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Disconnecting Symmetry Breaking From Seeded Growth for Reproducible Synthesis of High Quality Gold Nanorods

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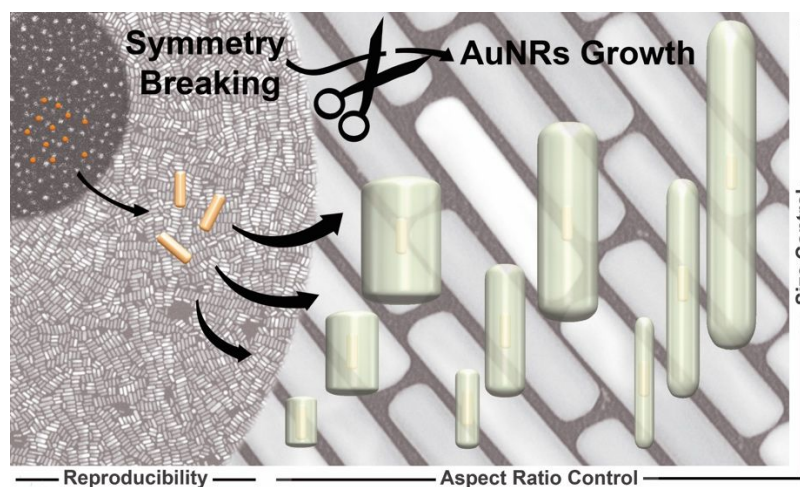
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ABSTRACT

One of the major difficulties hindering the widespread application of colloidal anisotropic plasmonic nanoparticles is the limited robustness and reproducibility of multistep synthetic methods. We demonstrate herein that the reproducibility and reliability of colloidal gold nanorod (AuNR) synthesis can be greatly improved by disconnecting the symmetry breaking event from the seeded growth process. We have used a modified silver-assisted seeded growth method in the presence of the surfactant hexadecyltrimethylammonium bromide and *n*-decanol as a co-surfactant, to prepare small AuNRs in high yield, which were then used as seeds for the growth of high quality AuNR colloids. Whereas the use of *n*-decanol provides a more rigid micellar system, the growth on anisotropic seeds avoids sources of irreproducibility during the symmetry breaking step, yielding uniform AuNR colloids with narrow plasmon bands, ranging from 600 to 1250 nm, and allowing fine tuning of the final dimensions. This method provides a robust route for the preparation of highly-quality AuNR colloids with tunable morphology, size and optical response, in a reproducible and scalable manner.

KEYWORDS: gold nanorods, CTAB, *n*-decanol, symmetry breaking, seeded growth

Table of Contents Graphic



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3 Noble metal nanocrystals have become an essential component for the development of
4 improved technologies for biomedicine,¹ energy harvesting,² or chemical synthesis,² among
5 others.^{3,4} Importantly, the overall usefulness and potential relevance of metal nanocrystals
6 relies on our capacity to control their shape and, hence, their optical properties. Although the
7 nature, purity, and concentration of chemical reactants are pivotal toward obtaining the desired
8 metal nanocrystals, the uniformity in shape and size of the final metal nanoparticles relies
9 ultimately on the employed methodology.^{5,6}

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20 The advent of colloidal seed-mediated growth methods in the early 2000's entailed a
21 breakthrough in the synthesis of noble metal nanoparticles.^{7,8} Based on the spatial and temporal
22 separation between nanocrystal nucleation and growth, this methodology provided access to
23 colloidal metal nanocrystals⁹ in a wide variety of shapes, including spheres,¹⁰ rods,¹¹ or
24 triangles.¹² Moreover, seeded growth has proven to be the most efficient method toward gaining
25 insight into the growth mechanisms of anisotropic nanocrystals.¹³⁻¹⁵ The concept was first
26 introduced by Murphy *et al.* for the synthesis of gold nanorods (AuNRs),⁷ which is probably
27 the most alluring case of anisotropic noble metals synthesis. Due to the high-symmetry face-
28 centered cubic lattice of gold (as well as of other noble metals), its growth into low-symmetry
29 nanocrystals is highly disfavored.⁵ Nonetheless, the silver-assisted seeded growth of AuNRs
30 demonstrated that anisotropic nanoparticles can be prepared in shape yields over 99%.¹⁶⁻¹⁸ Not
31 surprisingly, the underlying mechanism responsible for AuNR formation has been the focus of
32 intense research during the last decade.

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51 Nevertheless, the complexity of the mixture of surfactant and salts where AuNR growth takes
52 place, makes it difficult to unravel the underlying mechanisms and to achieve the desired
53 reproducibility. For instance, the role of the surfactant hexadecyltrimethylammonium bromide
54 (CTAB, required for the synthesis of AuNRs), has been claimed to be related to the induction
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3 of strain, favoring anisotropic growth, and the modification of the electrochemical potential of
4 gold ions.^{19,20} Additionally, when single crystal seeds are used, the presence of silver ions in
5 solution is required for symmetry breaking to occur.^{11,15–18} In addition, a certain degree of
6 truncation should be allowed in the seed to initiate anisotropic growth, thereby restricting the
7 seeds size to the range between 4 - 7 nm. In this regard, the aspect ratio is determined by the
8 [HAuCl₄]/[AgNO₃] ratio, symmetry breaking occurring at the smaller seed sizes for high silver
9 concentration, thereby producing AuNRs of higher aspect ratio.^{13–15} Finally, solution pH,
10 temperature, and concentration of ascorbic acid (weak reducing agent) also influence the
11 outcome of AuNR growth. Therefore, symmetry breaking occurs only within a narrow range
12 of reactant concentrations, seed sizes, and experimental conditions. As a result, the lack of
13 reproducibility remains the main drawback of the currently used methods for AuNR growth.²¹
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29 In this work, we explored a different concept toward a reproducible and reliable method for the
30 silver-assisted seed-mediated synthesis of AuNRs. As such, we envisioned that control over
31 the formation of AuNRs can be achieved by optimizing separately the symmetry breaking and
32 seeded growth stages. This concept requires the preparation of intermediate anisotropic seeds
33 (small AuNRs), which then serve as universal seeds for the growth of AuNRs with selected
34 aspect ratio and size. This approach thus becomes much more robust and scalable than current
35 methods, so that the plasmonic properties and dimensions of the obtained AuNRs can be readily
36 tuned with high simplicity and reproducibility. Furthermore, we introduce the use of *n*-decanol
37 as a co-surfactant that can enter CTAB micellar aggregates, as an important additive for
38 optimization of the symmetry breaking step and the overall success of the method.
39 Computational studies on the interactions between surfactant aggregates and different gold
40 facets, support a model that allowed us to understand the underlying mechanism of *n*-decanol
41 action.
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RESULTS AND DISCUSSION

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7 It has been established that, besides the experimental conditions, the shape, size, and crystal
8 habit of the seeds determine the quality of the products resulting from the seed-mediated
9 growth of metal nanoparticles.^{9,15,22–24} In the particular case of AuNR synthesis, the efficiency
10 of the symmetry breaking process is highly sensitive to small variations in the 1–2 nm
11 nanocrystalline seed.^{21,25} However, the reproducible synthesis of 1–2 nm seeds of sufficient
12 quality remains a challenge. Furthermore, the small seeds are only stable for a few hours (due
13 to Ostwald ripening processes) and freshly prepared seed solutions are required whenever a
14 new batch of AuNRs is prepared.²⁶ In this context, the main idea behind our work is that the
15 reproducibility of the seed-mediated silver-assisted synthesis of AuNRs could be significantly
16 improved by optimizing the symmetry breaking process in a step that is separated from
17 anisotropic growth, both in space and time. Accordingly, the preparation of stable anisotropic
18 gold seeds (where the symmetry breaking process has been completed) should allow us to
19 improve the reproducibility of current methods for AuNR synthesis. In practice, this involves
20 the synthesis of small gold nanorods in high yield and their subsequent use as small anisotropic
21 seeds to obtain AuNRs of different aspect ratios and/or dimensions (**Figure 1**).

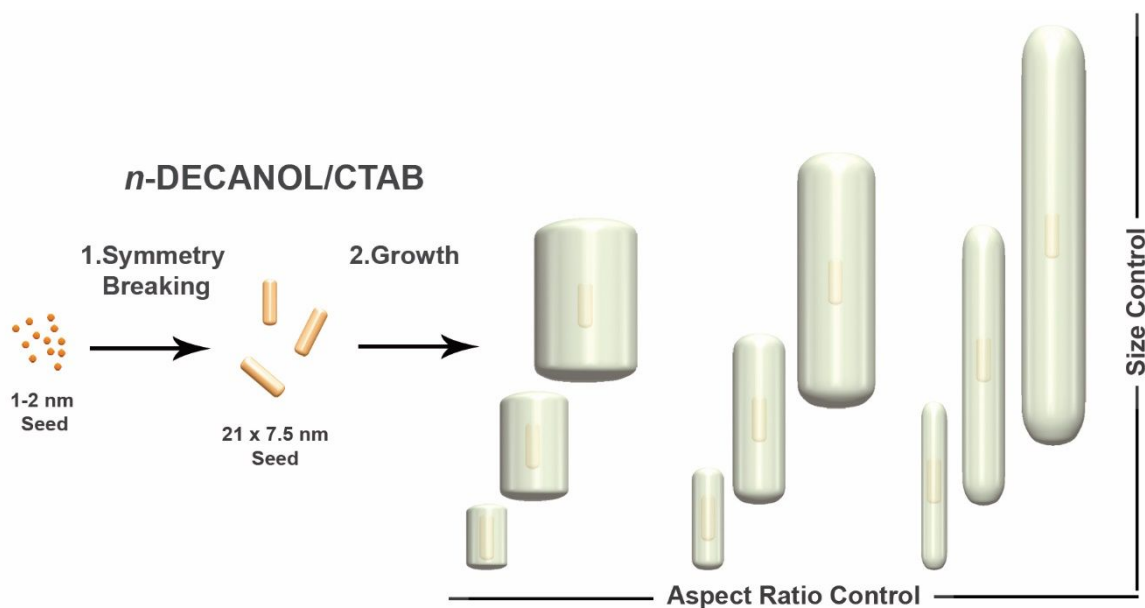


Figure 1. Schematics of the proposed method for the reproducible synthesis of AuNRs. Small 1-2 nm gold seeds are used to prepare anisotropic 21 × 7.5 nm gold nanocrystals, where symmetry breaking (1) has been completed, The anisotropic seeds are then used for the controlled growth (2) of colloidal AuNRs with low dispersity in both aspect ratio and size.

Although both seed-mediated and seedless approaches have been developed for the synthesis of anisotropic nanocrystals of reduced dimensions (volume *ca.* 10^3 nm^3), their preparation in high yield has remained elusive.^{27–29} Several issues are encountered, most of them related to the shape yield (usually below 90%) and overall size dispersity. Still, reproducibility remains the main obstacle toward the synthesis of small anisotropic nanocrystals with low size dispersity. Aromatic molecules (*e.g.* bromo salicylic acid)^{16,18} and oleic acid¹⁷ have been introduced as additives to modify the nature of micellar CTAB aggregates, thereby significantly improving the preparation of standard AuNRs in high yield (99%). Therefore, we propose that the use of an additive can cooperate with CTAB in favoring the preparation of small anisotropic nanocrystals in high yield. However, such additives present a concomitant

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3 co-reducing role that makes the analysis of their colloidal effects on the synthesis process
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5 difficult. As an alternative, long linear-chain alcohols such as *n*-decanol, can be solubilized
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7 within CTAB micelles as co-surfactants, stimulating their growth and leading to structural
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9 transitions from spherical to worm-like micelles and lamellar structures.³¹ For this reason, we
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11 decided to investigate the use of *n*-decanol in the synthesis of small anisotropic nanocrystals,
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13 affording (i) high shape yield, (ii) controlled dimensions, and (iii) improved reproducibility
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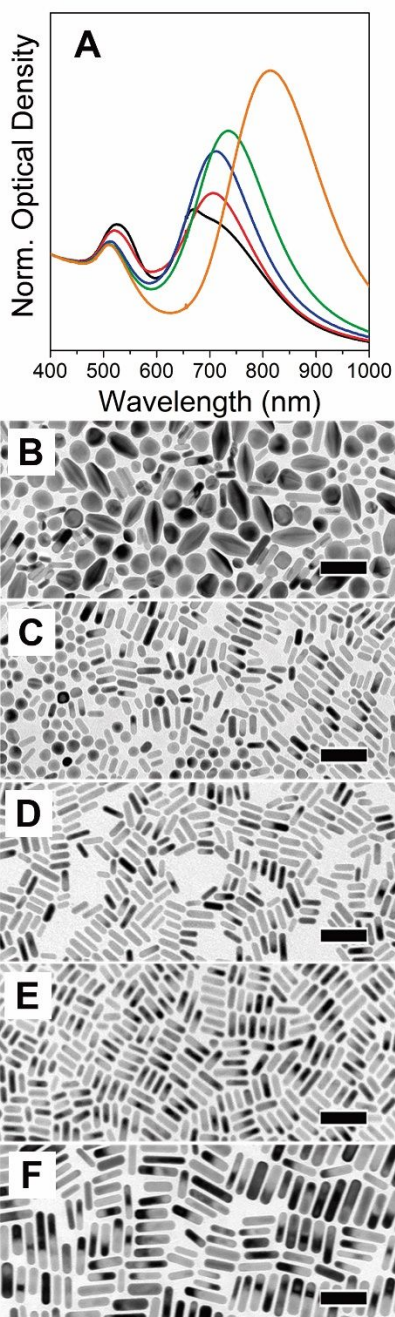


Figure 2. Synthesis of small anisotropic seeds. (A) Normalized optical density spectra and (B–F) representative TEM images of small AuNRs obtained at different *n*-decanol/CTAB ratios: 0.23 (black, B), 0.25 (red, C), 0.27 (blue, D), 0.29 (green, E), and 0.31 (magenta, F). Scale bars: 50 nm.

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3 The synthesis of small AuNRs was carried out following the standard method with some
4 modifications (see Methods Section and Supporting Information for details) but introducing *n*-
5 decanol in different *n*-decanol/CTAB ratios between 0.23 and 0.31 for optimization. The UV-
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10 Vis spectral analysis of the products showed the presence of two distinct extinction bands,
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12 suggesting the formation of AuNRs (for which the bands can be assigned to transversal and
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14 longitudinal LSPR modes). The longitudinal LSPR band became more intense and gradually
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16 red-shifted (from 710 to 750 nm) with increasing *n*-decanol content (**Figure 2A**). Analysis of
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18 TEM images revealed that small anisotropic seeds were successfully produced, only at *n*-
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20 decanol/CTAB ratios between 0.27 and 0.29 (yield = 98%; length = 20 ± 3.5 nm, width =
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22 7.5 ± 1.5 nm, volume: $(0.9 \pm 0.2) \times 10^3$ nm³, **Figures 2B–F, S1, S2**). Below the optimal *n*-
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24 decanol/CTAB ratio, the products mostly contained large spheres and short bipyramids (**Figure**
25
26 **2B**) or a mixture of small anisotropic and spherical nanocrystals (**Figure 2C**). At the highest
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28 studied *n*-decanol content, they were also produced in high yield, but their dimensions were
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30 significantly larger (length = 36 ± 9 nm, width = 10 ± 1.5 nm, **Figure 2F**). In the absence of *n*-
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32 decanol, small anisotropic seeds can also be obtained after the growth conditions have been re-
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34 optimized. However, the dispersion in size and shape are much wider (**Figure S3**).
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41 We hypothesized that the role of *n*-decanol would be related to the selective passivation and
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43 stabilization of certain facets in the seeds, by CTAB aggregates during the symmetry breaking
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45 event. It has been demonstrated that seeded growth of single crystal gold nanorods requires the
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47 use of cuboctahedral seeds, *i.e.* gold nanocrystals enclosed by six {001} and eight {111} facets.
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49 As the size of the seed increases, truncating {110} facets may stochastically appear as a way
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51 to remove high-energy edge atoms located at intersections between {111} facets. For small
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53 nanocrystals (4–6 nm) this could lead to truncating surfaces appearing only at certain
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55 intersections between {111} facets and the rupture of the nanocrystal symmetry.^{13–15} Then, the
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57 presence of silver ions could render preferential stabilization of newly formed {110} facets
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3 over the {001} and {111} ones, *via* an underpotential deposition mechanism and the growth of
4 the nascent AuNRs develops orthogonally on the new facets (along the $\langle 100 \rangle$ direction)^{14,31} In
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6 addition to silver ions, CTAB has also been proposed to play a key role in the stabilization of
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8 emerging facets.^{32,33} As such, CTAB remains the most employed surfactant for the synthesis
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10 of AuNRs. The hypothesis is that CTAB colloidal aggregates adsorb strongly on high-index
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12 facets, reducing the accessibility for gold ions. Therefore, modification of the CTAB
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14 aggregation behavior by insertion of *n*-decanol molecules should affect the passivation of
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16 truncating surfaces, possibly explaining the observed increased efficiency in the symmetry
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18 breaking process and synthesis of small AuNRs.
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25 To validate this hypothesis, we confirmed the insertion of *n*-decanol in CTAB aggregates by
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27 means of diffusion-ordered NMR spectroscopy (DOSY) (**Figure S4**).³⁴ The analysis of DOSY
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29 spectra upon addition of *n*-decanol to small gold nanorods stabilized with CTAB under
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31 experimental conditions of synthesis (see Methods Section), showed: (i) a significant decrease
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33 in the self-diffusion coefficient of CTAB (from $6.7 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ to $2.9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$), and (ii)
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35 the same self-diffusion coefficients for *n*-decanol and CTAB. Additionally, we found no
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37 changes in the self-diffusion coefficient of water ($1.98 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), which confirms that there
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39 are no significant changes in the global viscosity of the solutions.³⁴ Interestingly, no
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41 modifications of the self-diffusion coefficient of CTAB were observed upon addition of *n*-
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43 decanol in the absence of gold nanorods (Figure S4A, B). Therefore, all these results point to
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45 an increase in the effective size of surfactant aggregates adsorbed onto gold nanorods, due to
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47 the formation of mixed *n*-decanol/CTAB systems.
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54 Then, we carried out a series of Molecular Dynamics (MD) simulations of the aggregation
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56 behavior of *n*-decanol/CTAB mixtures on different gold surfaces using the GROMACS
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58 Package (**Figure S5, Table S1**).³⁵ Whereas it has been reported that CTAB bilayers in solution
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3 are unstable and small spherical micelles are preferred,⁶ *n*-decanol/CTAB solutions form stable
4 bilayers at ratios between 0.20–0.30, in good agreement with the concentrations at which we
5 experimentally found better results in the formation of AuNRs. Lower and higher *n*-decanol
6 contents destabilize the bilayer in favor of micellar aggregates. Preassembled CTAB bilayers,³⁶
7 with varying concentrations of *n*-decanol, are initially deposited on {001}, {111}, and {110}
8 gold surfaces, which are expected to form during the early stages of AuNR growth.¹⁴ Higher-
9 index facets such as {250} were also studied regarding their emergence at increasing AuNR
10 dimensions.^{37,38} The system was then solvated with AuCl₂⁻ anions acting as the gold source and
11 H₃O⁺ cations to maintain the neutrality of the system. The simulations revealed highly surface-
12 specific interactions of gold with the *n*-decanol/CTAB aggregates, in good agreement with the
13 DOSY analysis, resulting in different self-assembled morphologies, affecting the diffusion of
14 gold ions from the bulk solution toward the AuNR surface. On {110} and {250} facets, pre-
15 assembled bilayers remain highly ordered and homogeneously cover the gold surface; on the
16 {100} and {111} surfaces, however, the bilayer gets destabilized and tends to form micellar
17 aggregates with a heterogeneous coverage. The structure of *n*-decanol/CTAB aggregates was
18 found to have a large impact on the ability of gold ions to diffuse toward the particle surface.
19 When CTAB forms micelles, *e.g.* on {100} and {111}-type facets, gold ions can readily access
20 the gold surface from solution by diffusion on the micelle surface (**Figure 3A**). On the contrary,
21 when a rigid bilayer is formed on the particle surface, gold ions would be required to cross such
22 a *n*-decanol/CTAB bilayer to reach the gold surface, but this effect was not observed in the
23 timescale of our simulations. Instead, gold ions diffused along the surface of the bilayer, still
24 exposed to the solution (**Figure 3B**). We quantified these different behaviors by measuring the
25 separation distance of gold ions to the surface (**Figure 3C**). We found that, whereas gold ions
26 were able to reach the gold surface in the presence of micelles, they fluctuated and moved along
27 the bilayer interface when more compact aggregates were present. Upon close observation, one
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3 can see that gold ions can also penetrate the aggregates in this instance, but they are swiftly
4 expelled out again. We additionally calculated the probability of finding gold ions at a threshold
5 distance of 1 nm from the surface (**Figure 3D**). The availability of gold ions exhibits a
6 maximum for {100} facets at *n*-decanol/CTAB ratios between 0.20 and 0.30, in agreement
7 with the concentrations at which the experiments showed growth of more uniform small
8 AuNRs. The availability of gold ions on the {111} surfaces is also significant for *n*-
9 decanol/CTAB ratios in the range of 0.10–0.30, though much lower than on {100} surfaces.
10 On the contrary, the availability of gold ions on {110} and {250} facets is very low for all the
11 studied *n*-decanol percentages. Computer simulations thus support a significant influence of *n*-
12 decanol to enhance the selective CTAB passivation of high-index facets. Since the presence of
13 silver ions is pivotal for the symmetry breaking event to occur, we also studied the role of *n*-
14 decanol/CTAB aggregates in the availability of silver ions on different gold facets (Figure S6).
15 We found that diffusion of silver ions through the *n*-decanol/CTAB aggregates is not favored
16 and the differences between different facets are negligible. This result might indicate that the
17 effect of *n*-decanol is mainly related to changes in the diffusion of gold ions, but hardly
18 affecting Ag⁺ diffusion. Therefore, in the presence of *n*-decanol (and silver ions), symmetry
19 breaking in the crystalline gold seed is more efficient and thus small anisotropic seeds are
20 systematically obtained in high yield.
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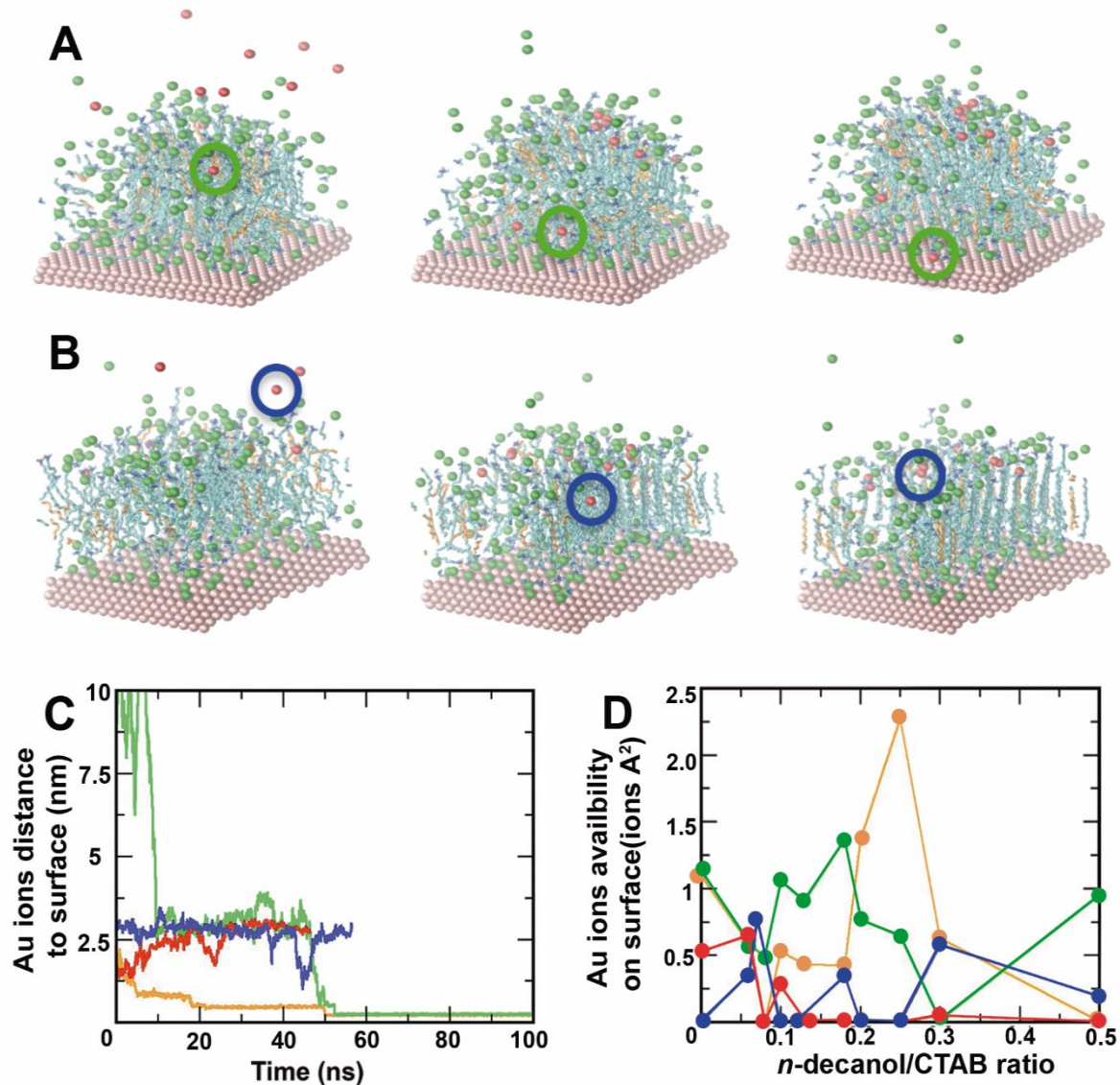


Figure 3. Role of *n*-decanol in the synthesis of small anisotropic seeds. (A,B) Mechanism of diffusion of AuCl_2^- anions in the presence of *n*-decanol/CTAB aggregates (green and blue lines depict the trajectory of gold ions at different times of the simulation). (A) On {111} surfaces, the micelles cover the surface heterogeneously and the diffusion of gold ions toward the gold surface is facilitated. (B) On {250} surfaces, the surfactants form bilayers with homogeneous coverage, hindering the diffusion of gold ions toward the surface. Gold ions are shown as red spheres, bromide ions as green spheres, surfactant chains as blue lines, *n*-decanol in orange, and gold surfaces in pink. (C) Distance of gold ions to the gold surface for selected trajectories: orange ({100} facets) and green ({111} facets) lines show the trajectories corresponding to the mechanism in (A), while red ({110} facets) and blue ({250} facets) lines show the typical diffusion expected for the mechanism shown in (B). (D)

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3 Probability of finding gold ions at a distance smaller than 1 nm from the gold surface for the
4 different facets: {100} (orange), {111} (green), {110} (red), and {250} (blue).
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11 Once the fabrication of small anisotropic seeds was successfully optimized by the addition of
12 *n*-decanol, we focused on the seeded growth of high-quality AuNR colloids. Even though the
13 concept of growth on pre-formed AuNRs has been widely reported in the literature,^{39–41} the
14 tunability of longitudinal LSPR frequency that can be achieved by this method is rather limited.
15 Similarly, when larger anisotropic seeds are used, the growth homogeneity is again reduced,
16 resulting in asymmetric and/or broad LSPR bands (**Figure 4A, Figures S7–S11, Table S2**).
17 Collectively, these pieces of evidence suggest that the use of AuNRs with reduced dimensions
18 is central toward the synthesis of high-quality AuNR colloids with widely tunable LSPR bands.
19 We hypothesized that high-index facets form at the tips of AuNRs as their dimensions increase,
20 which are subsequently stabilized by deposition of silver and surfactant micelles.^{14,41} While we
21 expect the sides of AuNRs at early stages of growth (*i.e.* small AuNRs) to be enclosed by {001}
22 and {111} facets, truncating surfaces appear at more advanced stages thereby suppressing
23 edges between existing facets. Anisotropic growth is favored when such surfaces are
24 exclusively located at the sides. However, as AuNRs keep growing, the formation of high-
25 index facets may also develop at the tips. Silver and surfactant aggregates thus stabilize both
26 the tips and sides, so that gold deposition is no longer preferential at the tips. As a consequence,
27 anisotropic growth is enhanced in small AuNRs due to the lower proportion of high-index
28 facets expected at the tips.
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53 Considering the effect of *n*-decanol in small anisotropic seeds formation, the additive was also
54 used in the homogeneous seeded growth on the AuNRs (**Figure 4B,C**). At *n*-decanol/CTAB
55 ratios around 0.22, the intensity of the LSPR bands was consistently highest, regardless of the
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3 growth conditions. Importantly, the amount of HAuCl_4 was fixed in all experiments, whereas
4 the amounts of AgNO_3 and HCl (pH), as well as temperature were varied. In summary, we
5 carried out experiments at three different temperatures: 18 °C, 28 °C, and 38 °C; two
6 $[\text{HAuCl}_4]/[\text{AgNO}_3]$ ratios: 3.3 and 1.7; and two $[\text{HCl}]/[\text{HAuCl}_4]$ ratios: 60 and 120 (**Figure**
7 **4B,C, Figures S12–S14, Table S3**). The aspect ratio dispersity (D , defined as the standard
8 deviation from the mean value, expressed in percentage) was calculated by means of optical
9 fits to the LSPR bands of AuNRs prepared at different *n*-decanol concentrations (see
10 Supporting Information for details; **Figures S12–S14**).^{6,43,44} This method is more reliable than
11 the usual analysis based on TEM images (see also **Figures S12–S14, Table S3**), where a much
12 smaller number of particles are actually analyzed (few hundreds *versus* ca. 10^{11}), distortions
13 may be introduced during TEM sample preparation, and low image quality (poor image
14 resolution and/or low contrast) may lead to errors in the analysis.^{6,43} The lowest aspect ratio
15 dispersity (6.25–7%) was obtained at *n*-decanol/CTAB ratios ranging from 0.20 to 0.24. In
16 contrast, pure CTAB ($D = 9.5\%$ at all three temperatures) and 0.30 *n*-decanol/CTAB ($D = 11$ –
17 12.5%) afforded less homogeneous growth.
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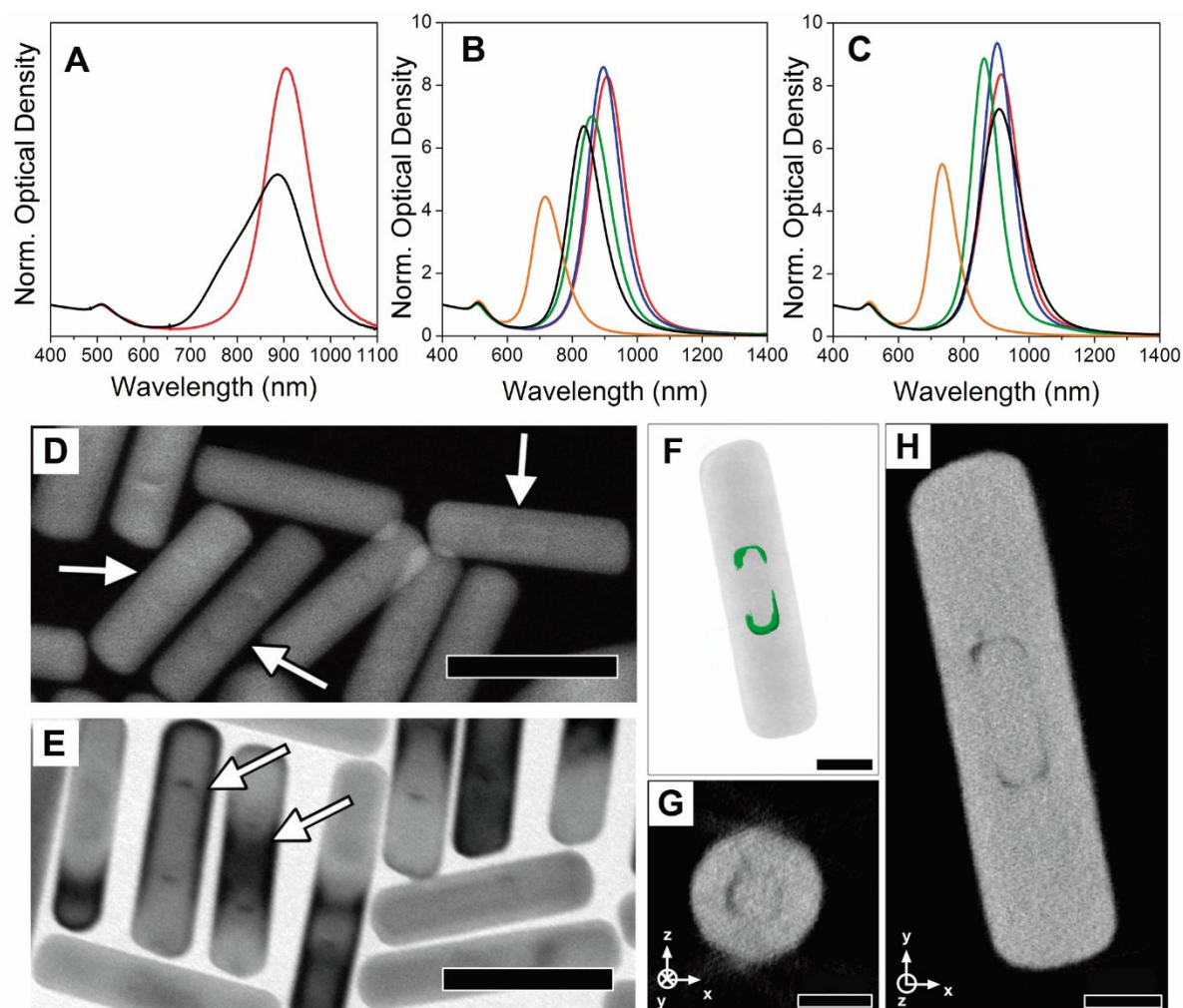


Figure 4. Effect of small anisotropic seeds dimensions and *n*-decanol proportion on the growth process, and their location inside the final AuNRs. (A) Normalized optical density spectra of AuNRs obtained by seeded growth on small anisotropic seeds (length: 21 nm, width: 7.5 nm, red) and on anisotropic seeds of similar aspect ratio but larger size (length: 36 nm, width: 10.5 nm, black). (B,C) Normalized optical density spectra of small AuNRs prepared in the presence of increasing *n*-decanol/CTAB ratios: 0 (pure CTAB, black), 0.20 (red), 0.22 (blue), 0.24 (green), and 0.30 (orange), under different experimental conditions: (B) $[\text{HAuCl}_4]/[\text{AgNO}_3] = 3.3$ and $[\text{HCl}]/[\text{HAuCl}_4] = 60$ at 18 °C; (C) $[\text{HAuCl}_4]/[\text{AgNO}_3] = 1.7$ and $[\text{HCl}]/[\text{HAuCl}_4] = 120$ at 28 °C. (D) Low magnification HAADF-STEM and (E) TEM images of AuNRs prepared by seeded growth on small anisotropic seeds coated with a thin shell of Pd. The white arrows indicate the position of the Au@Pd seeds inside the final AuNRs. Scale bars: 50 nm. (F) 3D visualization of the reconstructed volume of an individual AuNR, where the Au@Pd seed is indicated in green (manual segmentation). Scale bar: 10 nm. (G,H) Orthoslices in the *xz* (G) and *xy* (H) planes through the reconstruction, showing a

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3 lower intensity at the Pd location (Pd has a lower atomic number than Au). Scale bars: 10
4 nm.
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8 An interesting advantage of this method is that it allows the visualization of the small
9 anisotropic seed inside the final AuNR. For this purpose, a thin layer of palladium was grown
10 on the small anisotropic seeds (Au@Pd seeds, see Methods Section), prior to seeded
11 growth.^{22,45} Because of the lower atomic number of palladium relative to that of gold ($Z_{\text{Pd}} = 46$
12 and $Z_{\text{Au}} = 79$), the position of the small Au@Pd seeds could be observed in high angle annular
13 dark field scanning transmission electron microscopy (HAADF-STEM) mode, since the
14 intensity in such images scales with the projected thickness of the structure and the atomic
15 number of the elements (**Figure 4D–H**).²² By using high angle annular dark field STEM
16 (HAADF-STEM) tomography, we were able to determine that the deposition of Pd atoms
17 occurs preferentially at the tips of the AuNR seeds (**Figure 4F–H**). More importantly, the
18 HAADF-STEM images show that anisotropic growth is clearly imposed by the geometry of
19 the small Au@Pd seeds, which is located around the geometrical center of the grown AuNR
20 (Figure 4F–H).
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39 Beyond the narrower LSPRs bands obtained (**Figure S15–S18**) during optimization of the
40 CTAB/*n*-decanol system (compared to standard two-steps methods, where symmetry breaking
41 event is not disconnected from the growth process), we identified the most appealing feature
42 of this method: the straightforward tunability of the longitudinal LSPR. For instance, by simply
43 increasing the [HCl]/[HAuCl₄] ratio from 40 to 160, the LSPR band was readily shifted from
44 760 to 1125 nm, barely affecting the AuNR size and shape dispersity ($D < 10\%$, **Figure 5A**,
45 **Figures S15–S22**, **Table S4** and **S5**). This effect can be related to a lower redox potential of
46 ascorbic acid at low pH, which results in a slower growth kinetics and favored anisotropic
47 growth.¹⁴ On the contrary, when the growth was seeded on 1–2 nm gold nanocrystals (the
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3 standard two-step method), only [HCl]/[HAuCl₄] ratios in a narrow range (60–80) lead to high
4 yields of high-quality AuNRs (**Figure 5B**, **Figure S17**). In this case, the LSPR can also be
5 tuned within a similar range, above the optimum HCl amount, but at the expense of increasing
6 the population of spherical impurities, as indicated by a shoulder at 525–535 nm and seen in
7 TEM images (**Figures S19–S22**). We further note that, the overall size of the overgrown
8 AuNRs could be better adjusted when the symmetry breaking is disconnected from the growth
9 (**Figure 5C–H**, **Tables S4 and S5**).

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20 We also compared the growth of AuNRs using either small anisotropic nanocrystals or 1–2 nm
21 spherical nanocrystals as seeds, both at the same [HAuCl₄]/[AgNO₃] ratio of 3.3. The optimal
22 growth temperature was different in both cases. For instance, the use of 1–2 nm gold seeds
23 required a temperature of 28 °C to afford the highest AuNR yield. Interestingly, narrower LSPR
24 bands were obtained when using small AuNRs at 16 °C instead of 28 °C (**Figure S23**). This
25 fact suggests that, for the studied [HAuCl₄]/[AgNO₃] ratios, symmetry breaking and
26 subsequent growth may be favored at 28 °C, but narrower bands (higher size and aspect ratio
27 dispersity) can be obtained when anisotropic growth is disconnected from symmetry breaking
28 and performed at 16 °C. Similar results were obtained for other [HAuCl₄]/[AgNO₃] ratios
29 (**Figure S23**).

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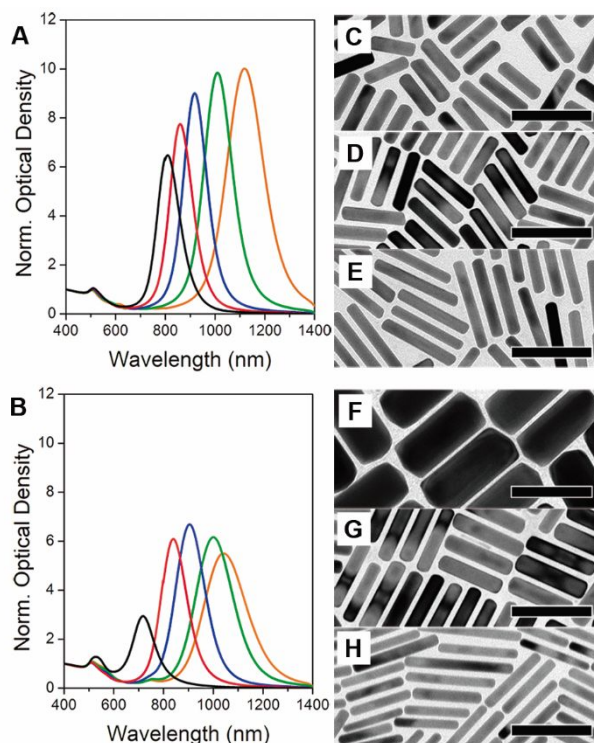


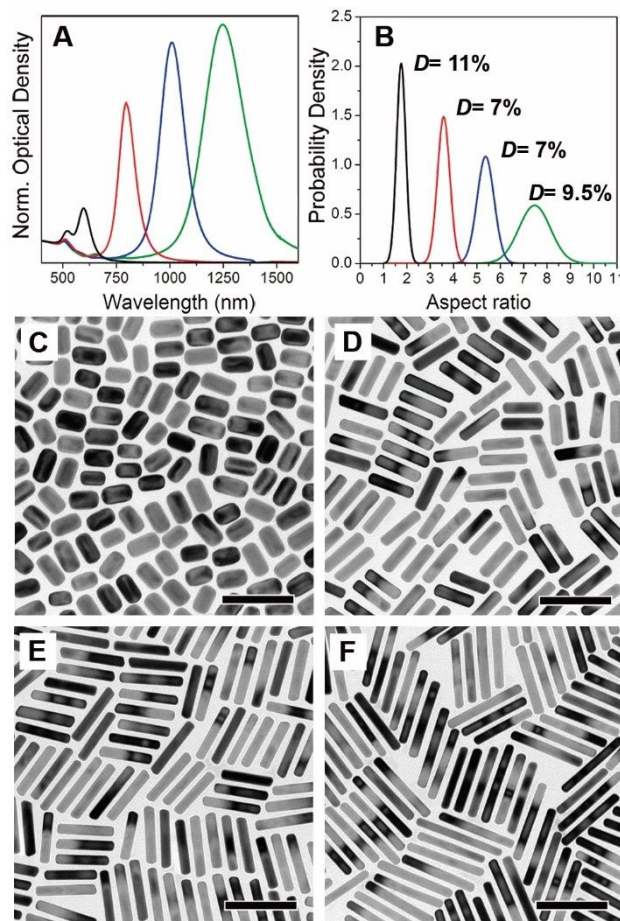
Figure 5. Comparison between the use of small anisotropic seeds and standard Au nanocrystal seeds in the growth of AuNRs at increasing $[\text{HCl}]/[\text{HAuCl}_4]$ ratios. (A,B) Normalized optical density spectra of AuNRs obtained *via* seeded growth on either small AuNRs (A) or 1–2 nm Au nanocrystals (B), at $[\text{HCl}]/[\text{HAuCl}_4]$ ratios of 40 (black), 60 (red), 80 (blue), 120 (green), and 160 (orange). (C–H) TEM images of AuNRs synthesized at $[\text{HCl}]/[\text{HAuCl}_4]$ ratios of 40, 80, and 160 by seeded growth on either 21×7.5 nm anisotropic seeds (C–E) or 1–2 nm Au nanocrystals (F–H), respectively. Scale bars: 100 nm.

To explain how silver ions enable control over AuNR growth, a mechanism based on underpotential deposition (UPD) on lateral, high-index facets has been proposed.^{14,31} The deposition of silver ions *via* UPD in the presence of excess gold ions during the growth process favors the formation of a self-sustaining cycle of silver co-reduction and galvanic replacement by gold ions. This process is affected by temperature, which is in agreement with the above described dependence of the optimal $[\text{HAuCl}_4]/[\text{AgNO}_3]$ ratio with temperature. Indeed, we

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3 found that at 16 °C the optimal [HAuCl₄]/[AgNO₃] ratio ranged from 2.5 to 3.3, whereas ratios
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5 higher than 3.3 were required at 28 °C and 38 °C (**Figure S23**).

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9 By controlling pH, temperature, Ag⁺ concentration and reducing agent, AuNRs with LSPR
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11 bands ranging from 600 up to 1270 nm could be successfully grown with high-quality (**Figure**
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13 **6A–F, Figure S24, S25, Tables S6 and S7**). Our methodology yields AuNRs featuring narrow
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15 LSPR bands, regardless of the aspect ratio (FWHM = 0.250 eV at 600 nm; FWHM = 0.177 eV
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17 at 800 nm; FWHM = 0.165 eV at 1000 nm; FWHM = 0.187 eV at 1250 nm). AuNR dimensions
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19 could be readily varied between 40 and 103 nm in length and between 15 and 25 nm in width,
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21 with an average volume of $(18 \pm 2) \times 10^3 \text{ nm}^3$ (**Figure 6E–H, Figure S24, Tables S6 and S7**).
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23 The dispersity in aspect ratio, as determined from LSPR bands, consistently ranged between
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25 7% and 11%, *i.e.* within the state-of-the-art values of typical syntheses of short rods (**Figure**
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27 **6B, Figure S24, Tables S8 and S9**). Although selected approaches for the preparation of
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29 AuNRs with LSPR wavelengths either above 1150 nm^{29,46,47} or below 650 nm⁴⁸ have been
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31 reported, the dispersity and/or shape purity of the products was generally poor. In our case,
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33 when the [HCl]/[HAuCl₄] ratio was increased up to 240 and temperature decreased down to 16
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35 °C, the growth kinetics was slowed down to such an extent that the synthesis of AuNRs in the
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37 1200–1300 nm range was readily achieved (an interesting advantage of using *n*-decanol as co-
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39 surfactant is the resulting decrease in the Kraft temperature of CTAB. The *n*-decanol/CTAB
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41 systems remains stable at temperatures above 16 °C, [HAuCl₄]/[AgNO₃] = 3.3; **Figure 6A,F**).
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43 Above 1300 nm, the polydispersity in aspect ratio starts to increase and further addition of HCl
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45 does not lead to further increasing the aspect ratio (Figure S25). This is the standard limit in
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47 the synthesis of high-quality single crystal gold nanorods.⁴⁶ Furthermore, the use of reducing
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49 agents other than ascorbic acid, for instance hydroquinone, allowed us to obtain low aspect
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51 ratio AuNRs, with LSPRs close to 600 nm (**Figure 6A,C**). Due to the different nature and
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53 redox potential of hydroquinone (lower than that of ascorbic acid), we found that the optimal
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3 [HAuCl₄]/[AgNO₃] ratio was also significantly different (*ca.* 10) and HCl was not even
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40 **Figure 6.** Preparation of AuNRs with tunable, narrow LSPR bands by seeding the growth
41 with small anisotropic seeds. (A) Normalized optical density spectra for selected syntheses.
42 (B) Corresponding D derived from optical fits. (C,D) representative TEM images of AuNRs
43 from the colloidal samples in (A,B). Scale bars: 100 nm.
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51 Another important advantage of the synthesis of colloidal AuNRs seeded with small AuNRs is
52 related to control over the absorption and scattering cross-sections. It has been well established
53 that absorption dominates in the case of small AuNRs, whilst scattering may become dominant
54 at larger sizes.^{28,49} Herein, by simply adjusting the amount of small AuNRs added to the growth
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3 solution, we were able to fine-tune the size of the final AuNRs. A proof-of-concept test was
4 carried out by growing AuNRs with a five-fold increased volume (standard AuNR volume:
5 $(15\text{--}25) \times 10^3 \text{ nm}^3$, **Figure 7C–F**). The LSPR wavelength was mainly governed by pH, while
6 size uniformity was ensured by a suitable $[\text{HAuCl}_4]/[\text{AgNO}_3]$ ratio. For a volume of (74 ± 4)
7 $\times 10^3 \text{ nm}^3$, the LSPR wavelength could be tuned from 600 to 1110 nm, while length and width
8 varied from 60 to 140 nm and 20 to 40 nm, respectively (**Figure 7A–D**, **Figure S26**, **Tables**
9 **S8 and S9**). When the seed concentration was increased, colloidal AuNRs were obtained with
10 an average volume of $(4.3 \pm 0.7) \times 10^3 \text{ nm}^3$ and LSPR bands ranging from 600 to 1050 nm.
11 The corresponding dimensions varied between 30 and 55 nm in length and between 8 and 13
12 nm in width (**Figure 7E–H**, **Figure S26**). It should be noted that, in conventional methods a
13 variation in the number of seeds requires re-optimization of the synthesis and modification of
14 multiple parameters, whereas hardly any optimization was required to obtain high-quality
15 AuNRs with the present method (D values of 9–13% and 12–15% for AuNRs with large and
16 small volumes, respectively; see **Figure S26**, **Tables S8 and S9**).

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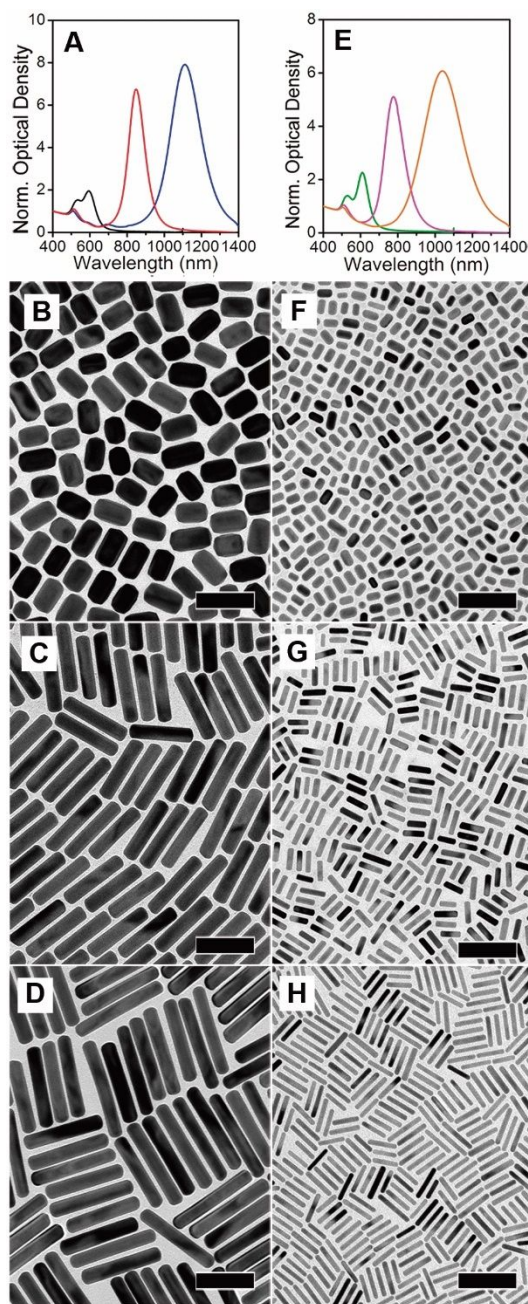


Figure 7. Tuning AuNR size. (A) Normalized optical density and (B–D) TEM images of AuNRs displaying an average volume of $(74 \pm 4) \times 10^3 \text{ nm}^3$ and LSPR bands located at 600 (black, B), 850 (red, C), and 1110 (blue, D) nm. (E) Normalized optical density and (F–H) TEM images of AuNRs displaying an average volume of $(4.3 \pm 0.7) \times 10^3 \text{ nm}^3$ and LSPR bands located at 610 (green, F), 775 (magenta, G), and 1040 (orange, H) nm. Scale bars: 100 nm.

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3 Optimization of a synthetic procedure requires modification of multiple parameters, which in
4 practice implies that only a narrow range of conditions are allowed.^{19–21,29} Furthermore, the
5 symmetry breaking event is highly sensitive to small variations in the concentrations of various
6 reagents during 1–2 nm seed preparation (*e.g.* stirring speed during NaBH₄ addition or its
7 decomposition).^{21,25,26} Therefore, the reproducibility and reliability of commonly employed
8 methods becomes elusive. We found that the superior control obtained through the use of small
9 anisotropic nanocrystals as seeds and the addition of *n*-decanol, significantly improves the
10 reproducibility of the method. To illustrate this idea, we carried out a series of AuNR syntheses.
11 Furthermore, we used water provided by colleagues from different laboratories worldwide and
12 CTAB with different qualities to introduce plausible sources of non-reproducibility (water and
13 CTAB have been claimed as common sources of reproducibility).²¹ Water samples were thus
14 obtained from labs in Australia, Brazil, China, USA, Germany, India, and Italy (see details in
15 the Supporting Information). Our results show that high-quality AuNR colloids were
16 systematically obtained, thereby confirming the high reproducibility of the present method. A
17 high level of control over the LSPR, aspect ratio dispersity and NR size was demonstrated
18 (**Figure S27-S31, Table S10**), even though no further optimization was performed (see the re-
19 optimization route in the Supplementary Information, **Figure S32, Tables S11-S13**).

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43 The robustness of this method lies on the disconnection of the symmetry breaking event and
44 the growth process. While the range of reagent concentrations and temperatures is still very
45 narrow for the synthesis of small anisotropic seeds (see **Figure 2**), the homogeneity of the
46 growth process is much less sensitive to variations in the experimental conditions (**Figures 4–**
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7). Hence, once small AuNRs have been obtained in high yield, after symmetry breaking under
optimal experimental conditions, it is very unlikely that low quality AuNRs will be obtained
or that control over their aspect ratio and dimensions will be lost during the growth step.

CONCLUSIONS

In summary, we demonstrate that the reproducibility, tunability and even quality of colloidal gold nanorods can be largely improved by dealing separately with symmetry breaking and seeded growth. Symmetry breaking is first optimized to produce uniform small AuNRs, using *n*-decanol to enhance the face-selective capping properties of CTAB. In a second step, these anisotropic nanocrystals are employed as universal, anisotropic seeds for the growth of high-quality AuNR colloids with tailored aspect ratios and/or dimensions. This approach yields AuNRs with LSPRs that can be broadly tuned, with high simplicity, from 600 up to 1250 nm. Additionally, low aspect ratio dispersity is obtained, regardless of the aspect ratio and size of the prepared colloidal AuNRs. We also demonstrate that disconnecting symmetry breaking from growth leads to improved reproducibility and reliability of the synthesis, which has traditionally been one of the main pending issues toward large scale AuNR synthesis. The uncertainty associated with the symmetry breaking process is significantly reduced in comparison with standard methods, where each AuNR synthesis requires manipulation of both symmetry breaking and growth, regardless of the final aspect ratio and size. Finally, whereas most syntheses are based on one-pot approaches, where the experimental conditions for symmetry breaking and growth are the same, we show that both stages require different experimental conditions and independent optimization leads to high-quality AuNRs.

METHODS

Chemicals. All the starting materials were obtained from Sigma Aldrich and used without further purification: hexadecyltrimethylammonium bromide (CTAB for molecular biology $\geq 99\%$, batch code BCBBT066; CTAB 96%, batch code: BCBB0800; CTAB BioXtra $\geq 99\%$ batch code: BCBS1424V), hexadecyltrimethylammonium chloride (CTAC, 25% w/w aqueous solution), 1-decanol (*n*-decanol, 98%), hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$), silver nitrate (AgNO_3 , $\geq 99.0\%$), hydroquinone ($\geq 99.0\%$), sodium tetrachloropalladate (Nd_2PdCl_4 , 98%), L-ascorbic acid ($\geq 99\%$), and sodium borohydride (NaBH_4 , 99%) were purchased from Aldrich. MilliQ grade water (resistivity 18.2 M Ω cm at 25 °C) was used in all experiments.

***n*-decanol/CTAB Solution.** The growth solution was prepared by dissolving 9.111 g of CTAB (50 mM) and 1.068 g (13.5 mM for 1-2 nm and 21×7.5 nm seeds) or 870.5 mg (11 mM for AuNR synthesis) of *n*-decanol in 500 mL of warm water (stirring at ~ 60 °C for 1 h or 30 °C overnight) in a 500 mL Erlenmeyer flask. Importantly, CTAB and *n*-decanol were weighted directly in the Erlenmeyer flask. Once *n*-decanol is incorporated in CTAB micelles, the solution is stable while the temperature is kept above 16°C.

Synthesis of 1–2 nm Gold Seeds. A 0.05 M HAuCl_4 solution (200 μL) and 100 μL of a 0.1 M ascorbic acid solution were added to 20 mL of a 50 mM CTAB and 13.5 mM *n*-decanol solution in a 50 mL glass beaker at 25–27 °C. A colorless solution was obtained. After 1–2 min, 800 μL of a freshly prepared 0.02 M NaBH_4 solution was injected under vigorous stirring (1000 rpm using a PTFE plain magnetic stirring bar: 30×6 mm) at 25–27 °C giving rise to a brownish-yellow solution (Movie S1). Excess borohydride was consumed by ageing the seed solution for at least 60 min at 25–27 °C prior to use. In the case of standard AuNRs, 1-2 nm

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3 gold seeds were prepared using a 100 mM CTAB solution instead of 50 mM CTAB and 13.5
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5 mM *n*-decanol solution.
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9 **Synthesis of Small Anisotropic Seeds (21 nm in length and 7.5 nm in width).** In a typical
10 synthesis, 2400 μL of 0.01 M AgNO_3 , 21 mL of 1 M HCl, 3000 μL of 0.05 M HAuCl_4 , and
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12 3900 μL of 0.1 M ascorbic acid were added to 300 mL of a 50 mM CTAB and 11 mM *n*-
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14 decanol solution at exactly 25 °C. Then, 18 mL of the seed solution was added under stirring.
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16 The mixture was left undisturbed at exactly 25 °C for at least 4 h. The solution changed from
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18 colorless to grey and finally dark brownish gray. The longitudinal LSPR of the small
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20 anisotropic nanocrystals at this point should be located at 725–730 nm. The obtained small
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22 anisotropic seeds were centrifuged at 14000–15000 rpm for 45–60 min in 2 mL tubes. The
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24 precipitate was re-dispersed with 4 mL of a 10 mM CTAB solution. The concentrated gold
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26 nanorod colloid was centrifuged twice under the same conditions. Finally, the final Au^0
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28 concentration was fixed to 4.65 mM ($\text{Abs}_{400\text{nm}}$: 10, optical path: 1 cm).
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35 **Synthesis of Small Anisotropic Seeds in the absence of *n*-decanol.** In a typical synthesis,
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37 120 μL of 0.01 M AgNO_3 , 20 μL of 1 M HCl, 100 μL of 0.05 M HAuCl_4 , and 80 μL of 0.1 M
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39 ascorbic acid were added to 10 mL of a 100 mM CTAB at exactly 28 °C. Then, 12 μL of the
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41 seed solution (prepared following the same protocol described for the 1-2 nm gold cluster
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43 synthesis but using 100 mM CTAB instead of 50 mM CTAB and 13.5 mM *n*-decanol solution)
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45 was added under stirring. The mixture was left undisturbed at 28 °C for at least 4 h. The solution
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47 changed from colorless to grey and finally dark brownish orange. The longitudinal LSPR of
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49 the small anisotropic nanocrystals at this point should be located at 800 nm. The obtained small
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51 anisotropic seeds were centrifuged at 14000–15000 rpm for 45–60 min in 2 mL tubes. The
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53 precipitate was re-dispersed with 4 mL of a 10 mM CTAB solution. The concentrated gold
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55 nanorod colloid was centrifuged twice under the same conditions.
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3 **Synthesis of Small Gold@Palladium Anisotropic Seeds.** A protocol previously described
4 was followed.¹⁸ Briefly, 1.2 mL of a small anisotropic nanocrystals suspension (Au conc. =
5 4.65 mM, Abs_{400nm}: 10, optical path: 1 cm) was centrifuged at 14000–15000 rpm for 45–60
6 min using 2 mL tubes. The precipitate was re-dispersed in 2 mL of a 50 mM CTAC solution.
7 This step was repeated twice and the nanoparticles were finally re-dispersed in 20 mL of 50
8 mM CTAC. Then, 250 μ L of 5 mM Na₂PdCl₄ and 250 μ L of 0.1 M ascorbic acid were added
9 under mild stirring. The mixture was left undisturbed at 40 °C for 12 h. The final colloids were
10 removed from the growth solution by centrifugation at 14000 rpm for 45–60 min and re-
11 dispersed in 1-2 mL of 2 mM CTAC.
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25 **Synthesis of Gold Nanorods with Tunable LSPR Bands and Dimensions.** In a typical
26 synthesis, a certain amount of a 0.01 M AgNO₃ solution (**Table S11–S13**), 100 μ L of 0.05 M
27 HAuCl₄, 80 μ L of a 0.1 M ascorbic acid solution (LSPRs between 660 nm and 1270 nm) or
28 500 μ L of a 0.1 M hydroquinone solution (LSPRs close to 600 nm) were added under stirring
29 to 10 mL of a 50 mM CTAB and 11 mM *n*-decanol solution at a given temperature (**Table**
30 **S11-S13**). Then, a certain volume of 1 M HCl was added (**Table S11-S13**). The size of the
31 AuNRs was controlled by the addition of: 10 μ L (V_f : 74×10^3 nm³), 50 μ L (V_f : 16×10^3 nm³), or
32 250 μ L (V_f : ca. 3000×10^3 nm³) of the small anisotropic seed suspension.
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44 **Synthesis of Gold Nanorods Using the Standard Method.** A two-steps standard method for
45 the synthesis of AuNRs was used with minor modifications.¹¹ In a typical synthesis, 120 μ L of
46 a 0.01 M AgNO₃, 100 μ L of 0.05 M HAuCl₄, 200 μ L of 1M HCl and 80 μ L of 0.1 M ascorbic
47 acid solution were added under stirring to 10 mL of a 100 mM CTAB solution at a 28°C. Then,
48 the growth was initiated by adding 12 μ L of seed solution. The mixture was left undisturbed
49 until the growth was completed (4 hours).
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3 **Characterization.** *Transmission Electron Microscopy (TEM):* Low magnification TEM
4 images were obtained on a JEOL JEM-1400PLUS transmission electron microscope operating
5 at an acceleration voltage of 120 kV. Carbon-coated 400 square-mesh copper grids were used.
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10 *Small Gold@Palladium Anisotropic Seeds:* HAADF-STEM images were acquired using a FEI
11 Tecnai Osiris electron microscope operated at 200 kV. Acquisition of the electron tomography
12 tilt series was performed in HAADF-STEM mode and a Fischione model 2020 single-tilt
13 tomography holder was used. The tilt series were acquired over an angular range of $\pm 74^\circ$ with
14 a tilt increment of 2° . The reconstruction was performed using the Simultaneous Iterative
15 Reconstruction Technique (SIRT) implemented in the ASTRA toolbox, where 100 iterations
16 were used. *Gold cluster characterization:* HAADF-STEM images were acquired using an
17 aberration corrected cubed FEI-Titan electron microscope operated at 300kV. *TEM Grid*
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Preparation: 5 mL of the mixture (Au(0) concentration of 0.5 mM and surfactant concentration of 50 mM) was centrifuged and redispersed in 1 mL of a 1 mM CTAB solution; then, the NRs were centrifuged again (same parameters) and redispersed with 200 μ L of water (Au(0) concentration of 25 mM and CTAB concentrations ranging 0.1–0.2 mM). Finally, one drop (3 μ L) was allowed to dry slowly on a carbon-coated 400 square-mesh copper grid (placed on Parafilm). *UV-vis-NIR Spectroscopy:* Extinction spectra were recorded using Agilent 8453 UV-vis diode-array and Cary 5000 UV-Vis-NIR spectrophotometers. All experiments were carried out at 298 K using quartz cuvettes with an optical path length of either 2 mm or 1 cm. *¹H NMR Spectroscopy:* All the NMR measurements were carried out at 298 K in a Bruker AVIII 700 MHz spectrometer (16.4 T). The proton spectra were recorded by averaging 32 scans, with a digital resolution of 0.30 Hz. The signal assignment of the surfactant was established by conventional NMR methods. *Diffusion-ordered NMR spectroscopy (DOSY):* A stimulated echo sequence incorporating bipolar gradients (BPPLIED) with a longitudinal eddy current delay of 5 ms was used for acquiring DOSY spectra. The duration of the magnetic field

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3 pulse gradients and the diffusion times were optimized for each sample to observe the complete
4 signal decay with the maximum gradient strength. Gradient strengths of 2.0-2.5 ms were
5 incremented in 32 steps ranging between 2% and 95% of the total gradient using a linear ramp.
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7 An exponential window function with 1 Hz line broadening was applied before Fourier
8 transformation.³⁴
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15 ***n*-Decanol/CTAB Micelles on Gold:** With the aim of understanding the role of *n*-decanol on
16 the structure of CTA⁺ aggregates and its effect on the nanorod growth, we performed Molecular
17 Dynamics simulations of a CTA⁺ bilayer deposited on top of a gold surface. The co-surfactant
18 *n*-decanol was inserted at random positions of the CTAB bilayer. Both amphiphilic molecules
19 were modeled with the GROMOS53-a6 force fields as the starting point.⁵⁰ However, the partial
20 charges of CTA⁺ and *n*-decanol were assigned values obtained from the *ab-initio* calculations
21 described in our previous works.⁵¹ Bromide, which acts as the counter-ion of CTA⁺, was
22 described as a Lennard-Jones (LJ) potential with a negative charge at its center.⁵² The atoms
23 forming the surface were described with the model developed by Heinz *et al.*⁵² The system was
24 then solvated with SPC water, adding gold ions in the form of AuCl₂⁻ and hydronium (H₃O⁺)
25 to neutralize the system. AuCl₂⁻ was described with the same model used by Mena *et al.*,⁵³
26 whereas hydronium was modelled as an LJ center with charges in tetrahedral symmetry. Three
27 positive charges +0.529 were placed one in each hydrogen, and a negative charge (-0.587) at
28 the oxygen atom. The hydronium charges were obtained with the Automated Topology
29 Builder. The O–H bond length was set to 0.0983 nm, and the strength in the bond was constant
30 at 9 831 400 kJ mol⁻¹ nm⁻².⁵¹ Simulations were performed at varying CTA⁺/ *n*-decanol ratios
31 from 0 to 0.5 for four different gold surfaces, namely, {100}, {110}, {111}, and {250}. Further
32 details about the simulated systems are provided in **Table S1** of the Supporting Information.
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3 Simulations were performed with the GROMACS package in the NPT ensemble at 1 bar and
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5 298 K. The temperature was controlled with a velocity-rescale thermostat and the pressure with
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7 a Berdensen barostat.^{54,55} Equations of motion were integrated with a time step of 0.003 ps.
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10 The relaxation times of the barostat and thermostat were set at 2 ps. The LJ potential as well as
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12 the real part of electrostatic interactions were truncated at 1.2 nm. The Particle–Particle mesh
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14 technique was used to deal with electrostatic interactions.⁵⁶ Initial pre-assembled
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16 configurations of the CTA⁺Br/ *n*-decanol bilayers were created using Packmol.³⁶ The gold
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18 surface and the bilayer were placed perpendicular to the *z*-axis. Gold surfaces were placed at
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20 the bottom and top of the simulation box. Periodic boundary conditions were applied in the
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22 three dimensions of space but leaving 10 nm of vacuum between the two gold surfaces to avoid
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24 interactions between neighboring images of the cell. To correct overlaps in the initial
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26 configuration, a steep descent minimization was performed until the maximum force converged
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28 at 1000 kJ mol⁻¹ nm⁻¹. Simulations were extended over rather long times of about 45–425 ns,
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30 since the diffusion of gold ions through the CTA⁺ aggregate to the gold surface is a rather slow
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32 process (see **Table S1** in Supporting Information). Previous simulations of the assembly of
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34 CTAB in the presence of the *n*-decanol showed that the co-surfactant stabilizes the bilayers
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36 over a rather wide *n*-decanol concentration range. Here, we analyzed the structure of the
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38 aggregates as a function of the *n*-decanol concentration when deposited on top of the gold
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40 surfaces by plotting 2D density maps. The orientational order of CTA⁺ molecules was
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42 quantified by evaluating the parameter $S_z = 1/2 \langle 3 \cos^2 \theta - 1 \rangle$, where θ is the angle formed by
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44 the head-to-tail vector of each surfactant molecule with the *z*-axis. The availability of gold ions
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46 on the gold surfaces was estimated by measuring the distribution of ions as a function of the
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48 distance to the surface $P(z)$ along the *z*-axis (see Figure S3 in the Supporting Information) and
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50 calculating the average distribution function within a distance of 1 nm from the surface.
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3 **Dispersity Measurements and Calculations.** The size and aspect ratio distributions of the
4 AuNRs were obtained from analysis of the TEM images, following the protocol previously
5 reported by Hubert *et al.*⁵⁷ The Image J software with the algorithm “Measure_ROI.class” was
6 employed to obtain the length and diameter of the gold nanorods from the TEM images. About
7 50–300 nanoparticles per sample were measured.
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12 **Simulating the optical response of Au nanorods ensemble and fitting to the optical**
13 **spectra.** The simulation of the optical density of an ensemble of gold nanorods, or any other
14 nanoparticles, implies a large number of calculations (equation 1). This fact requires that the
15 selected method for calculating the optical extinction of the particles cannot be computationally
16 expensive due to the long time it would demand. In this work we have used an approach to
17 calculate the ensemble extinction cross section ($\langle\sigma_{ext}\rangle$, equation 2) which is based on an
18 extension of the electrostatic approximation.⁴³ This extension of the electrostatic
19 approximation includes retardation effects for arbitrary geometries like cylinders, spheroids or
20 hemispherically capped cylinders, allowing a rapid calculation of their cross sections without
21 the necessity of expensive numerical methods. The hemispherically capped cylinder geometry
22 is used directly due to its similarity with the synthesized colloidal nanorods. Also the medium
23 refractive index does not need to be corrected, so in this case, a refractive index slightly lower
24 than the CTAB index (*i.e.* 1.435)⁵⁸ of 1.400 is used due to the presence of water molecules
25 around the surface of the particles. The broadening and position of the optical spectra depends
26 on the aspect ratio dispersity to a great extent and less to the volume distribution of the particles.
27 Because of this, we consider nanorods with constant volume (V , with equivalent sphere radius
28 of R_v) and a normal distribution of aspect ratios ($n(\rho)$), where the mean value (ρ_n) and standard
29 deviation (σ_n) are the fitting parameters.
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$$\langle OD \rangle = \log(e) CL \langle \sigma_{ext} \rangle \quad (1)$$

$$\langle \sigma_{ext} \rangle = \int_{\rho_{min}}^{\rho_{max}} n(\rho) \sigma_{ext}(V, \rho) d\rho = \sum_{i=1}^M u_i n(\rho_i) \sigma_{ext}(V, \rho_i) \quad (2)$$

$$\sigma_{ext}(V, \rho_i) = \frac{2 \cdot \sigma_{ext,trans}(V, \rho_i) + \sigma_{ext,long}(V, \rho_i)}{3} \quad (3)$$

The calculation of the ensemble optical density and the fitting procedure to the optical measurements can be revised elsewhere (see Supporting Information for more detailed discussion).^{6,44,59} To take in account unpolarized light and random orientation of the nanoparticles, the longitudinal ($\sigma_{ext,long}$) and transversal ($\sigma_{ext,trans}$) responses are averaged and the fitting results compared to the T-matrix method (equation 3, see Supporting Information).

ASSOCIATED CONTENT

The following files are available free of charge on ACS Publications website:

Information about the: symmetry breaking process, computational simulation of the *n*-decanol/CTAB system, the role of small-AuNR size on the synthesis of high-quality AuNRs, the effect of *n*-decanol/CTAB ratio on the growth process, comparison of the use of small AuNRs and standard Au nanocrystal seeds in the growth of AuNRs at increasing [HCl]/[HAuCl₄] ratios, the dependence of the optimal [HAuCl₄]/[AgNO₃] ratio with the temperature, the preparation of AuNRs with tunable, narrow LSPR bands by seeding the growth with small AuNRs, tuning the AuNR size, the growth of AuNRs using water from different countries, protocol for small-AuNR synthesis optimization and the simulation of the optical response of AuNR ensembles and optical spectrum fitting (pdf).

Movie S1 shows the synthesis of 1-2 nm gold seeds.

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