Seedless Synthesis of Single Crystalline Au Nanoparticles with Unusual Shapes and Tunable LSPR in the near-IR

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Supporting Information

ABSTRACT: The plasmonic properties of metal nanoparticles have acquired great importance because of their potential applications in very diverse fields. Metal nanoparticles with localized surface plasmon resonances (LSPR) in the near-infrared (NIR, 750−1300 nm) are of particular interest because tissues, blood, and water display low absorption in this spectral range, thus facilitating biomedical applications. Cetyltrimethylammonium chloride (CTAC) was used to induce the seedless formation of highly anisotropic, twisted single crystalline Au nanoparticles in a single step. The LSPR of the obtained particles can be tuned from 600 nm up to 1400 nm by simply changing the reaction temperature or the reagents concentrations. The tunability of the LSPR is closely associated with significant changes in the final particle morphology, which was studied by advanced electron microscopy techniques (3D Tomography and HAADF-STEM). Kinetic experiments were carried out to establish the growth mechanism, suggesting that slow kinetics together with the complexation of the gold salt precursor to CTAC are key factors favoring the formation of these anisotropic particles.

KEYWORDS: gold nanoparticles, NIR absorption, surface plasmon resonance, electron tomography

INTRODUCTION

The special optical properties of metal nanoparticles arise from localized surface plasmon resonances (LSPR), which occur when conduction electrons in metal nanostructures collectively oscillate, as a result of their interaction with an incident electromagnetic radiation of appropriate frequency.† Such nanoplasmonic properties of metal nanoparticles have acquired great importance because of their potential applications in fields as diverse as photonics, electronics, sensing, and biomedicine.²,³ Since the specific optical response might determine the final application, many efforts are focused on tailoring the LSPR frequency range, which in turn is mainly determined by nanoparticle size, shape, and composition.⁴ Additionally, the excitation of an LSPR mode gives rise to energy confinement at certain regions of the particles surface, creating a localized enhanced electromagnetic field. This effect is of special relevance at sharp corners and edges, as well as narrow gaps, making particles with sharp tips particularly appealing toward surface enhanced spectroscopy techniques.⁵ Thus, a tight control over nanoparticle synthesis is critically important.

The synthesis of metal nanoparticles, gold in particular, is mature and it can be safely stated that the present understanding allows us to obtain particle sizes within a broad range for a variety of shapes,⁶ so that the LSPR can be tuned in the visible and the near-infrared (NIR) regions. Metal nanoparticles with LSPRs in the NIR (750−1300 nm) are of particular interest because tissues, blood, and water do not absorb in this spectral range, thus facilitating biomedical applications.³ LSPR bands in the NIR can be achieved by increasing the anisotropy of Au nanoparticles, typically in the form of rods, stars, and plates.⁶−⁸

The growth of anisotropic gold nanoparticles through wet-chemical seed-mediated methods typically requires the use of a surfactant as “shape-directing agent”, and quaternary ammonium surfactants have become the most common choice.⁹ Previous works have demonstrated that cetyltrimethylammonium bromide (CTAB) is particularly efficient as directing agent and has allowed the preparation of Au nanoparticles with different shapes, such as nanorods, stars, and plates.⁶ CTAB’s chloride counterpart (CTAC) has also been used in the synthesis of anisotropic particles, however with more regular shapes, such as concave cubes, trisoctahedra, or rhombic dodecahedra.¹⁰−¹⁵ The reason for such different morphologies obtained with CTAB and CTAC has been attributed to the different ability of bromide and chloride ions to bind on Au surfaces.¹⁶,¹⁷

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In this work, we demonstrate that CTAC can induce the seedless formation of highly anisotropic, twisted single crystalline Au nanoparticles in a single step. The advantage of this method is that the LSPR of the obtained particles can be tuned from 600 nm up to 1400 nm by simply changing the reaction temperature (between 30 and 10 °C) and the reagents concentration. The tunability of the LSPR is closely associated with significant changes in the final particle morphology.

### EXPERIMENTAL SECTION

**Materials.** HAuCl₄ × 3H₂O, Na₂S, and CTAC solution (25% in water) were supplied by Aldrich; ascorbic acid (AA) was purchased from Sigma. All chemicals were used as received. Milli-Q grade water was used as solvent.

**Particle Preparation.** CTAC solution in water was stabilized in a thermostatic bath at a fixed temperature (between 10 and 30 °C, in 5 °C intervals) for 10 min, and then a HAuCl₄ solution was added until a final concentration of 6.25 × 10⁻³ M was reached. Immediately after (to avoid the reduction of Au³⁺ by CTAC), a selected amount of AA solution was added. Then, the solution was mixed and allowed to react inside the thermostatic bath for at least 2 h. The [CTAC]:[Au] molar ratio was varied between 15 and 120, and the [AA]:[Au] molar ratio was varied between 2 and 32. The use of different final volumes (from 3 to 20 mL) and the magnetic stirring did not affect the final particle size and shape. The excess of AA and CTAC was removed from the solution by centrifugation—redispersion steps (15 min, 6000 rpm).

Particle growth was followed by transmission electron microscopy (TEM). Several tubes containing 3 mL of HAuCl₄, CTAC, and AA solution at selected concentrations in water were kept in a thermostatic bath at the desired temperature. After a fixed time, the same volume of Na₂S solution (0.5 mM, final S: Au ratio 4:1) was added to the sample in order to stop particle growth. After one hour for stabilization at the reaction temperature, the sample was cleaned as described above and observed in TEM.

**Characterization.** Optical characterization was carried out by using UV−visible−NIR spectroscopy in a Cary 5000 UV−visible−NIR spectrophotometer, using 1 mm path length quartz cuvettes. Conventional TEM analysis was performed with a JEOL JEM1010 microscope operating at an acceleration voltage of 100 kV. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6700F FEG microscope operating at an acceleration voltage of 15 kV and with a secondary-electron detector. Tilt series for 3D tomography were acquired with a FEI Tecnai G2 microscope, operated at 200 kV. A single tilt tomography holder (Fischione model 2020) was used for acquisition, and the alignment and reconstruction were carried out using the FEI Inspet3D software. High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were acquired using a double aberration corrected Titan 50–80 microscope operating at 300 kV in STEM mode.

### RESULTS AND DISCUSSION

The synthesis of Au nanoparticles was performed via reduction of AuCl₄⁻ with ascorbic acid, in the presence of CTAC. The addition of AA immediately followed the preparation of the gold salt/CTAC solution. Preliminary experiments revealed a strong dependence of the nucleation and growth processes on temperature. Therefore, experiments at different temperatures (between 10 and 30 °C) were carried out. In all cases the molar ratio [Au]:[CTAC]:[AA] was 1:60:16. Figure 1 shows the optical response of the obtained colloidal dispersions as a function of reaction temperature. Remarkable changes were observed, mainly related to the LSPR shifting from ca. 600 nm up to 1400 nm as temperature was decreased from 30 to 10 °C. These results suggest a strong variation in nanoparticle morphology, which was confirmed by both TEM and SEM, as can be seen in Figure 2.

Whereas the particles grown at 10 °C are highly anisotropic, with long branches and planar appendices, particles obtained at 15 °C, 20 °C, and 25 °C can be described as formed by the intersection of planar structures, with different degrees of filling between the planes. Finally, the 30 °C sample seems to be a mixture of more rounded and solid shapes, resembling trisected gold nanoparticles. It is important to note that, though not all the particles obtained at a certain temperature present identical shape, each sample as a whole is uniform both in size and general morphology. The presence of nanoparticles with different shapes was not observed for any of the obtained samples.

Since conventional TEM techniques only provide 2D projections and SEM has limited resolution, the morphology of the Au nanoparticles was elucidated using 3D analysis by electron tomography in HAADF-STEM mode. Such a 3D reconstruction was carried out from a tilt series of 2D projection images (each time the sample was tilted by 2°, with an angular range of −76° to +76°). Figure 3 shows the 3D morphology of representative Au nanoparticles obtained at 10 and 20 °C (see also 3D rendering videos in the Supporting Information, SI).

The tomography images show that highly anisotropic particles synthesized at 10 °C display numerous long and flat appendices, while the particles synthesized at 20 °C present an intricate structure with high internal curvature and often presenting holes inside the particles, somehow resembling a crushed piece of paper.

With such unusual shapes, it was necessary to understand whether the curvature is dictated by defects in the crystalline lattice. Thus, we carried out high resolution HAADF-STEM imaging on selected samples to investigate the crystalline structure of the Au nanoparticles and the overall orientation of the sample. Using HAADF-STEM, a fine electron probe scans across an area of interest, and a HAADF detector will only collect electrons that have been scattered to high angles (>60 mrad) with respect to the optical axis. This results in images where the intensity scales with thickness as well as with the square of the atomic number Z of the elements present in the sample.
High resolution HAADF-STEM images and their corresponding Ronchigrams\textsuperscript{22,23} acquired at 6 different positions on these two types of particles are presented in Figure 4. The Ronchigrams are the undiffracted disks of electrons at the center of the convergent beam electron diffraction (CBED) patterns. The diffraction spots in these patterns are disk-shaped instead of small points because the incident angle of the electron beam increases for a smaller probe such as the one used in STEM mode. The recorded diffraction patterns are symmetric when the sample is correctly oriented along a zone-axis. Deviations from perfect symmetry consequently correspond to deviations from perfect zone-axis orientation. The analysis of the obtained images revealed that while in particles synthesized at 20 °C the whole particle is oriented along the same zone-axis (variation below 1°), the particles obtained at 10 °C present a mistilt of 3−4° between different orientations, i.e. some of the analyzed areas are oriented along the [001] zone axis, but others are not. Interestingly, both types of particles were found to be free of defects, indicating that they are single crystals. Thus, the HAADF-STEM results confirm that despite the extreme shape anisotropy of these
nanoparticles, they are constituted by defect-free single crystals and with only slight variations in the crystalline orientation.

**Effect of Temperature.** The effect of reaction temperature on the growth process was evaluated through the time evolution analysis of visible-NIR absorbance spectra during particle formation, along with the morphology information (also for different reaction times) obtained from TEM. Figure 5 shows the time evolution of the visible-NIR spectra during growth of the particles at 10 °C, together with representative TEM images of samples obtained by stopping the growth by addition of sulfide (see the Experimental Section), at different times. At this temperature, the main LSPR band is evidenced around 550 nm after ca. 10 min of reaction, and then it gradually red-shifts and broadens. This spectral evolution can be ascribed to the initial formation of spheroidal nanoparticles with several protuberances (Figure 5b) that evolve into tips or branches as the reaction proceeds (Figure 5c,d). The variety of length and width of those tips/branches is responsible for the observed red-shift and broadening of the LSPR band.8

Although the evolution of the LSPR bands is similar for the different temperatures (see Figure S1, SI), the reduction rate of the Au salt by AA is clearly temperature dependent. Figure 6 shows the evolution of the absorbance at 400 nm (A400 as an indication of the amount of metallic gold present in the sample), as a function of time. The kinetic traces evidence that the rate of reduction is higher when the temperature is increased. While at 10 °C the formation of the particles is completed (A400 reaches a plateau) within around 120 min, at 30 °C maximum absorbance is reached in only 40 min.

**Effect of CTAC and AA Concentrations.** It should be taken into account that the temperature effect was studied at a particular [Au]:[CTAC]:[AA] molar ratio of 1:60:16. Therefore, one could also expect an influence of the concentrations of CTAC and AA on the final particle size and morphology. The effect of CTAC concentration was analyzed keeping constant the temperature and [AA]:[Au] molar ratio (16), while the [CTAC]:[Au] molar ratio was varied between 15 and 120, at a fixed HAuCl4 concentration (6.25 × 10⁻⁵ M). Figure 7 shows the visible-NIR spectra of the dispersions (T = 10 °C) with different [CTAC]:[Au] ratios, as indicated, together with representative TEM images. At first sight, it can be clearly observed that the average particle size increases as the CTAC concentration increases, i.e. CTAC favors growth over nucleation. The strong influence of CTAC concentration on both processes is also reflected on the final morphology of the particles; at low [CTAC]:[Au] ratios (15 and 30) they could be described as ellipsoidal and monopod nanoparticles, respectively, with average sizes below 100 nm (see Figures 7a-7b). Further increase of CTAC concentration leads to the formation...
of particles with an increased number of pods, spikes, or appendices that eventually evolve into branched nanostructures along with an increase in the average size (see Figures 7c-7e). The different particle shapes obviously lead to different optical properties of the corresponding aqueous dispersions (Figure 7f). At low CTAC concentrations the ellipsoidal/monopod particles give rise to two well-differentiated LSPR bands, shown in the red and green spectra in Figure 7f, which are associated with the short and the long axes of the particles (similar to gold nanorods24). An increase in the number and size of branches leads to broadening and red-shift of the main LSPR associated with the plasmon mode localized at the tips.8 The visible-NIR spectra show an evolution of the main LSPR band from ca. 900 up to 1400 nm as the CTAC concentration is increased. Besides, a more anisotropic growth is promoted by the lower reduction rates as CTAC concentration increases. Thus, we observe that changing the CTAC concentration may be an alternative way to control the final particle shape and optical properties.

In the case of samples prepared at 30 °C, small variations in both the spectra and particle shape were observed (Figure S2, SI) for different CTAC concentrations. It is thus obvious from these results that the effect of temperature on the reaction kinetics is more pronounced than the effect of CTAC concentration.

Taking into account the influence of the reduction kinetics on particle size and morphology, a strong influence of the AA concentration on the nucleation and growth processes should also be expected. To evaluate its influence, the [AA]:[Au] molar ratio was varied between 2 and 32, while keeping constant the temperature and the [CTAC]:[Au] ratio (60). Figure 8 shows representative TEM images together with the visible-NIR spectra of the particles obtained at 10 °C.

In this case, as the AA concentration was increased, the LSPR band was observed to shift toward lower wavelengths. This blue-shift is directly related with a decrease in the number and length of appendices in the particles, as shown in Figure 8a-c. Once again, the kinetics of the reaction plays a key role: increasing the AA concentration accelerates the reaction and thus the obtained particles are less anisotropic. The effect of AA concentration on the particles morphology is minimized at temperatures where the growth kinetics is rather fast (see experiments at different [AA]:[Au] ratios performed at 30 °C, Figure S3, SI).

**Growth Mechanism.** In an attempt to figure out the formation mechanism of the anisotropic single crystal Au nanoparticles, we consider the growth kinetics as the key point in determining the final particle morphology. In this respect, particles with higher anisotropy were obtained when slower kinetic rates were induced by either decreasing the reaction kinetics.
temperature, the ascorbic acid concentration, or increasing the CTAC concentration (see Figures 2a, 8a, and 7e, respectively). Bearing these effects in mind, in what follows a number of facts are listed that should help us understand the mechanism.

First of all, the obtained highly anisotropic particles could resemble dendritic structures, which are known to form more readily when a growth system moves farther away from equilibrium,25 that is, when diffusive transport cannot keep up with the demand at the growing surface. However, to consider a critical mass transport process, only the growth of a preformed seed should be taken into account and this is not the case, since nucleation should be considered apart from the growth process.

Second, we need to consider that the gold complex ions (AuCl₄⁻) are quantitatively and strongly bound to CTA⁺ monomers, giving rise to a water insoluble complex with 1:1 stoichiometry.26 These complexes could be solubilized within CTAC micelles when working above the critical micelle concentration of CTAC (ca. 1 mM) and at an optimal CTAC:HAuCl₄ ratio >10:1. Assuming a micelle aggregation number of ca. 60, one AuCl₄⁻–CTA complex will be solubilized in each CTAC micelle.27 The solubilization of the complex within the CTAC micelle will necessarily affect the balance between the nucleation and growth processes and therefore the kinetics of the reduction. In fact, we found that at low CTAC:Au ratios nucleation is favored (smaller particles), while at high CTAC:Au ratios (above 60) growth is promoted over nucleation (larger particles).

The complexation of gold ions with CTA⁺ monomers also leads to an increase in their reduction potential, and, initially upon addition of ascorbic acid, the AuCl₄⁻–CTA complex gets reduced only to AuCl₂⁻–CTA.28 Subsequently, nucleation takes place at a rate determined by ascorbic acid concentration and temperature. Once the nuclei are formed, they grow due to the catalytic reduction of gold ions on their surface. It should be pointed out that the use of CTAB (with bromide as counterion) does not lead to the formation of metal nanoparticles under these conditions.27 The difference between CTAC and CTAB can be attributed to the different redox potentials of AuCl₄⁻ and AuBr₄⁻ (1.002 and 0.854 V vs NHE, respectively).

The final morphology of the particles can also be influenced by the use of CTAC as capping agent. It is well-known that the stabilization of gold nanoparticles by cationic surfactants implies the formation of a bilayer29 and involves the adsorption of the counterion, in this case chloride. Chloride ions present a lower adsorption affinity on gold surfaces than bromide or iodide but at the same time present a higher oxidative etching power that has been shown to play an important role in the formation of single crystalline gold nanoparticles.30

Therefore, at the present stage, we propose that the slow reaction kinetics together with the oxidative etching power of chloride ions give rise to the formation of single crystalline, highly anisotropic gold nanoparticles.

\section*{CONCLUSIONS}

We have prepared highly anisotropic Au nanoparticles with unusual shapes and LSPRs in the visible-NIR range, through a simple synthetic method involving only three reagents: H\text{AuCl}_4, CTAC, and AA. Different shapes were reproducibly obtained in high yield by varying the synthesis temperature and the reagents concentrations. Advanced microscopy techniques (3D Tomography and HAADF-STEM) were used to fully characterize the obtained particles, which demonstrated that the particles are monocrystalline and present planar sections that explain the interesting optical properties observed. It has been postulated that the slow kinetics together with the complexation of the gold salt precursor with CTAC are the key factors that favor anisotropic growth.
**ASSOCIATED CONTENT**

- **Supporting Information**
  Visible-NIR spectra of solutions during nanoparticle growth at 15 and 30 °C, visible-NIR spectra and TEM pictures of samples prepared at 30 °C with different CTAC and AA concentrations; and videos of 3D tomography reconstruction of 10 and 20 °C samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.

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