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Surfactant-Assisted Symmetry Breaking in Colloidal Gold Nanocrystal Growth

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Abstract: Colloidal anisotropic gold nanocrystals play a central role in the field of plasmonics owing to their tunable optical activity across a wide spectral range. However, achieving sufficient optical quality for practical implementation requires advanced synthetic protocols yielding gold nanocrystals with the desired morphology and plasmonic properties. This Minireview focuses on a fundamental step during the growth of anisotropic nanocrystals, namely symmetry breaking. In connection with thermodynamic and kinetic control of nanocrystal growth, we discuss the complex

interplay between the role of seed morphology and that of surfactants, shape-directing additives and reducing agents. We revisit some iconic syntheses of anisotropic gold nanoparticles, including nanorods, nanotriangles, and nanobipyramids. Finally, we analyze the use of co-surfactants as an emerging strategy to disconnect the symmetry breaking event from the anisotropic growth process, overcoming current limitations in the synthesis of anisotropic gold nanocrystals.

1. Introduction

Control over light emission processes and light-matter interactions holds transformative implications for the realization of next-generation technologies such as ultra-small light sources, quantum-computing, and advanced optoelectronic and optomechanical devices.^[1] The discovery and understanding of plasmonic effects in the early 20th century set a landmark in this direction, enabling the confinement of light into subwavelength volumes, thereby revolutionizing the fabrication of optical and photonic materials.^[2–4] A surface plasmon is created by the coherent oscillation of conduction electrons at a metal–dielectric interface, in response to an external electromagnetic field. If the dimensions of the metallic object are smaller than the wavelength of the exciting radiation, plasmons become localized, resulting in absorption and scattering of photons at specific resonant frequencies.^[5] The energy associated with plasmon oscillations varies as a function of nanocrystal composition, size, morphology, surface chemistry, and organization.^[6] Nanocrystals can display much larger extinction cross-sections (by 10^5 – 10^6 times) than conventional molecular

dyes.^[7] These features have generated huge interest in plasmonic nanoparticles, fostering their applications in solar energy harvesting, hydrogen production, catalysis, biosensing, and nanomedicine, among others.^[8–10]

The advanced study and translational implementation of metal nanoparticles ultimately rely on the efficient synthesis of nanocrystals with the desired plasmonic, physical, and chemical properties. The field of plasmonics has thus been deeply entangled with the development of advanced synthetic protocols. Among plasmonic nanomaterials, gold is the most studied one, owing to an excellent balance between high plasmonic activity, high chemical stability, and ease of synthesis. However, plasmon resonances in the near- and mid-infrared spectral ranges can be achieved for gold, only when the nanocrystal symmetry is reduced, i.e., for anisotropic plasmonic structures.^[5] In this regard, gold nanoparticles can be produced in different shapes, from nanospheres to nanorods and nanostars, using reproducible and scalable protocols, with tunable plasmon bands from ~500 nm to beyond 2000 nm.^[6,11] Among various available fabrication strategies, surfactant-based wet chemistry methods provide access to a wide variety of morphologies.

This minireview focuses on the role of surfactants assisting symmetry breaking during the synthesis of anisotropic gold nanocrystals. We first cover the fundamental aspects of the seed-mediated growth of colloidal anisotropic gold nanocrystals, assisted by surfactants. Fundamental concepts, such as the role of seed crystal structure, concentration of reactants and other shape-directing agents, are discussed from the perspectives of thermodynamic and kinetic control of symmetry breaking. In the following two sections, the synthesis of gold nanorods, nanotriangles, and bipyramids will be revisited under this perspective, with particular attention to the symmetry-breaking event. The last section focuses on the use of co-surfactants and the separation of symmetry breaking from anisotropic growth, two approaches that have emerged as promising ways to overcome historical limitations in the synthesis of gold colloids. We intend this minireview to offer a different angle toward understanding symmetry breaking phenomena in gold nanocrystals, which will ultimately foster new ideas and research in the field.

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2. General Concepts in Anisotropic Nanocrystal Growth

2.1. Seed-Mediated Growth of Anisotropic Gold Nanocrystals

The surfactant-assisted synthesis of anisotropic gold nanocrystals involves three fundamental steps: (i) nucleation of atoms into isotropic clusters or small nanocrystals, (ii) reduction of nanocrystal symmetry by spontaneous asymmetric fluctuations during deposition of additional atoms, and (iii) amplification of symmetry reduction via anisotropic growth (Figure 1a). The gold precursor (e.g., HAuCl_4) is reduced to Au^0 until supersaturation conditions are reached, inducing the formation of isotropic stable clusters or nanocrystals. Then, by non-symmetric deposition of Au^0 atoms over the nuclei, crystal symmetry can be broken, thereby supporting anisotropic growth. The synthesis of high quality anisotropic nanoparticles requires the separation of nucleation and growth, as the formation of new nuclei once growth has been initiated (secondary nucleation) would lead to broad size distributions and undesired morphologies. On one hand, the nucleation step

is intended to tailor the seed dimensions and their crystallographic structure, as the crystalline habit of the seed determines how symmetry reduction can be induced and stabilized (see Section 3). On the other hand, in the growth step, one aims to achieve a high degree of control over symmetry breaking and anisotropic growth, to obtain the desired size, morphology, and composition.^[12]

The concept of seed-mediated growth has enabled a physical and temporal separation of these two steps, thus facilitating their individual study and optimization.^[13] As a result, anisotropic structures such as gold nanorods, nanotriangles, or nanobipyramids were obtained.^[13] Practically, gold seeds (typically below 5 nm) are prepared through fast nucleation using a strong reducing agent (e.g., NaBH_4), usually at high surfactant concentrations (100 mM). The seeds are then transferred into a growth mixture containing surfactant, Au^+ and a mild reducing agent (e.g., ascorbic acid), as the starting point of symmetry reduction and subsequent growth into a controlled shape.^[12] Interested readers are referred to Refs. [12,14] for additional information on the history of seed-mediated growth. It is important to underline that all the synthetic aspects discussed here can be applied for the synthesis of nanocrystals made of

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Figure 1. (A) Schematic view of the seed-mediated synthesis of anisotropic gold nanoparticles. i) Nucleation stage: the gold precursor is reduced into small spherical nanocrystals. ii) Symmetry breaking: more gold atoms are deposited asymmetrically. iii) Anisotropic growth: the deposition of gold atoms leads to anisotropic nanoparticles. (B) Schematic of all possible scenarios for the growth of nanoparticles with different anisotropies, and related Gibbs free energies. Kinetic control (blue lines) of gold atom deposition on spherical seed favors spontaneous symmetry breaking, while symmetry is conserved under thermodynamic conditions (red lines). Stabilization of broken symmetry usually requires the combination of kinetic and thermodynamic aspects (pink lines). Symmetry reduction, preferentially stabilized under kinetic conditions (SB I), enables the growth of nanoparticles with higher anisotropy than those stabilized under thermodynamic conditions (SBII).

different noble metals, bimetallic systems and metal/semiconductor nanostructures.^[15,16]

2.2. Thermodynamic and Kinetic Control

An often overlooked but essential consideration toward understanding anisotropic nanocrystal growth is the influence of both thermodynamic and kinetic aspects. In a general sense, we can distinguish a *thermodynamic product*, as the one lying on the global Gibbs energy minimum (i.e., with the lowest surface energy), while kinetic products would be located at local Gibbs energy minima (i.e., meta-states in which the growing crystal can be “trapped” by controlling the reaction evolution).^[17–19] For an elegant description of these concepts, we recommend reading Ref. [17]. At a fixed nanocrystal volume, the global minimum for the Gibbs free energy of the system is reached when the surface free energy is minimized, modifying the obtained morphology shape. For a non-crystalline material (i.e.,

when the surface free energy is isotropic) this corresponds to spherical nanoparticles. Consequently, any kind of symmetry reduction is accompanied by an increase of the free energy of the system, leading to out-of-equilibrium structures (Figure 1b).

Gold crystallizes naturally into a highly symmetric cubic close packed – or face centered cubic structure,^[20] where distinct crystallographic planes have different surface free energies: $\gamma(111) < \gamma(100) < \gamma(110)$. According to Wulff construction rules for a perfect fcc crystal, the shape with the lowest global Gibbs energy (in the absence of twin-defects in the crystal, see Section 3) corresponds to a truncated octahedron, which offers the optimum balance between facets with the lowest surface energy (a mix of {100} and {111} facets) and a low surface-to-volume ratio.^[19,21–23] A symmetry breaking event is therefore needed to induce anisotropic growth.^[24] This process can occur occasionally due to non-symmetrical fluctuations, but such spontaneous deformations are not energetically favorable and usually self-correct during growth. A reduction of the symmetry would lead to a change in the relative proportion

between {100} and {111} facets and the emergence of an out-of-equilibrium structure with higher surface energy facets (e.g., elongation). The system would then tend to compensate this perturbation and return to the most stable, symmetric truncated octahedron. This would happen through the migration of the gold atoms along the surface of the crystals towards a most stable position. The whole phenomenon can be described by two different kinetic processes: deposition (V_{dep}) and diffusion (V_{dif}). Deposition refers to the speed at which new gold atoms are added to the growing crystal, while diffusion is related to the speed at which they diffuse on its surface.^[17]

As a direct consequence, the growth of “out-of-equilibrium symmetry-reduced” (anisotropic) nanocrystals demands two phenomena to take place: i) kinetics-promoted symmetry fluctuations and asymmetric deposition of gold atoms; ii) thermodynamic or kinetic stabilization of these anomalies, thereby amplifying asymmetric growth. These two effects typically occur at the same time but occasionally one can predominate over the other (see Sections 3 and 4). Through the first effect, symmetry breaking is favored by kinetic control of the growth process. Due to symmetry perturbation, V_{dep} can be accelerated at certain locations of the nanocrystal. If diffusion of atoms from the deposition location (typically higher energy {100} facets) toward lower surface energy sites (e.g. {111}) is much slower than deposition ($V_{\text{dep}}/V_{\text{dif}} \gg 1$), the symmetry is not restored and an anisotropic crystal will be obtained. On the contrary, when $V_{\text{dep}}/V_{\text{dif}} \ll 1$, migration of atoms to the most stable sites will result in thermodynamically favored nanostructures.^[17] Through the second effect, the symmetry breaking process is regulated from a thermodynamic standpoint, using face-selective capping agents or so-called *shape-inducing agents*.^[17,20] These are chemical species that can selectively chemisorb on certain crystallographic facets. They can thereby modify the specific free surface energies and change the equilibrium shape, effectively stabilizing symmetry-reduced states and amplifying the asymmetry of the final product. In this context, silver and halides are iconic examples of shape-inducing agents. The full description of their surface activity is beyond the scope of this minireview, and we refer the readers to Refs.[25] and [26] for additional information.

2.3. The Role of Surfactants

Among many potential surfactants, we center our attention on the role of hexadecyltrimethylammonium halides (CTAX, where X = Cl, Br), which are also considered shape-directing agents.^[11,13,24–35] The extent of the thermodynamic control normally exerted by surfactants on symmetry breaking and anisotropic growth, depends on the nature of the hydrophobic and hydrophilic groups. In the case of CTAX, the length of the hydrocarbon chain and the quaternary ammonium group provide a good balance between high solubility and relatively low critical micellar concentration (~1 mmol/L at 25 °C). Computational simulations of the adsorption of CTA⁺ micelles on different gold facets revealed a preference for surfaces with higher free energy. Therefore, {111} facets are less covered by

micelles than {100} and {110} ones.^[29,36] Related studies have shown a strong influence of the halide counterions, with denser micellar layers being formed on gold facets for bromide, compared to chloride (Figure 2a).^[37,38] This can be explained by the lower affinity of chloride ions for gold surfaces compared to that of bromide. These results suggest a synergic interplay between halides and CTA⁺ micelles in the passivation of different gold facets.

The synthesis of gold nanocubes vs. nanooctopods can be used to illustrate the effect of surfactants as shape-inducing agents and the importance of kinetic control to grow anisotropic nanostructures. In the presence of CTA⁺ and bromide, the {111} facets of truncated octahedron seeds are less efficiently passivated than {100} facets. Thus, gold deposition preferentially occurs at {111} facets. When growth occurs at low reducing agent concentration, $V_{\text{dep}}/V_{\text{dif}} \ll 1$, the growth of {100} facets remains favored, giving rise to cubic shapes. However, as V_{dep} increases, $V_{\text{dep}}/V_{\text{dif}} \gg 1$, the growth along the {111} direction leads to octopods (Figure 2b).

In what follows, we discuss how surfactants can be used to influence the symmetry-breaking process in gold nanocrystals

Figure 2. (A) Snapshots from molecular dynamics simulations of the adsorption of CTAB (left) and CTAC (right) micelles on {111} gold facets. Adapted with permission from ref. [37] (Published by the PCCP Owner Societies). (B) Schematic illustration (top) and TEM images (bottom) showing the thermodynamic (left) and kinetic (right) products that result from the growth of a cuboctahedron seed enclosed by {100} and {111} facets in the presence of CTAB. Under thermodynamic control ($V_{\text{dep}}/V_{\text{dif}} \ll 1$), CTAB promotes the stabilization of {100} facets directing the formation of a cube. In contrast, kinetic control ($V_{\text{dep}}/V_{\text{dif}} \gg 1$) favors the growth of octopods covered by {100}, {111}, and high-index facets. Scale bars: 100 nm. Adapted with permission from Refs. [39] and [40] (Copyright 2018 American Chemical Society and Frontiers in Chemistry, respectively).

and to induce distinct “out-of-equilibrium” structures in case of both defect-free and twinned nanoparticles. The synthesis of gold nanorods, nanotriangles and nanobipyramids will be discussed in terms of its kinetic and thermodynamic parameters.

3. Symmetry Breaking in the Absence of Twin-Defects

The synthesis of gold nanorod colloids is a paradigm of symmetry breaking in single crystal nanoparticles.^[24,27,32,34,41] This was the first demonstration of the feasibility of symmetry reduction in colloidal gold nanocrystals with high yield (> 90%), enabling narrow plasmon bands with unprecedented tunability in the visible and near-infrared regions.^[27,35] The complexity of this method arises from the need to control a delicate interplay between various parameters. First, small seeds (1–2 nm) are needed for symmetry breaking to occur. Therefore, the reduction rate of the gold ionic precursor should be high and CTAB should be present at high enough concentrations (typically 100 mM), to create a micellar layer that can hinder nanoparticle coalescence (e.g., Ostwald ripening), which can introduce twin defects in a post-nucleation phase.^[42]

Once the seeds have been obtained, they are transferred to a complex aqueous mixture of CTAB, Ag^+ , Au^+ , ascorbic acid in small excess, and HCl (Figure 3A). Under these conditions, the initial 1–2 nm cuboctahedral seeds grow isotropically until they reach a critical size of ca. 4 nm, when the nanocrystals are large enough to support the emergence of {110} facets (Figure 3B).^[45] This truncation can appear at the intersection of two {111} faces, to remove the high-energy atoms located at the edges. However, they form asynchronously as occasional deformations of the symmetry. In the presence of Ag^+ and CTAB, the rate of gold deposition shifts toward the {111} and {100} planes, thereby supporting symmetry reduction and anisotropic growth along the $\langle 001 \rangle$ direction (Figure 3C). This process can efficiently occur until the size reaches ca. 5–7 nm, point at which the emergence of truncations is more favorable at the {111} intersections without reducing nanocrystal symmetry.^[41,45,46] The final single crystal gold nanorod products are typically enclosed by {100} and {111} facets at the tips, while higher index planes such as {110} or {250} can be found at the sides (Figure 3D).^[47–51]

The aspect ratio of gold nanorod colloids, their quality (dispersion in size and aspect ratio), and the shape yield of the synthesis (hindered by spherical impurities) are primary determined by the efficiency of the symmetry-breaking process. This is controlled by an interplay between $[\text{Ag}^+]$ and V_{dep} . On the one hand, Ag^+ plays a thermodynamic role in the stabilization of high-index facets ({110} or {520}), directing the symmetry breaking of the gold nanocrystal (either by underpotential deposition mechanism or the adsorption of the CTAB- Ag^+ complex, although the exact mechanism remains unfortunately unknown).^[44,52–55] On the other hand, kinetic control is introduced by modifying V_{dep} through the pH-dependent redox potential of ascorbic acid.^[56] More acidic pH values lower the

Figure 3. (A) Schematic representation of symmetry breaking and anisotropic growth of cuboctahedral seeds into single-crystal gold nanorods. (B) High-resolution phase-contrast TEM images (top) and corresponding schematic models (bottom) of gold nanocrystals during symmetry breaking of cuboctahedral seeds, oriented in the [011] direction. Adapted with permission from ref. [43] (Copyright 2015 American Chemical Society). (C) Wulff construction of a single-crystal gold seed and preferential adsorption of CTAB- AgBr complex on {100} planes (green), as determined by density functional theory calculations. Adapted with permission from ref. [44] (Copyright 2014 American Chemical Society). (D). Three orthogonal slices through an atomic-resolution electron tomography reconstruction of a single-crystal gold nanorod, showing {110} and {100} facets at the sides and {101} planes at the rounded tips. Adapted with permission from ref. [44] (Copyright 2012 Nature Publishing Group).

reduction rate of Au^+ and favor deposition on less passivated facets ({111} in the presence of CTAB). Thus, the efficiency of symmetry breaking is enhanced in the presence of HCl and a larger fraction of seeds evolve into anisotropic structures.

It is worth noting that gold nanorods can serve as starting point for the growth of more complex single-crystal anisotropic nanostructures such as nanodumbbells, nanocuboids or spiky nanostructures among others.^[57,58] In the presence of CTAC, Ag^+ and a large excess of reducing agent, nanorods overgrowth can be directed to form nanoarrows, i.e. a concave nanostructure enclosed by {110} at the tips and high-index facets at the sides.^[59]

4. Twin-Directed Symmetry Breaking

The identification of truncated octahedra as the most thermodynamically stable structure only applies for nanocrystals with a defect-free internal structure. When twin-defects are introduced additional strain arises within the nanocrystal, thereby increasing the nanoparticle free energy and leading to a rearrangement of gold atoms to compensate the loss of thermodynamic stability.^[60,61] As a result, nanocrystals adopt shapes that are enclosed by {111} facets (with the lowest surface energy), thus “violating” the Wulff construction rules (see “General Concepts”).^[62] This crystallographic modification affects the ways in which particle symmetry can spontaneously be reduced during growth, and supporting the synthesis of anisotropic nanostructures with different morphologies. Depending on the number of twin-defects in the internal structure, the morphology of the nanocrystal varies: one twin plane gives rise to truncated triangular bipyramids (Figure 4A,B), five twin planes to decahedra (Figure 4C-E) and twenty twin planes to icosahedra.^[62,63] Therefore, the introduction of defects in the crystalline structure has become one of the most useful approaches to thermodynamically promote the growth of anisotropic gold nanoparticles with morphologies such as

nanotriangles, penta-twinned gold nanorods, and nanobipyramids.

The conditions required for the growth of anisotropic nanostructures from seeds containing a single twin or stacking faults are quite similar to those required for the introduction of defects in single-crystal gold seeds. As a result, this type of anisotropic nanoparticles is usually grown from single-crystal seeds in the presence of an “appropriate” shape- (and twin-defect-) inducing agent. The dimensions of the seeds need be taken into account as they play an important role when introducing defects during the growth process. For example, mono-twinned gold nanotriangles (i.e., truncated right bipyramids) can be more efficiently synthesized from 10 nm than from 20 nm single-crystal seeds. In this case, iodine ions are used as a shape-inducing agent that can strongly bind {111} facets and promote twinning during nanocrystal overgrowth (Figure 4A,B).^[28,38,66] These results were corroborated by relativistic *ab initio* thermodynamics calculations, suggesting that single-crystal gold nanoparticles (enclosed by {100} and {111} facets) are favored at sizes above 15 nm, while twinned ones (enclosed by {111} facets) would be more stable at smaller sizes.^[67]

A different scenario applies to the synthesis of penta-twinned anisotropic nanocrystals, which typically requires

Figure 4. (A) Schematic view symmetry breaking and anisotropic growth of mono-twinned seeds into gold nanotriangles enabled by iodine in CTAC. (B) TEM images of a mono-twinned 7 nm gold nanocrystal seed (left) and nanotriangles (right). Adapted with permission from ref. [22] (Copyright 2005 Elsevier). (C) Scheme of the different shapes that can be obtained by reducing the symmetry of penta-twinned seeds and promoting their anisotropic growth. (D) High-resolution high-angle annular dark-field scanning transmission electron microscopy image of a penta-twinned seed. (E) Low-angle annular dark-field scanning transmission electron microscopy image of a penta-twinned nanocrystal. (F) TEM images of penta-twinned gold nanorods (left) and bipyramids (right). Adapted with permission from Refs. [64,65] (Copyright 2016 and 2018, American Chemical Society). Red planes (A and C) and arrows (B and D) indicate the presence of twin-defects. Scale bars: 3 nm (B left), 100 nm (B right and F), 2 nm (D), and 20 nm (E).

separation of twin formation from symmetry breaking and anisotropic growth.^[11,30,64,68] The symmetry breaking of penta-twinned nanocrystals is generally favored at sizes close to 5 nm, although depending on the experimental conditions larger seeds can also be used.^[68] The symmetry reduction depends primarily on the nature of the surfactant and the presence of shape-inducing agents (Figure 4C,D). For instance, preferential stabilization of {100} facets can promote the growth of penta-twinned gold nanorods in the presence of CTAB. Amplification of the anisotropy can then be ensured in the presence of low reactants concentration at relatively low temperatures (20 °C) to favor deposition on {111} facets at the nanorod tips (the most active sites in the presence of CTAB).^[29,36,64,68,69] This strategy can be used for the synthesis of high aspect ratio gold nanorods.^[30] However, when symmetry reduction takes places in the presence of CTAB and Ag⁺, penta-twinned bipyramids enclosed by high-index facets instead of nanorods enclosed by {100} and {111} facets are formed.^[54,64,70] The presence of Ag⁺ imposes again a strong thermodynamic effect to stabilize high-index facets.^[54] This implies that gold bipyramids are closer to a thermodynamic product than penta-twinned gold nanorods. In fact, for bipyramids, growth at low temperature is not required.

5. Optimizing Symmetry Breaking: Co-Surfactants Help Disconnecting from Anisotropic Growth

Despite the success of seed-mediated growth methods in the synthesis of anisotropic gold nanocrystals, the lack of reproducibility remains a significant drawback. For this reason, great efforts have been directed toward the development of novel strategies that help increase control over the symmetry breaking and anisotropic growth processes. Once again, single-crystal gold nanorods serve as the benchmark platform for research in this direction. Among various attempts (e.g., using gemini surfactants and other structures), modification of the micellar

properties of CTAB by inserting co-surfactants has likely been the most successful approach, setting the basis for a most recent strategy toward disconnecting symmetry breaking from growth.

The effect of co-surfactants is related to modification of the CTAX micellar behavior. It has been observed that the morphology of CTAB micelles and the resulting rheological properties of the solution, vary as a function of CTAB/co-surfactant ratio (e.g., from spherical micelles to worm-like aggregates).^[71–73] For example, the effect of both salicylic acid derivatives and sodium oleate as co-surfactants was investigated in the context of gold nanorod synthesis. As a result, the tunability of gold nanorods morphology, quality and reproducibility were significantly improved (Figure 5).^[32–34] The co-surfactant could be used both to provide additional rigidity to the CTAB micellar structure, and as a secondary reducing agent to control V_{dep} during growth (Figure 5B). Ultimately, this modification resulted in a narrower size distribution and a significant expansion of the average aspect ratio that could be accessed (Figure 5C).

Unfortunately, the detailed role of co-surfactants on the improvement of the symmetry-breaking process remains unclear, as it is somehow entangled with its effect on anisotropic growth. The understanding and optimization of both processes could be significantly improved by separating them in space and time. Our group recently proposed a first example of this strategy, where co-surfactants allowed the preparation of high-quality gold nanocrystals where the symmetry-breaking process was completed but anisotropic growth was hindered (Figure 6).^[24] In practice, this process relied on the synthesis of small gold nanorods with dimensions 10–50 times smaller than those for standard nanorods. High yield synthesis was made possible by using appropriate concentrations of *n*-decanol as co-surfactant. Molecular dynamics simulations of the interaction of CTAB micelles with different gold facets, supported the experimental results and revealed an increased rigidity of CTAB micelles on {110} facets. Consequently, *n*-decanol helps reduce V_{dep} on {110} facets by steric hindrance (due to the increased

Figure 5. (A) Normalized extinction spectra of single crystal gold nanorods with different aspect ratios, obtained in the presence of sodium oleate as a co-surfactant. Adapted with permission from ref. [33] (Copyright 2013, American Chemical Society). (B,C) In the presence of 5-bromo salicylic acid, the gold precursor is pre-reduced to Au⁺ (reduction in the Au³⁺-CTAB complex absorption band intensity at 396 nm). The extent of pre-reduction influences the kinetics of gold nanorod growth, enabling fine-tuning of the aspect ratio (C). Adapted with permission from ref. [34] (Copyright 2013, American Chemical Society).

Figure 6. (A) Schematic description of the separation between symmetry-breaking and anisotropic growth of single-crystal seeds into gold nanorods. *n*-decanol assists the formation of high-quality small gold nanorods (1), which are then anisotropically grown in a physically and temporally separated event (2). (B) TEM image of small gold nanorods used as anisotropic seeds. (C,D) UV-Vis-NIR (C) and TEM images (D) of gold nanorods with variable aspect ratio and tunable plasmon bands, grown from anisotropic seeds under different thermodynamic (CTAB and silver concentration) and kinetic (pH, reducing agent, and low temperature) conditions. Adapted with permission from ref. [24] (Copyright 2019, American Chemical Society). Scale bars: 100 nm.

rigidity of CTAB micelles), suggesting that co-surfactants may improve the kinetic control of symmetry-breaking by CTAB micelles, rather than affecting the strength of micelle adsorption (thermodynamic control). Once the synthesis of small nanorods was optimized, it enabled the independent optimization of anisotropic growth and symmetry breaking. The concentrations of Ag^+ , ascorbic acid, HCl, or temperature, could be varied in a much wider range without affecting the quality of the final nanorods. The overgrowth of such small gold nanorods in the presence of *n*-decanol and CTAB systematically yielded high-quality gold nanorod colloids with tailored plasmon bands from 600 up to 1250 nm (Figure 6C,D). Overall, the uncertainty in the seeded-growth process is reduced upon disconnecting the symmetry breaking and anisotropic growth steps. We are confident that similar concepts will be developed

for other morphologies and materials, thereby broadening the synthetic possibilities for anisotropic plasmonic nanostructures.

6. Conclusion

The reduction of gold nanocrystal symmetry is a central process in the synthesis of plasmonic nanoparticles featuring Vis-NIR optical bands. This Minireview describes the symmetry-breaking process in the formation of gold nanocrystals assisted by CTAX surfactants. The seed-mediated synthesis of gold nanorods, nanotriangles, and nanobipyramids is discussed using the concepts of thermodynamic and kinetic control, as a foundation to understand the role of the distinct parameters determining the complex evolution of shape during symmetry breaking and anisotropic growth. On the one hand, kinetic control is needed to favor spontaneous seed symmetry deformation, initiate the symmetry breaking process, and induce anisotropic growth. On the other hand, CTAX and shape-directing agents modify the nanoparticle's free surface energy, thus serving as thermodynamic parameters that decrease the Gibbs energy of symmetry-reduced nanocrystals and enabling their stabilization, thus sustaining anisotropy in the final product.

Overall, we show that symmetry breaking and anisotropic growth processes require a delicate balance between thermodynamic and kinetic control. The in-depth analysis that we presented above is intended to demonstrate that often it is difficult to completely separate the different thermodynamic and kinetic effects involved in the symmetry reduction of gold nanocrystals to promote anisotropic shapes. We propose that the next leap in colloidal synthesis will indeed consist in a complete separation of all three steps discussed in this minireview: nucleation, symmetry breaking, and anisotropic growth. Finally, the synthesis of ultra-small anisotropic nanostructures together with the search for new co-surfactants may set the basis for the growth of novel anisotropic nanoparticles. For instance, the use of chiral co-surfactants may enable the synthesis of plasmonic nanocrystals with chiroptical activity.

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Conflict of Interest

The authors declare no conflict of interest.

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