

This item is the archived peer-reviewed author-version of:

Silver Ions Direct Twin-Plane Formation during the Overgrowth of Single-Crystal Gold Nanoparticles

Reference:

Grzelczak Marek, Sanchez-Iglesias Ana, Heidari Mezerji Hamed, Bals Sara, Pastoriza-Santos Isabel, Perez-Juste Jorge, Liz-Marzan Luis M.- Silver Ions Direct Twin-Plane Formation during the Overgrowth of Single-Crystal Gold Nanoparticles

ACS OMEGA - ISSN 2470-1343 - 1:2(2016), p. 177-181

Full text (Publisher's DOI): <https://doi.org/10.1021/ACSOMEGA.6B00066>

To cite this reference: <https://hdl.handle.net/10067/1403980151162165141>

Silver ions direct twin plane formation during the overgrowth of single crystal gold nanoparticles

Marek Grzelczak,^{†,||} Ana Sánchez/ Iglesias,[†] Hamed Heidari,[‡] Sara Bals,[‡] Isabel Pastoriza/ Santos,[§] Jorge Pérez/ Juste,[§] and Luis M. Liz/ Marzán^{*,†,||}

[†] *Bionanoplasmonics Laboratory, CIC biomaGUNE, Paseo de Miramón 182, 20009 Donostia - San Sebastián, Spain*

[‡] *EMAT-University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium*

[§] *Departamento de Química Física, Universidade de Vigo, 36310 Vigo, Spain*

^{||} *Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain*

KEYWORD: *Nanoparticles, Twin engineering*

ABSTRACT: It is commonly agreed that the crystalline structure of seeds dictates the crystallinity of final nanoparticles in a seeded/ growth process. Although the formation of monocrystalline particles does require the use of single crystal seeds, twin planes may stem from either single/ or poly/ crystalline seeds. However, experimental control over twin formation remains synthetically difficult to achieve. Here we show that a careful interplay between kinetics and selective surface passivation offers a unique handle over the emergence of twin planes (in decahedra and triangles) during the growth over single/ crystalline gold nanoparticles of quasi/ spherical shape. Twinning can be suppressed under conditions of slow kinetics, in the presence of silver ions, yielding single/ crystalline particles with high/ index facets.

INTRODUCTION

The mechanistic understanding of the emergence of twin planes is of great importance in nanoparticle synthesis, since the presence of defects can alter the physical properties of nanostructures, thereby opening new avenues toward the design of novel systems.^{1/ 7} Experimental monitoring of twin emergence attracted recently attention of several groups. For example, Mirkin and co/ workers showed that single/ crystalline gold nanoparticles can develop twin defects during their growth with silver, to yield core/ shell nanoparticles with a twinned structure.⁸ Although the initial single crystal particles used in their work were prepared by conventional surfactant/ assisted methods, the

emergence of twin planes originated from photochemical reduction of silver in the presence of additives that are not commonly used in established methods. Thus, the need for further experimental advancement is more than justified, which will not only ensure generalization of the current growth models, but also open up opportunities for new synthetic pathways and crystal diversity at the nanoscale.

It is commonly agreed that reaction kinetics and selective surface passivation are primary factors behind nanoparticle growth mechanisms.^{9,10} *Kinetic effects* dominate at high rates of metal reduction, and usually result in thermodynamically unstable products (displaying high/ index facets). On the contrary, at

slow reduction rates thermodynamically more stable particles emerge, which display low/ index facets. *Selective surface passivation*, on the other hand, involves the use of chemical additives. Silver ions (Ag^+) are known to bind preferentially onto certain gold facets, which can result in anisotropic crystal growth through the well/ known underpotential deposition mechanism (UPD). UPD occurs under conditions of seed/ mediated synthesis in which ascorbic acid cannot reduce Ag^+ in bulk, thereby facilitating the formation of a silver (sub)monolayer on a gold surface and hindering further deposition of Au atoms. As a result, particle growth slows down, affecting the final nanoparticle shape and crystalline structure. At high Ag^+ concentrations, seeded growth has been reported to lead to anisotropic shapes with high/ index facets.¹¹ Although, these design considerations – kinetic/ and surface/ controlled growth – were established from single/ crystalline nanoparticle, further experimental work is required to understand how twinned structures fits within this context.¹²

RESULTS AND DISCUSSION

Here we define experimental conditions for the emergence of twin planes during the overgrowth of single/ crystalline nanoparticles in typical seeded/ growth synthesis. We observed that relatively fast kinetics and high concentration of silver ions are crucial to forming twinned particles (decahedra, triangles) with low/ index facets from single crystalline seeds (10 nm). Our findings indicate that kinetic/ and surface/ controlled growth does not necessarily apply to the formation of twinned particles, as recently proposed for single/ crystalline analogues.

It is well known that very small seeds can significantly change in solution due to spontaneous ripening processes at room temperature.¹³ We therefore decided to use larger seeds, which are more stable, but still maintaining a single/ crystalline structure. By following a protocol recently reported by Xia's group,¹⁴ we synthesized 10.0 ± 0.3 nm spherical particles in the presence of the cationic surfactant cetyltrimethylammonium chloride (CTAC) and ascorbic

acid as reducing agent. Detailed inspection of the obtained nanocrystals by high/ resolution transmission electron microscopy (HRTEM) revealed that 93 % of the particles were monocrystalline (Figures 1 and 2d). Importantly, extended storage in the surfactant solution did not affect particle size, suggesting higher stability than their 3 nm analogues commonly used in seed/ mediated synthesis.

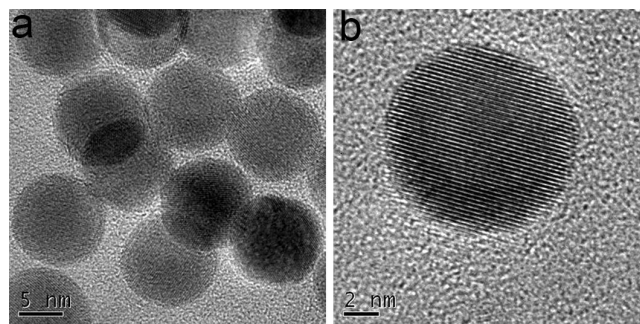


Figure 1. TEM (a) and HRTEM (b) images of single crystalline gold nanoparticles used as seeds in overgrowth experiments. The average diameter was 10 ± 0.3 nm, 93% were single crystals, 7% were polycrystalline.

Since our aim was to evaluate the role of silver in selective surface passivation and emergence of twin planes, we tried to keep our system as simple as possible, using chemicals that contain chloride counterions only.¹¹ the cationic surfactant benzyldimethylhexadecylammonium chloride (BDAC), gold precursor (AuCl_4^-) and acid (HCl). Note that Cl^- is the halide with the lowest binding affinity to gold surfaces, as compared to bromide or iodide,¹⁵ which minimizes the risk of undesired symmetry breaking in the growing particles. Therefore, the growth over the crystals is dominated by the presence of Ag^+ ions.¹⁶ In a typical experiment, the solution containing the initial nanoparticle seeds was mixed with a growth solution containing AuCl_4^- (0.5 mM), ascorbic acid (0.067 mM), BDAC (100 mM), and different concentrations of AgNO_3 and HCl. The solution was stored at 30 °C for 2 hours to ensure complete reduction.

Mirkin and coworkers reported that silver ions drive the formation of single crystal particles with high/ index facets by adsorption on the particles surface.⁹ We

indeed confirmed that, when increasing the concentration of silver nitrate up to 0.04 mM. The resulting particles had the shape of concave cubes (Figure 2b). Supported by previous studies,¹⁰ we assume that these particles are of single/ crystalline nature. Overgrowth in the absence of silver nitrate rendered nearly spherical nanoparticles, thus preserving the shape of the initial seeds (Figure 2a). Interestingly, when increasing Ag^+ concentration to 0.12 mM, twinned nanoparticles were obtained with either decahedral (34%) or triangular (66%) shapes. The absence of spherical nanoparticles and the similar dimensions of triangles and decahedra (46.8 ± 3.4 nm for decahedra; 47.9 ± 4.6 nm for triangles), excluded a scenario involving the nucleation of new particles away from the seeds surface. We therefore postulate that twinned particles emerged from single crystal seeds under these conditions. To provide further arguments, we found that the volume of decahedra and triangles is $\sim 70\%$ fold higher than in the initial seeds. Thus, the size of final particles that contained twin defects is sufficient to accommodate 10 nm seeds between the boundaries of twin planes.

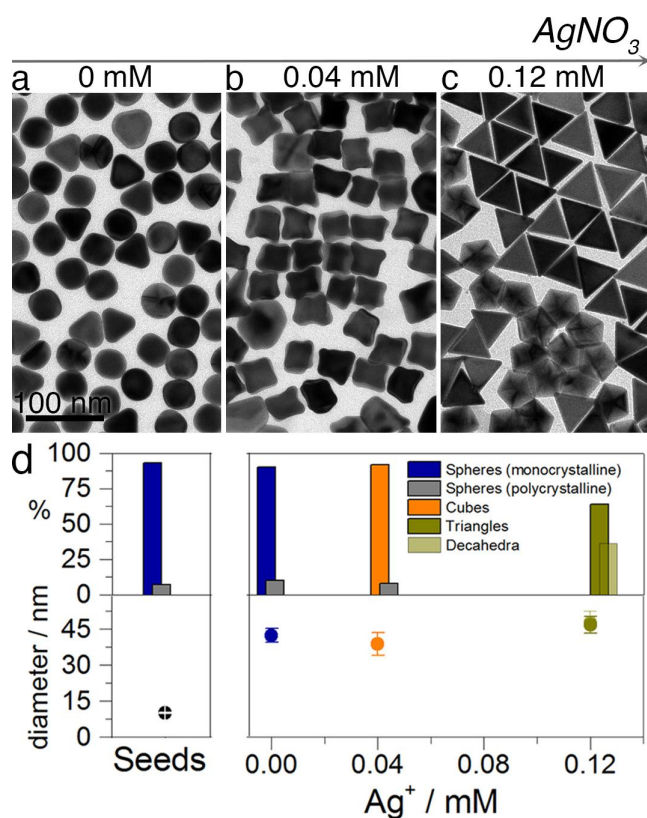


Figure 2. Effect of selective surface passivation. (a/ c) Effect of silver ions on the final nanoparticle shape: twinned particles formed at $[\text{AgNO}_3] = 0.12$ mM. (d) Population of single/ and polycrystalline particles in seeds and particles grown at selected silver concentrations; diameters of the seeds and final products. UV/ Vis spectra of the corresponding solutions are available in the Supporting Information (Figure S1).

Interestingly, the formation of twinned particles from single crystal seeds can be suppressed by adding extra HCl. At low HCl concentration (2.5 mM) nanoparticles with a variety of poorly defined shapes formed (Figure 3b). Further increase of HCl concentration up to 19 mM rendered particles with unconventional shapes (Figure 3c). High resolution electron microscopy, electron diffraction and tomography confirmed the single crystalline nature of the nanoparticles prepared at higher HCl content (Figure 4 and Figures S3&S4). The morphology of these particles, with dominating high index surface facets, $\{311\}$, $\{110\}$ and $\{100\}$, is close to truncated ditetragonal prisms¹⁷ (for simplicity, named DTP, from this point on). UV/ Vis spectroscopy showed that the LSPR position blue/ shifted from 620 to 555 nm when the amount of acid was increased, suggesting the formation of more isotropic nanoparticles (Figure 3e). We should however note that, at the higher acid concentration a new plasmon band emerged at 846 nm. SEM analysis revealed the presence of bipyramids (Figure S5). The population of bipyramids ($\sim 10\%$) is in good agreement with the initial population of twinned seeds.

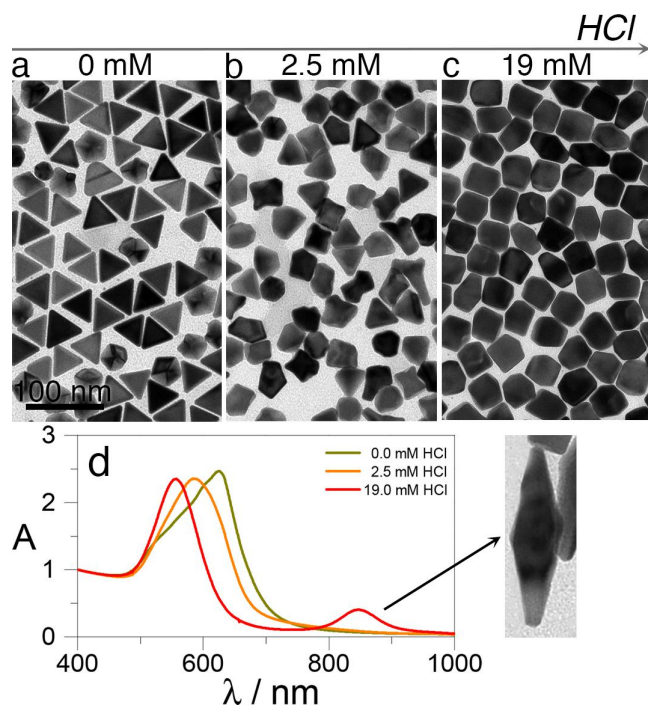


Figure 3. Effect of pH on shape evolution. (a/ c) Effect of HCl concentration on the final nanoparticle shape. (d) UV/ Vis/ NIR spectra of solutions prepared at different HCl concentrations.

Above results suggest that the right combination of HCl and Ag^+ as additives defines shape and crystallinity of the final particles. To better understand the role of additives on the crystal growth we evaluated the reduction kinetics for given experimental conditions. We carried out time/ dependent UV/ Vis analysis of the reactions during the formation of (1) spheres (no Ag^+ , no HCl), (2) twinned nanoparticles with mixed shapes (Ag^+ no HCl), and (3) DTP nanoparticles (Ag^+ and HCl). The results are summarized in Figure 4a. Whereas the formation of spheres was fast (10 min), 70 min were needed to complete the reduction in the presence of Ag^+ (0.12 mM), which yielded twinned products. The presence of both Ag^+ and HCl slowed the kinetics further down so that 160 minutes were required to obtain the final single/ crystalline DTP nanoparticles. Control experiments showed that addition of only acid yielded spherical, single/ crystalline nanoparticles (Figure S6), but when doubling the concentration of ascorbic acid / keeping HCl (0.19 mM) and Ag^+ (0.12 mM) constant / we could again

obtain twinned particles (Figure S7). These results show that, indeed, kinetics is the main parameter behind the formation of twinned particles, but only in the presence of a surface passivation/stabilizing agent / silver ions.

We analyzed further the amount of silver ions and their distribution in the particles of different crystallinity. Mirkin and co/ workers showed that, the number of Ag atoms that can deposit onto a particular facet is equivalent to the number of surface atoms for that facet.¹¹ Thus, it is possible to estimate the Ag/Au ratio in nanoparticles of given shape and crystallinity. Comparison of the calculated Ag/Au ratio with the experimental one obtained by elemental analysis (IPC/ MS, Table S1) allowed us to estimate silver incorporation in the nanoparticles.

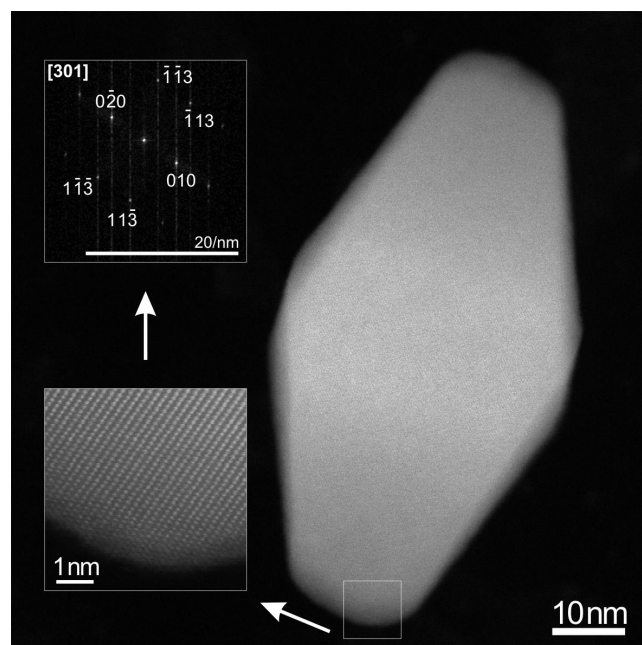


Figure 4. High angle annular dark field STEM image of a single DTP particle, indicating the absence of twin planes. The insets show HRTEM of a selected area and the corresponding Fourier transform, which confirm the monocrystalline structure.

The surface energy of twinned particles (decahedra, triangles) is lower than that of DTPs. Twinned particles display low/ index $\{111\}$ surface facets, with a greater number of exposed surface atoms than higher index facets in DTPs. We thus hypothesize that twinned nanoparticles can accommodate a larger amount of silver atoms,⁹ which was confirmed by comparing

experimental and calculated Au/Au ratios for three different samples: (a) spheres prepared in the absence of the silver, (b) mixture of twinned nanoparticles, (c) DTPs (For theoretical estimation of the Au/Ag ratio, see supporting information). To our surprise, the calculated and experimental Ag/Au ratios for twinned and DTP nanoparticles are nearly identical and equal to 0.04, and 0.013, respectively (Figure 5b). The amount of silver in spherical nanoparticles is negligible ($\text{Ag}/\text{Au} = 0.0003$). Relatively good agreement between experimental and calculated Ag/Au ratio suggest that (1) silver locates only on the surface of the nanoparticles and (2) twinned nanoparticles (decahedra and triangles) carry triple amount of silver than single/ crystalline nanoparticles that is related to their surface facets.

Next, we evaluate the effect of the particle size. It has been suggested that gold nanoparticles exhibit different structural motifs and twinning as a function of particle size.¹⁸ Thus to evaluate the size effect, we used conventional seeds (1/ 3 nm) prepared by fast reduction with borohydride and subjected them to overgrowth in the presence of silver ions and/or hydrochloric acid. We observed a similar trend in the morphologies of the final products for smaller seeds as those obtained using the 10 nm ones, but with less defined shapes. In the presence of Ag, twinned particles emerged whereas single/ crystal particles were obtained in the presence of both Ag^+ and HCl (Figure S8). This finding therefore shows that controlled twin engineering is possible for different size ranges.

We also evaluated the influence of the nature of the surfactant, as well as the counterion. For instance, it has been demonstrated that the presence of bromide is essential for symmetry breaking in gold nanorod synthesis. Thus, we evaluated the influence of the surfactant by employing CTAC instead of BDAC. We again observed a similar trend in the final products (twinned particles in the presence of silver ions) by using CTAC in the growth solution (Figure S9). Interestingly, the surfactant counterion clearly plays an important role. When the synthesis was performed in CTAB, irregular shapes were obtained regardless of the experimental conditions used (Figure S10).

We finally discuss the origin of twin planes. Our results show that when the Ag/Au ratio in the growth solution is 0.08 the particles adopt a concave cubic shape. Ag underpotential deposition (UPD) has been proposed as a key mechanism to control the final nanoparticle shape while retaining the single/ crystalline structure.¹¹¹ When the Ag/Au ratio is increased to 0.24, i.e. three/ fold higher, twinned particles are formed (Figure 2c). This seems to indicate that Ag^+ ions determine the formation of twins under our experimental conditions: Ag^+ (0.12 mM); Cl^- (100 mM from BDAC). Note that the formation of argentichloride ions^{19,20} (AgCl_2^-) and insoluble AgCl is favorable under these conditions. It is thus reasonable to assume that small clusters of silver chloride can co/ precipitate on the surface of gold particles during growth, facilitating the formation of defects. This reasoning is supported by the fact that there is a low energy barrier to the formation of twin defects.²¹ Once the twin is formed, the final morphology will be determined by a balance between surface energy and the elastic strain needed to form the non/ space filling structure.^{22,23} Therefore, increasing the content of low energy {111} surface facets could also drive the formation of twins by minimizing overall surface energy. The previous assumption is supported by the fact that an increase of chloride concentration up to 19 mM produced a transition from twinned to single/ crystalline particles enclosed by high index facets (Figure 3c). It has been reported that high chloride concentrations increase the solubility of AgCl as the formation of $\text{AgCl}_n^{-(n+1)}$ complexes becomes favorable.²⁴ Such an increase in silver chloride solubility could inhibit twin formation. Additionally, the presence of HCl reduces the reduction kinetics. On the other hand, when doubling the concentration of ascorbic acid (keeping HCl constant) twinned particles were also formed (Figure S7), thus supporting the kinetically controlled nature of the process. Bearing all this in mind, we propose a mechanism in which, at low pH and in the presence of Ag^+ ions, the UPD mechanism dominates the growth of the particles leading to a thermodynamically controlled process.²⁵ At high silver

ion concentrations in the absence of HCl, the higher pH increases the redox potential of ascorbic acid favoring the reduction of the gold precursor, in such a way that process is kinetically controlled.

In the later case, we should also consider the Ag/Au ratio in the final product is 0.04, which corresponds to the estimated value of monolayer coverage of Ag. Therefore, silver could be reduced on the gold surface via the UPD mechanism stabilizing selectively the {111} facets and the entire structure through favoring twin formation.

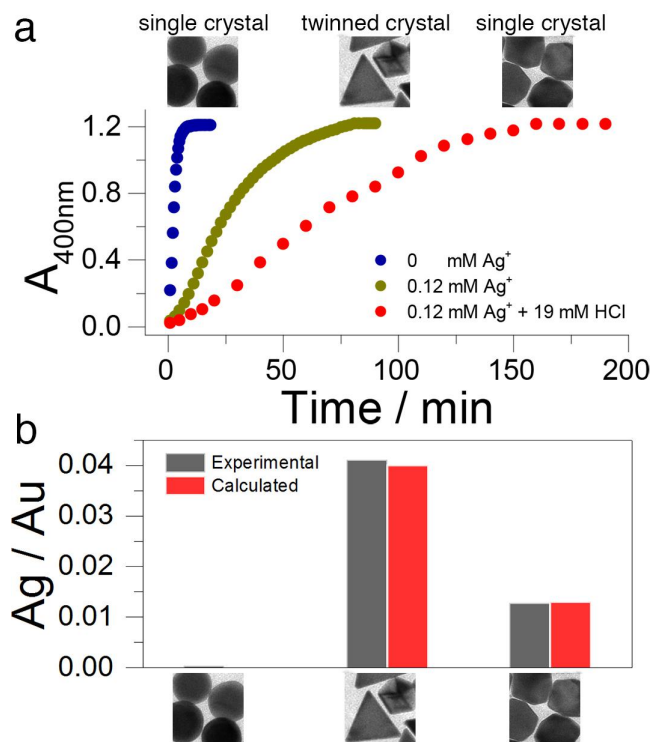


Figure 5. Kinetics and surface passivation effects. (a) Kinetic traces for three different samples, as labeled. (b) Ag/Au ratio for each particle type, as obtained from ICP/MS analysis (grey), and estimated values for monolayer coverage of Ag (red).

CONCLUSIONS

In conclusion, we have determined the experimental conditions required to obtain twinned nanoparticles with mixed shapes (decahedra, triangles), using as seeds single/ crystalline 10 nm spherical particles. We showed that not only a fast reduction rate is necessary to induce formation of twin planes, but also the

presence of a surface passivation agent / silver ions. Our results open up possibilities for stepwise monitoring of emerging twin plane on the single/ particle level that may contribute to further development of twin engineering at the nanoscale.

EXPERIMENTAL

Chemicals. Gold (III) chloride trihydrate ($\text{HAuCl}_4 \times 3\text{H}_2\text{O}$), sodium borohydride (NaBH_4), ascorbic acid (AA), cetyltrimethylammonium chloride (CTAC), benzyltrimethylhexadecylammonium chloride (BDAC), silver nitrate (AgNO_3) and hydrochloric acid (HCl) were purchased from Sigma/ Aldrich and used without further purification. Milli/ Q water was used in all experiments.

Synthesis of 10 nm single/ crystal gold nanoparticles.²⁶

Initial seeds were prepared by reduction of HAuCl_4 (5 mL, 0.25 mM) with freshly prepared NaBH_4 (0.3 mL, 10 mM) in aqueous CTAC solution (100 mM). A brown solution formed upon addition of NaBH_4 . The mixture was left undisturbed at 27 °C for 2h to ensure complete decomposition of NaBH_4 . An aliquot of seed solution (0.11 mL) was added to a solution containing CTAC (20 mL, 200 mM), HAuCl_4 (20 mL, 0.5 mM) and AA (15 mL, 100 mM). The mixture was left undisturbed at 27 °C for 30 min. The solution was then centrifuged (1 h, 14,500 rpm) to remove excess of reagents and redispersed in water to obtain a final concentration of gold equal to 2 mM. The 10 nm gold nanospheres were used as seeds in further growth experiments.

Main synthesis. In a typical experiment, a solution of 10 nm gold seeds (0.04 mL) was added under vigorous stirring to an aqueous growth solution containing BDAC (10 mL, 100 mM), HAuCl_4 (0.1 mL, 50 mM) and AA (0.075 mL, 100 mM), and the desired amounts of Ag^+ or HCl (vide infra) at 30 °C. The mixture was left undisturbed at 30 °C for 2 h. The solution was centrifuged twice (6,500 rpm, 30 min) to remove excess of reagents, and redispersed in Milli/ Q water.

The effect of Ag^+ and HCl. To study the effect of silver ions, additional experiments were performed in the presence of different amounts of 10 mM AgNO_3 (0.04 mL and 0.12 mL). Similarly, to study the effect of HCl, additional

- (13) Nikoobakht, B.; El/ Sayed, M. A. Preparation and Growth Mechanism of Gold Nanorods (NRs) Using Seed/ Mediated Growth Method. *Chem. Mater.* **2003**, *15*, 1957–1962.
- (14) Zheng, Y.; Zhong, X.; Li, Z.; Xia, Y. Successive, Seed/ Mediated Growth for the Synthesis of Single/ Crystal Gold Nanospheres with Uniform Diameters Controlled in the Range of 5/ 150 Nm. *Part. Part. Syst. Charact.* **2014**, *31*, 266–273.
- (15) Almora/ Barrios, N.; Novell/ Leruth, G.; Whiting, P.; Liz/ Marzán, L. M.; López, N. Theoretical Description of the Role of Halides, Silver, and Surfactants on the Structure of Gold Nanorods. *Nano Lett.* **2014**, *14*, 871–875.
- (16) Magnussen, O. M. Ordered Anion Adlayers on Metal Electrode Surfaces. *Chem. Rev.* **2002**, *102*, 679–726.
- (17) Quan, Z.; Wang, Y.; Fang, J. High/ Index Faceted Noble Metal Nanocrystals. *Acc. Chem. Res.* **2013**, *46*, 191–202.
- (18) Barnard, A. S.; Young, N. P.; Kirkland, A. I.; van Huis, M. A.; Xu, H. Nanogold: A Quantitative Phase Map. *ACS Nano* **2009**, *3*, 1431–1436.
- (19) Forbes, G. S.; Cole, H. I. The Solubility of Silver Chloride in Dilute Chloride Solutions and the Existence of Complex Argentichloride Ions. *J. Am. Chem. Soc.* **1921**, *43*, 2492–2497.
- (20) Hubert, F.; Testard, F.; Spalla, O. Cetyltrimethylammonium Bromide Silver Bromide Complex as the Capping Agent of Gold Nanorods. *Langmuir* **2008**, *24*, 9219–9222.
- (21) Elechiguerra, J. L.; Reyes/ Gasga, J.; Yacaman, M. J. The Role of Twinning in Shape Evolution of Anisotropic Noble Metal Nanostructures. *J. Mater. Chem.* **2006**, *16*, 3906–3919.
- (22) Howie, A.; Marks, L. D. Elastic Strains and the Energy Balance for Multiply Twinned Particles. *Philos. Mag. A* **1984**, *49*, 95–109.
- (23) Marks, L. D. Surface Structure and Energetics of Multiply Twinned Particles. *Philos. Mag. A* **1984**, *49*, 81–93.
- (24) Jonte, J. H.; Martin, D. S. The Solubility of Silver Chloride and the Formation of Complexes in Chloride Solution. *J. Am. Chem. Soc.* **1952**, *74*, 2052–2054.
- (25) Oviedo, O. A.; Vélez, P.; Macagno, V. A.; Leiva, E. P. M. Underpotential Deposition: From Planar Surfaces to Nanoparticles. *Surface Science* **2015**, *631*, 23–34.
- (26) Zheng, Y.; Zhong, X.; Li, Z.; Xia, Y. Successive, Seed/ Mediated Growth for the Synthesis of Single/ Crystal Gold Nanospheres with Uniform Diameters Controlled in the Range of 5/ 150 Nm. *Part. Part. Syst. Charact.* **2014**, *31*, 266–273.

For Table of Contents only

