential and future uses for these bipyramids may require high-temperature operation conditions, it is transcendental to study their thermal stability and to explore the role of capping agents in the thermal stability of these. Oxidative etching of Au bipyramids employing H2O2 or high temperatures and oxygen has been shown as a simple way to obtain Au nanorods of different morphologies using Au bipyramids as a starting point [12]. This process reshapes bipyramids by cyclic oxidations of Au (0) to Au (III) caused by the oxidizing agents and deposition/redeposition of Au (III) to form Au back onto the surface in low-energy and low-defect areas until the particles reach an energy minimum, which is attributed to a gold nanorod. From these studies, information related to the thermal and chemical stability of these particles can also be extracted and inferred, but there is a lack of information regarding the influence of capping agents over this process. It was reported elsewhere [12] that oxidative etching by heating over Au bipyramids capped with CTAB is slower in comparison with benzyltrimethylhexadecylammonium chloride (BDAC)-capped bipyramids because of BDAC acting as an etchant together with the dissolved oxygen in solution.

Reshaping Au NBPs by surface modification with the deposition of other metals on their surface is an interesting field of study. For example, decoration of the surface of Au nanostructures with metals can dramatically change the properties of the hybrid NP obtained. Those metals can form layers, 3D deposited structures or alloys [20, 29–35]. Also, photocatalytic properties can be targeted through the deposition of different metals or metal oxides, such as Pt, Pd, Co, ZnO, TiO2 and CuO2, in the synthesis of heterogeneous metallic particles [20, 36]. Selective growth of different materials such as Ag, Pt or SiO2 over Au NPs can be exploited as an alternative to change Au surface dependent properties, for example by tuning the plasmon resonance [37]. In the present work, the surface modification of Au NBPs by using organic molecules and covering them with a catalytic metal was studied. In the first stage, the capping agent replacement was performed. Its effect over the thermal stability of Au NBPs was followed by in situ and ex situ heating experiments under high vacuum conditions. The capping agent affects the surface energy of nanocrystals, influencing rearrangement of Au atoms under the heating process. Secondly, the surface modification was performed by the deposition of Pt, to obtain bimetallic NPs that present both the Au plasmonic properties and Pt catalytic properties.

The structural arrangement of Pt over the Au NBP’s surface was analyzed through atomic-resolution imaging [20, 31–33].

2. Results and discussion

2.1. Reshaping of Au NBPs by thermal annealing

The modification of the morphology and the surface reconstruction of Au NBPs can be optimized during the synthesis process. A fundamental step to obtain a high yield of pure NPs remains in the purification method, where the presence of CTAB or BDAC micelles purifies the final colloidal solution. The synthetic procedure employed and previously reported in [11, 12] yields highly reproducible Au NP batches. Two different types of Au NBPs were produced; Au regular bipyramids and Au nanodumbbells (Au NDBs). The main differences in the synthetic procedure to obtain both types of bipyramids are the employed surfactants. In the Au NBPs, only CTAB was employed, while for the Au NDBs a mixture of CTAB/cetyltrimethylammonium chloride (CTAC) was used. CTAC preferentially covers the extremes of bipyramids, and the bonding strength of CTAC is weaker than with CTAB, which causes a preferential growth over the apexes [12].
Figure 1 shows electron micrographs of the obtained Au seeds and the Au bipyramids, as well as their visible—NIR spectra. Au seeds of ~5 nm in diameter presented the five-fold decahedral structure, which eventually evolved into the elongated bipyramid morphology. Their absorbance spectrum showed the surface plasmon resonance maximum at 508 nm, which confirmed the small size of the NP seeds. Figures 1(b) and (c) correspond to scanning electron microscopy (SEM) images of Au NBPs and Au NDBs. The particle size increased from 100 nm to 150 nm (long-axis length), which is reflected in the red shift of the plasmon resonance maximum. On the other hand, the typical widths of Au NBPs and Au NDBs were 27 and 37 nm, respectively. Both, Au NBPs and Au NDBs show the presence of the characteristic two peaks; the first one at 525 nm and 540 nm corresponding to the transverse plasmon resonance. The second maximum at 750 nm and 1000 nm, for Au NBPs and Au NDBs, respectively, corresponds to the longitudinal plasmon resonance, being highly dependent on the aspect ratio of the bipyramids.

The surface reconstruction and reshaping of nanoscale materials under thermal annealing is an interesting aspect to deal with because it is related to their thermodynamic stability. Additionally, the role of surface capping molecules in the behavior of these nanostructures under high-temperature conditions arises as a corollary aspect to analyze. Au NPs in different solvents subjected to heating showed an increase in their size due to coalescence or Ostwald ripening [38, 39]. Reshaping of Au triangular nanodisks to softer-edges and spherical NPs was observed under heating, which was attributed to the lower melting point expected in nanoscale particles [40].

A study of the thermal stability of Au NBPs and Au NDBs was performed by ex situ and in situ heating...
experiments in high vacuum conditions. Figure 2 shows the effect of *ex situ* heating experiments on bipyramids after 1 h at 200 °C and 400 °C. As-synthesized bipyramids present a five-fold symmetry along their long-axis owing to the multi-twin nature of the seed particles. The five-fold symmetry is elucidated from the displayed electron diffraction pattern, showing the overlapping of the [112] and [001] patterns from three diffracting subunits [41]. Hence, the bipyramids grow along the [110] direction of each decahedral seed, ending in sharp tips. The ~16° angle corresponds to the angle between the 2D projection of the edges and the five-fold axis, indicating that the faces correspond to high-index facets. Considering a truncated bipyramidal shape as a model of 86 nm in length and 30 nm width, the expected angle between the five-fold axis and each facet is ~13.5°. This angle can be related to {116} high-index planes: the high-energy planes forming each facet of the bipyramids.

As warming takes place, bipyramids start to lose their morphology as edges start to smooth. After 1 h of heating at 200 °C, the bipyramids were converted to oval structures with a decrease in the length from 86 nm to 60 nm in comparison with the dimensions of the bipyramids before heating, and an almost imperceptible change in the width (figure 2). The elongated shape still remained. However, as shown in figure 2(b), the top edges became long {220} edges, and the tips presented two reconstructed facets, with approximated angles of 59° and 34° with respect to the [110] five-fold axis. Taking into consideration the same analysis for a truncated bipyramidal shape, the facets should form approximated angles of 53.5° and 28.7°, respectively. These angles were correlated with {111} and {2–25} facets, which form calculated angles of 54.5° and 29.3°, respectively. All these facets represent lower energy facets compared to the original {116} higher-index facets [42, 43]. After 1 h of heating at 400 °C, a more isotropic and spherical structure can be observed, following the trend of decreasing the length to 55 nm (approx. 30%–40% decrease in comparison with the non-annealed Au NBPs) and increasing the width to 45 nm (approx. 50% increase in comparison with the non-annealed Au NBPs).

**Figure 2.** TEM images and selected area electron diffraction (SAED) patterns of the Au plane-bipyramids (a)–(c) and dumbbell bipyramids (d)–(f), before and after heating annealing in vacuum for 1 h at different temperatures. The SAED patterns correspond to the projected patterns of the individual monoclinic crystals. Geometrical models of the beam direction over the NPs are shown as insets. After 200 °C, both types of particles underwent a marked reshaping. However, the five-fold symmetry was retained, indicating that atomic distribution takes place to lower the surface energy without reaching melting of the particle.
In the Au NDBs, the trends were similar, with a decrease of 30%–40% in length after annealing at 400 °C. The Au NDB in figure 2(d) taken along the [111]/[110] zone axis showed a 14° side, corresponding to {116} facets. The same angle was formed with the broad tip. After annealing at 200 °C, the particle underwent a shape transition exposing {220} edges at the top, and slightly sharper tips compared to the previous case. However, after annealing at 400 °C the particle retained its elongated shape, exposing longer {220} edges and shorter tips. From this analysis, it is inferred that both bipyramidal and dumbbell morphology correspond to a thermodynamically metastable structure, undergoing a shape transition from high-index facets to low-energy facets, and finally to a quasi-spherical morphology after annealing. Because of the high surface area exposed by the NPs, the spherical shape, with minute facets, represents a minimum energy configuration that lowers the surface energy for both types of bipyramids [44]. This is a consequence of the trend to decrease the surface area at the same volume, to lower the overall surface energy. From the selected area electron diffraction (SAED) patterns, it is clear that the five-fold symmetry of the NPs after thermal annealing remained, indicating that the melting point was not reached. The small particles that appear around the Au bipyramids while heating can be a consequence of the thermally assisted reduction of the remains of HAuCl₄.

The oxidation of gold bipyramids employing H₂O₂ [45] or oxidative etching with the oxygen dissolved on the surrounding media, while heating at 120 °C [12], causes a similar change in the bipyramid’s morphology in both cases. In the first case, it was reported that oxidation takes place preferentially at surface sites with a high curvature, such as apexes and edges and that both the length and the width of the bipyramids decrease as bipyramids tend to sphere, with the concomitant appearance of an absorption signal of dissolved Au (III). In our study, the length of the bipyramids is shortened but the width is increased, thus this is not a case of oxidation and loss of Au atoms as in oxidative etching cases that are known to reshape crystals via atomic addition and subtraction [46].

The influence of capping molecules or stabilizing agents on the thermal stability of Au bipyramids was analyzed. In the obtained bipyramids, the surfactant that they have after synthesis is CTAB. It is reported that CTAB is attached to the surface via an Au-Br bond, that can be detected from a characteristic signal at 190 cm⁻¹ [47] of the Raman spectrum, as can be extracted from figure 3. A procedure to replace CTAB molecules with dodecanethiol molecules was carried out. Although this ligand exchange was reported for nanorods [48], we could adapt the process for Au NBPs in the present work. The successful replacement of CTAB-capping molecules was demonstrated by Raman spectroscopy, following the disappearance of the Au-Br signal of CTAB-capped particles and the appearance of the Au-S signal near 250 cm⁻¹ [47, 49] for dodecanethiol-capped particles (figure 3).

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of bipyramids taken in situ while heating at 94 °C and the change in the dimension measurements over time are presented in figure 4 for Au NBPs with CTAB and in figure 5 for bipyramids with dodecanethiol. The chosen temperature to analyze the stability of the particles was slightly below 100 °C as one of the potential uses for these NPs is related to nanotheranostic and photothermal therapy applications, where the optimum temperature range lies between 37 °C and 60 °C [50, 51]. It is worth mentioning that the chosen temperature is far below the desorption temperatures of both capping agents. The CTAB-capped Au nanorods show three different desorption temperatures; that at 230 °C is due to the evaporation of weakly bounded surfactant monomers, while 273 °C and 344 °C are attributed to the outer and inner layer of the adsorbed membrane [52]. On the other hand, in the case of dodecanethiol bounded to a gold surface, the desorption temperature found in the literature was between 230 °C and 330 °C [53].

First, it can be observed that, for the CTAB case, the change in the morphology of Au bipyramids is less marked at 94 °C in comparison with the changes observed at higher temperatures (figure 2). However, by measuring the dimensions of the bipyramids after different heating times at 94 °C, it can be observed that there is a trend for a decrease in the length and an increase in the width over the heating time, even at the low temperature 94 °C. As a control, in each case one of the bipyramids was irradiated with the electron beam all the time during heating (see figures S1 and S2 of the supporting information available online at stacks.iop.org/NANO/30/205701/mmedia), and the trend was the same as for the other bipyramids that were only heated, not irradiated. These results indicate that the observed features depend exclusively on the temperature. This type of lattice contraction, where the contraction along one crystallographic direction is usually accompanied by expansion along the others, is common in anisotropic systems, and it is referred to as negative thermal expansion [54]. An interesting fact arises when measuring the dimensions of the bipyramids when they reached room temperature after being heated for 3 h at 94 °C. A small throwback in the trend can be observed, meaning that there is a slight increase in the length and a decrease in the width of the bipyramids when they return to room temperature. This effect can be related to a grade of elastic nature deformation capacity of gold bipyramids: in other words, a ‘memory’ effect. From a more in-depth study of this effect,
mechanical properties of this type of NPs can be inferred. Also, the whole trend is more marked in the case of bipyramids with CTAB in comparison with those stabilized with dodecanethiol. This effect is related to the bonding energy of the bipyramids; a strong bond has been found for Au-S ($40 \text{ kcal mol}^{-1}$) [54, 55] in comparison with the Au-CTAB bond. Therefore, the mobility of the Au surface atoms is reduced, allowing a favorable and higher stability in the crystalline structure of the bipyramids with dodecanethiol.

2.2. The decoration of Au NBPs with Pt nanostructures.

Another approach to the surface modification of Au bipyramids is the deposition of Pt over the NP’s surface. Mixing Au bipyramids’ plasmonic properties with the catalytic activity of other noble metals is an interesting option for several applications that require both features. Thus, to enhance the catalytic activity of metal NPs, the synthesis of nanosized bimetallic particles must be achieved. Depending on the synthetic method and on the nature of the metals that are mixed, core–shell systems or homogeneous alloys can be obtained [35], and aggregated phases can also be obtained [56].

Figures 6(a)–(d), show SEM micrographs of Au bipyramids decorated with Pt, employing Pt solutions of different concentrations. When the concentration of HPtCl$_6$ in the reaction solution is low, Pt forms deposited aggregates over the edges of the Au bipyramids. As the Pt concentration increases, the formed aggregates start to be located relatively uniform over the whole surface of the Au. It is reported that the growth of thin films of Pt over Au obeys the Stranski–Krastanov model for heterogeneous nucleation and growth theory [57]. This model represents a growth type in which the metal tends to form 2D islands over the substrate, and afterwards, these islands can grow in a 3D manner, generating particles. The growth mode is mainly determined by the lattice match and interactions between the overlayer and substrate; thus, the Stranski–Krastanov model [58] is an intermediate mode between layered growth (Frank–van der Merwe) [59] and the island growth (Volmer–Weber) [60]. Also, the ‘wettability’ of the substrate surface with the shell material, related to the relative electronegativity of both
metals, is a determinant in the growth model of the system [29].

As the degree of Au surface coverage with Pt increases, the surface plasmon signal decreases (figure 6(e)), because less amount of Au is present on the surface. Thus, the potential enhancement of the catalytic properties of these combined particles can be detrimental to applications that require the presence of the surface plasmon absorption band [31]. Also a red shift of the plasmon signals is observed when increasing the amounts of Pt deposited over Au NBPs. It has been reported that longitudinal surface plasmon resonance in non-spherical Au particles is very sensitive, not only to slight morphological changes but also to atomic level roughness due to crystallographic reconstructions [61]. Therefore, the observed red shift of the plasmon signals can be attributed to lattice reconstruction or an increase in Au NBP surface roughness as a consequence of the Pt deposition process. Among the obtained samples, the one that retained a notable plasmon resonance signal and that presented uniformly sized and distributed Pt aggregates was selected to be fully characterized. The HAADF images and energy-dispersive spectroscopy (EDS) elemental mapping images are shown in figure 7.

Also, figure 7 shows a low and high magnification STEM image of an Au–Pt pyramid (figures 7(a) and (b)) correspondingly). Additional HAADF analysis showed how the Pt particles tend to deposit over the edges of the bipyramids. Some of the Pt nanodeposits are faceted. Fast-Fourier transform (FFT) power spectrum analysis shows that both nanostructures are oriented along the [011] zone axes. The distance between Au–Au peaks is 0.23 nm, and Pt–Pt peaks are 0.225. These values are consistent with those corresponding to Au {111} and Pt {110} planes, respectively. The elemental map of the Au–Pt nanostructures was obtained using EDS (figures 7(c)–(e)). Different colors indicate the presence of different elements, where green and red refer to the presence of Pt and Au, respectively. Moreover, the overlap of both elements is shown in figure 7(f). Figures 7(g) and (h) show a line-scan EDS spectrum of Au and Pt through a yellow crossing line in an individual NP. The Au signal was obtained only across the core region, whereas the Pt signal was traced across the entire particle, especially at the edges of the bipyramid.

The geometrical-phase analysis (GPA) method was used to quantify the strain distribution field relaxation map in Au–Pt. To perform GPA, Fourier filtering and image processing are used in high-resolution electron microscopy images to improve the contrast, locate lattice mismatch sites and calculate the displacement and strain field mappings in a crystal lattice [62]. This is achieved by placing masks around

Figure 5. Changes in the dimensions ((a) width, (b) length and (c) width/length ratio) of dodecanethiol-capped Au bipyramids while heating. Each color corresponds to different particles. (d) STEM micrographs of bipyramids before and after heating.
the different Bragg spots in the Fourier transform images, and then forming the image by applying the inverse Fourier transform. From the image formed by the strong lattice reflections, it becomes possible to determine local variations in the structures, which is especially useful in nanomaterials with interfaces between two components [62].

The Au/Pt interface was studied by GPA. Figure 8(a) shows a low magnification HAADF-STEM image of a gold bipyramid that was decorated with Pt. Figure 8(b) corresponds to a magnified area of one facet oriented along the [110] axis zone. The (11-1) and (-11-1) spots were chosen for GPA, the Gaussian mask was placed around these spots to isolate them and the strain maps were calculated. It can be observed that high strain is accumulated at the interface between Au and Pt, originating from the lattice mismatch between both metals (figure 8(c)). The strain values are represented by a temperature scale, going from 10% tension strain to −10% compression strain. The intensity profile across the atomic columns, figure 8(d), indicated that strain was approximately constant along the Au bipyramid and

Figure 6. SEM micrographs of Pt-decorated Au bipyramids employing different concentrations of Pt: (a) $1.85 \times 10^{-6}$ M, (b) $9.25 \times 10^{-6}$ M, (c) $1.85 \times 10^{-5}$ M and (d) $1.85 \times 10^{-4}$ M. (e) The absorption spectra of the corresponding samples.
abruptly changed to ∼4% compressional strain at the interface with Pt. The magnified HAADF-STEM image and the intensity line profile on it showed the atomic displacement at the Au–Pt interface as a consequence of the accumulative lattice strain (figure 8(e)). This indicated that stacking faults were formed and accumulated during the growth of the lattice-mismatched shell.

3. Conclusion

Au NBPs represent a versatile platform for a wide range of applications tuning their properties by surface functionalization, either by capping exchange procedures or metal surface deposition. Thermal annealing of the bipyramids caused a drastic morphology change attributed to the minimization of the surface energy. CTAB-capping molecules can be easily replaced by dodecanethiol, and a difference in the behavior was detected when performing thermal annealing. The changes in dimensions while heating CTAB-capped particles is more prominent in comparison with dodecanethiol-capped particles, due to the stronger interaction between thiol molecules and Au surfaces. A little throwback in the deformation trend can be observed when Au NBPs return to room temperature after being annealed at 94 °C. It is interesting to explore this effect as it is related to a grade of elastic nature deformation capacity of Au NBPs.

The surface modification of Au bipyramids with Pt post-growth nanostructures was also studied as a possibility for combining the plasmonic properties of Au bipyramids with Pt catalytic properties. Pt was deposited onto the particles, forming agglomerates over the Au surface, especially over edges, obeying the Stranski–Krstanov epitaxy growth model. The amount of deposited Pt can be controlled by the synthetic conditions, which also determines the intensity of the Au plasmon band. Thus, to satisfactorily combine the catalytic and plasmonic properties of both metals, a balance between the amount of Pt and Au on the surface and strain engineering should be targeted.

4. Experimental section

4.1. Reagents

All the following reagents were purchased from Sigma Aldrich and used without further purification: tetrachlorauric acid (HAuCl₄·3H₂O, ≥99.9%), sodium borohydride (NaBH₄), citric acid trisodium salt dihydrate (≥99.9%), CTAB (Bioxtra, 99%), CTAC (≥98%), BDAC, L-ascorbic Acid (AA, Bioxtra, 98%), silver nitrate (AgNO₃, BioXtra, >99%), 1-dodecanethiol and hexachloroplatinic (IV) acid hydrate (H₂PtCl₆·7H₂O, ≥99.9%). Hydrochloric acid solution (HCl, 1N) was purchased from Fisher Scientific. Also, deionized water was used in all the experiments.

4.2. Synthesis of Au NBPs

The Au NBPs were synthesized according to the previous reported methods with some modifications [10, 11]. Briefly, to produce Au bipyramids, the first step was the synthesis of...
Au seeds by mixing ultrapure water (18.95 ml), HAuCl₄ (0.25 ml, 10 mM), and sodium citrate (0.5 ml, 10 mM), followed by a rapid addition of cold and fresh NaBH₄ (0.3 ml, 10 mM). This solution was kept under magnetic stirring at room temperature for 2 h. Then, the plain bipyramids were grown in a solution containing CTAB (10 ml, 0.1 M), HAuCl₄ (0.5 ml, 0.01 M), AgNO₃ (0.1 ml, 0.01 M), HCl (0.2 ml, 1 N), ascorbic acid (0.08 ml, 0.1 M), and the prepared Au seed solution (95 μl). The mixture was stirred and kept in an oil bath at 30°C for 2 h. The growth solution was centrifuged at 11 000 rpm for 15 min and washed twice with CTAB (1 ml, 1 mM). The obtained precipitate was dispersed in CTAB (3 ml, 1 mM) for further purification. First, to produce the selective precipitation of the pyramids separated from the seeds, 3 ml of CTAB solution was mixed with BDAC solution (6.2 ml, 0.5 M) and ultrapure water (0.8 ml) and left in an incubator at 37°C overnight. The supernatant was removed, and CTAB (3 ml, 1 mM) was added to the vial to disperse the precipitate helped with an ultrasonic bath. The resulting purified solution was centrifuged at 10 000 rpm for 8 min and washed with CTAB (1 mM), repeated twice, then dispersed in CTAB (1 mM) for further characterization.

Purification of bipyramids and dumbbells was performed by several centrifugation cycles at 4000 rpm in ultrapure water and mixtures of increasing ethanol proportion. The as-obtained Au NBPs and Au NDBs can be dispersed in water or ethanol.

4.3. Synthesis of Au NDBs

To prepare the NDBs (bipyramids with spheres in the apexes), CTAC solution (1.8 ml, 0.1 M) was mixed under stirring at 30°C with the sequential addition of CTAB solution (20 μl, 0.1 M), HAuCl₄ (100 μl, 0.002 M), AgNO₃ (20 μl, 0.002 M), HCl (20 μl, 1 N) and AA (40 μl, 0.02 M), and the colloidal solution was kept stirring for 5 min. Finally, purified bipyramid solution in 10 mM CTAB (200 μl) was added and kept under stirring for two hours. The resulting solution was centrifuged at 10 000 rpm for 8 min and washed with CTAB (1 mM), repeated twice, then dispersed in CTAB (1 mM) for further characterization.

4.4. Au NBP ligand exchange

The ligand exchange process, to replace CTAB from the surface of Au NBPs with dodecanethiol, is based on aqueous-to-organic phase transfer, according to a previous method.
The first step in the exchange reaction process was mixing the CTAB stabilized Au NBPs in aqueous solution with an excess of 1-dodecanethiol on the top of the solution, followed by the addition of acetone. The Au NBPs were extracted into the dodecanethiol phase after the mixture reaction was shaken vigorously for 1 min and left undisturbed until the phase separation occurred. After the procedure, it could be observed that the aqueous phase turned colorless, demonstrating the effectiveness of the proposed approach.

4.5. Au NBPs and Pt deposition

The as-prepared Au NBPs (100 μl) in CTAB (1 mM) were mixed with CTAB solution (900 μl, 0.1 M), AgNO₃ aqueous solution (10 μl, 0.01 M), ascorbic acid solution (8 μl, 0.02 M) and H₂PtCl₆ aqueous solution (70 μl) at different concentrations ranging from 10⁻⁷ to 10⁻⁴ M. The mixture was heated at 80 °C for 40 min under magnetic stirring.

4.6. Thermal experiments

For the thermal stability study of the bipyramids, the samples were seeded on molybdenum transmission electron microscope (TEM) grids. Ex situ thermal analysis was performed by heating the samples on the grids in an Evaporator-Inter-covamex TE12 (High Vacuum System) at 200 °C and 400 °C. In situ heating experiments were performed inside the STEM microscope by thermalizing the JEOL 21130 heating holder at 94 °C.

4.7. Characterization of the obtained Au NBPs

Au NPs were characterized employing a Hitachi 5500 field emission microscope operating at 30 kV, high-resolution SEM imaging and EDS. High-resolution TEM images were taken with a HRTEM JEOL 2010, and STEM imaging was carried out in a JEOL-ARM200F aberration-corrected microscope operating at 200 kV in STEM mode, coupled with a HAADF detector and EDS analysis. Optical characterization was carried out in a Thermo Scientific Evolution 220 UV–vis spectrophotometer. For the strain distribution in the interface of the Au/Pt bipyramid, GPA was used.

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Conflict of Interest

The authors declare no conflict of interest.

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