

ELECTRONIC SUPPLEMENTARY INFORMATION

Disentangling the Effect of Seed Size and Crystal Habit on Gold Nanoparticle Seeded Growth

Guillermo González-Rubio,^{a,b,c} Thais Milagres de Oliveira,^d Thomas Altantzis,^d Andrea La Porta,^d Andrés Guerrero-Martínez,^b Sara Bals,^d Leonardo Scarabelli,^{*a,e,f} Luis. M. Liz-Marzán.^{*a,c,g}

- a. BioNanoPlasmonics Laboratory, CIC biomaGUNE, Paseo de Miramón 182, 20014 Donostia-San Sebastián, Spain*
- b. Departamento de Química Física I, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040, Madrid, Spain*
- c. Ciber de Bioingeniería, Biomateriales y Nanomedicina, Ciber-BBN, 20014 Donostia-San Sebastián, Spain*
- d. EMAT-University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium*
- e. Department of Chemistry and Biochemistry, UCLA, Los Angeles, California 90095, USA*
- f. California NanoSystems Institute, UCLA, Los Angeles, California 90095, USA*
- g. Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain*

EXPERIMENTAL DETAILS

Characterisation Techniques

Transmission Electron Microscopy (TEM): Low magnification TEM images were obtained with a JEOL JEM-1400PLUS transmission electron microscope, operating at an acceleration voltage of 120 kV. Carbon-coated 400 square mesh copper grids were used. ADF-STEM, HAADF-STEM images and electron tomography series were acquired using a FEI-Tecnai and a FEI-Osiris electron microscopes operated at 200 kV. The acquisition of electron tomography series was performed in HAADF-STEM mode by using a Fischione model 2020 single tilt tomography holder. The series were acquired within a tilt range from -70° to $+70^\circ$ and a tilt increment of 2° . The reconstruction was performed by using the Simultaneous Iterative Reconstruction Technique (SIRT), implemented in the ASTRA toolbox¹. High resolution HAADF-STEM images were acquired using an aberration corrected cubed FEI-Titan electron microscope operated at 300 kV.

TEM grid preparation: 5 mL of the mixture (Au(0) concentration of 0.5 mM and surfactant concentration between 25 and 100 mM) was centrifuged and redispersed in 1 mL of 1 mM CTAC solution; then, the NPs were centrifuged again (same parameters) and redispersed with 200 μ L of water (Au(0) concentration of 25 mM and CTAC concentration between 0.1 - 0.2 mM). Finally, one drop (5 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 registered using using an Agilent 8453 UV-vis diode-array spectrophotometer. All experiments were carried out at 298 K using quartz cuvettes with optical path length of either 2 mm or 1 cm.

Experimental Details

Chemicals: Cetyltrimethylammonium chloride (CTAC, 25% w/w, 756 mM), cetyltrimethylammonium bromide (CTAB, 99%), hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$), L-ascorbic acid ($\geq 99\%$), 5-bromosalicylic acid (technical grade, 90%), sodium borohydride (NaBH_4 , 99%), silver nitrate (AgNO_3 , $\geq 99.0\%$), sodium iodide (NaI , $\geq 99.5\%$) and sodium bromide (NaBr , $\geq 99.5\%$) were purchased from Aldrich. All chemicals were used without further purification and Milli-Q water (resistivity $18.2 \text{ M}\Omega \cdot \text{cm}$ at 25°C) was used in all experiments.

Synthesis of Gold Nanorods: Gold nanorods were prepared, with some modifications, as previously described by Scarabelli et al.^{2,3} A CTAB/ NaBH_4 procedure was used to prepare the initial seeds: $25 \mu\text{L}$ of a 0.05 M HAuCl_4 solution was added to 4.7 mL of a 0.1 M CTAB solution; $300 \mu\text{L}$ of a freshly prepared 0.01 M NaBH_4 ($7.6 \text{ mg}/20 \text{ mL}$) solution was then injected under vigorous stirring. After 3 min the mixture was diluted 10 times in CTAB 0.1 M . In a synthesis of a 3 L nanorod suspension, 2.7 g of 5-bromosalicylic acid was added to 3 L of 0.05 M CTAB . The solution was mildly stirred for 15 min until complete dissolution and 28.8 mL of 0.01 M AgNO_3 and 30 mL of 0.05 M HAuCl_4 solutions were added to the mixture. After 2 h at 27°C (or once the absorbance of the Au(III) CTAB complex at 390 nm has decreased from 2.2 to 0.22) 7.8 mL of 0.1 M ascorbic acid solution was added under vigorous stirring, followed by 48 mL of diluted seed solution. The mixture was left undisturbed at room temperature for at least 4 h. Typically, the mixture was centrifuged twice (7000 rpm , 30 min) and finally, nanorods were redispersed in 100 mL of 25 mM CTAC solution. The resulting gold nanorods presented average length of $59 \pm 5 \text{ nm}$, and average diameter of $25 \pm 2 \text{ nm}$.

Synthesis of gold nanotriangles: The gold nanotriangles colloid was prepared, with some modifications, as previously described by Scarabelli et al.⁴ The initial seeds were prepared by the standard CTAC/ NaBH_4 procedure: $25 \mu\text{L}$ of a 0.05 M HAuCl_4 solution was added to 4.7 mL of 0.1 M CTAC solution; $300 \mu\text{L}$ of a freshly prepared 0.01 M NaBH_4 solution was then injected under vigorous stirring. The seed solution was aged for 2 h at room temperature prior to use and then diluted 10 times in a 0.1 M CTAC solution. In a typical synthesis, 37.5 mL of 0.05 M HAuCl_4 solution was added to 3 L of 50 mM CTAC solution, followed by 22.5 mL of a 0.01 M NaI solution. Subsequently, 30 mL of 0.1 M ascorbic acid solution was added under vigorous manual stirring, followed by 25 mL of the diluted seed solution. The gold nanotriangles dispersion was left undisturbed at room temperature for at least 1 h and then purified by addition of 100 mL of $25 \text{ wt}\%$ CTAC solution (final concentration: 150 mM). Flocculation of the gold nanotriangles was completed overnight and then, the supernatant was removed and the precipitated particles were redispersed in 100 mL of 0.25 mM CTAC solution. The resulting gold nanotriangles presented an edge length of $59 \pm 3 \text{ nm}$.

Synthesis of 20 and 12 nm gold seeds from gold nanotriangles and nanorods: An iterative oxidation approach, with Au(III) as oxidizing agent, was used to produce monodispersed spherical seeds from both gold nanotriangles and gold nanorods. Upon centrifugation, the nanoparticles were suspended in 4 L of an aqueous solution of 25 mM CTAC and 10 mM NaBr . The concentration in Au(0) (estimated using the absorbance at 400 nm) was set at 0.2 mM .³ Subsequently, a certain amount of 0.05 M Au(III) solution was added under vigorous stirring (final Au(0):Au(III) molar ratio of 4:1). The reaction was then gently stirred at 30°C until oxidation was completed (absorbance at 400 nm decreased by ca. 50%).³ Finally, the mixture was centrifuged (1h at increasing rpm as the number of oxidation cycles increases, from 8000 to 13000 rpm), the supernatant was discarded and the precipitate redispersed in 25 mM CTAC solution. The entire process was repeated several times until the desired size was achieved. Four and seven oxidation cycles

were required to produce gold seeds of 20 and 12 nm, respectively. An additional centrifugation step (2h at 2000 rpm for 20 nm seeds; 6000 rpm for 12 nm seeds) was performed to remove large particles which were not sufficiently etched. The final concentration of nanoparticles was fixed to $1.02 \cdot 10^{17}$ nanoparticles per litre.

Silver overgrowth of 20 and 12 nm gold seeds. Typically, 100 μL of 0.01 M AgNO_3 and 10 μL of 0.01 M ascorbic acid solution were added to 2 mL of 25 mM CTAC solution. The concentration of gold seeds was fixed to $1.02 \cdot 10^{15}$ nanoparticles per litre. The mixture was heated up to 65 $^\circ\text{C}$ and left undisturbed for 12 h. Finally, it was centrifuged for 30 min at 5000 rpm and redispersed in 1 mM CTAC solution.

Gold overgrowth of 20 and 12 nm gold seeds. Typically, 25 μL of 0.05 M HAuCl_4 solution and the desired amount of 0.01 mM NaI solution were added to 2 mL of 50 mM CTAC solution. Subsequently, 20 μL of 0.1 M ascorbic acid solution was added under vigorous manual stirring. The concentration of gold seeds was fixed to $1.02 \cdot 10^{15}$ nanoparticles per litre. The mixture was left undisturbed at room temperature for 1 h. Finally, it was centrifuged for 30 min at 5000 rpm and the precipitate was redispersed in 2 mL of 1 mM CTAC solution.

Synthesis of 20 nm gold seeds via standard bottom-up approach. Single-crystal gold nanospheres were prepared, with some modifications, as previously described by Zheng et al.⁵ and Hanske et al.⁶: 25 μL of a 0.05 M HAuCl_4 solution was added to 4.7 mL of a 0.1 M CTAB solution; 300 μL of a freshly prepared 0.01 M NaBH_4 (7.6 mg/20 mL) solution was then injected under vigorous stirring. The mixture was kept undisturbed for 3 h. Then, an aliquot of 500 μL was added to 20 mL of 0.2 M CTAC solution, followed by 15 mL of 0.1 M ascorbic acid solution. Subsequently, 20 mL of 0.5 mM HAuCl_4 was quickly injected under vigorous stirring. The reaction was allowed to proceed for 15 min at room temperature. The mixture was centrifuged twice (1 h at 13000 rpm) and the precipitate was redispersed in 1 mL of 25 mM CTAC solution. The size of gold nanospheres was characterised by TEM and determined to be 8 ± 0.5 nm. Overgrowth of such particles to obtain 20 nm single crystal seeds was performed in a 25 mM CTAC solution, in the presence of 0.25 mM of HAuCl_4 and 0.2 mM of ascorbic acid. The concentration of 8 nm gold seeds was fixed to $6.1 \cdot 10^{14}$ nanoparticles per litre.² The mixture was kept undisturbed for 1 h. Finally, the 20 nm seeds were washed twice by centrifugation (1 h at 9000 rpm) and redispersed in 25 mM CTAC solution. The resulting 20 nm gold seeds presented a diameter of 20 ± 1 nm.

EXPERIMENTAL RESULTS

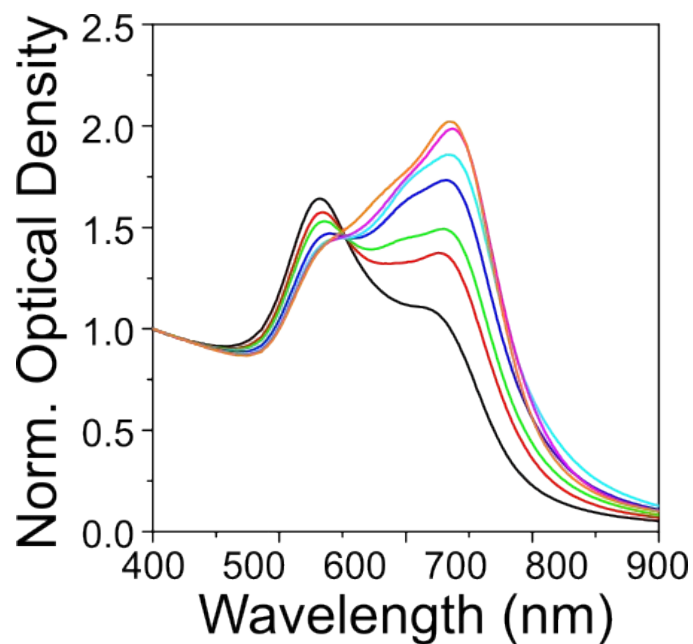


Fig. S1 UV-vis spectra of nanotriangles colloids, prepared with different aging time of the seeds solution: **black:** 0 min, **red:** 15 min, **green:** 30 min, **blue:** 1 hour, **cyan:** 1.5 hours, **pink:** 2 hours, **orange:** 3 hours.

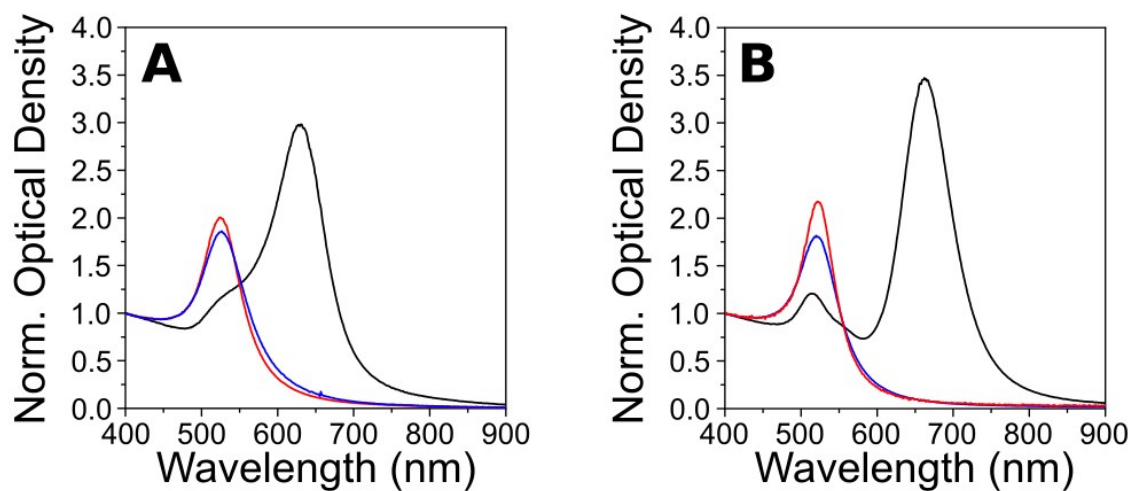


Fig. S2 UV-vis spectra of the starting nanoparticles and the seeds resulting from oxidative etching. **Black:** starting samples, **red:** 20 nm seeds, **blue:** 12 nm seeds. **A:** nanotriangles, **B:** nanorods.

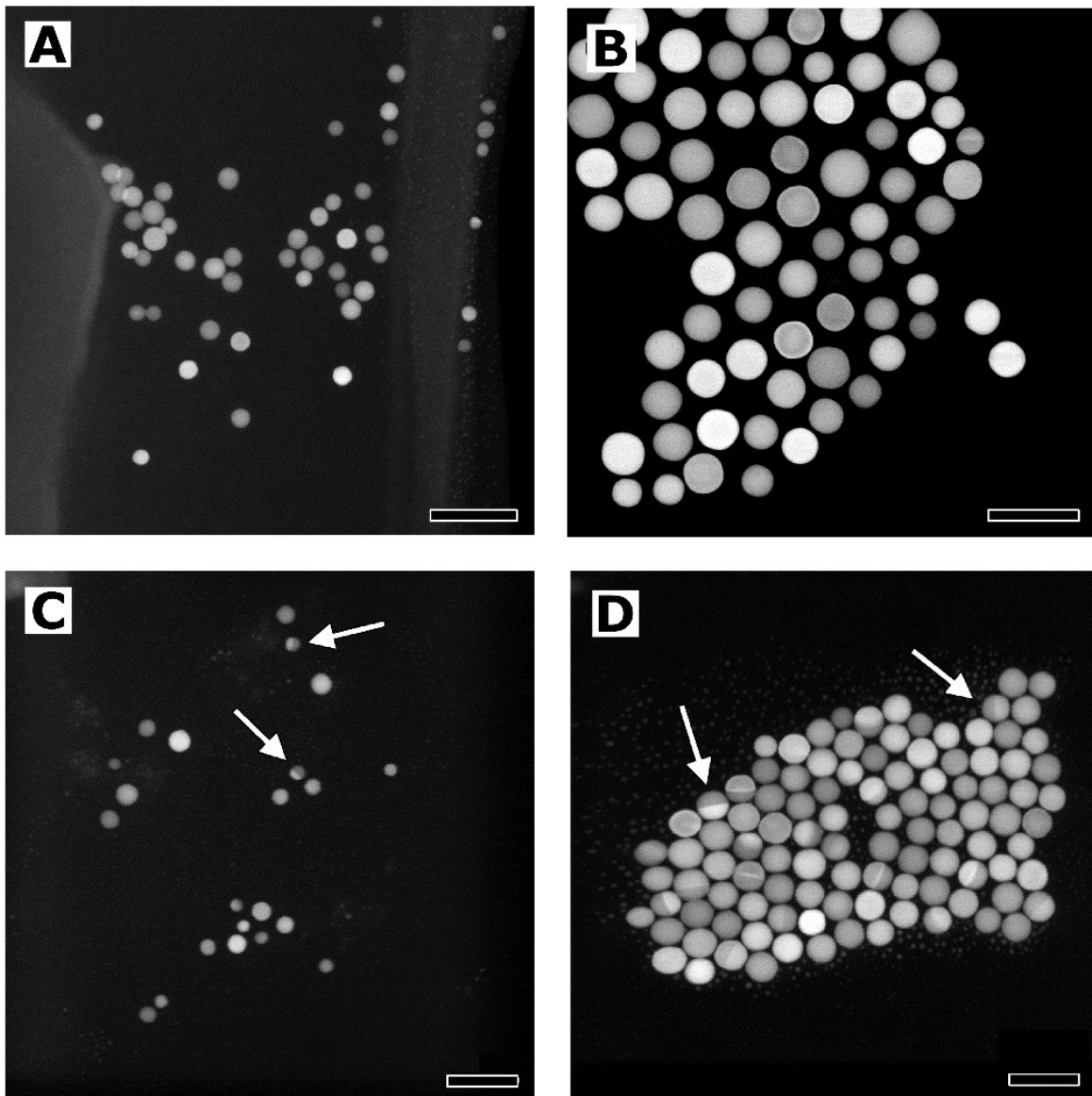


Fig. S3 ADF-STEM images of seeds: 12NR (A), 20NR (B), 12NT (C), 20NT (D). Diffraction contrast is present, which indicates the presence of twins (as indicated in some representative particles by white arrows). For the single crystal seeds (12NR, 20NR), twins could not be observed in the vast majority of the particles.

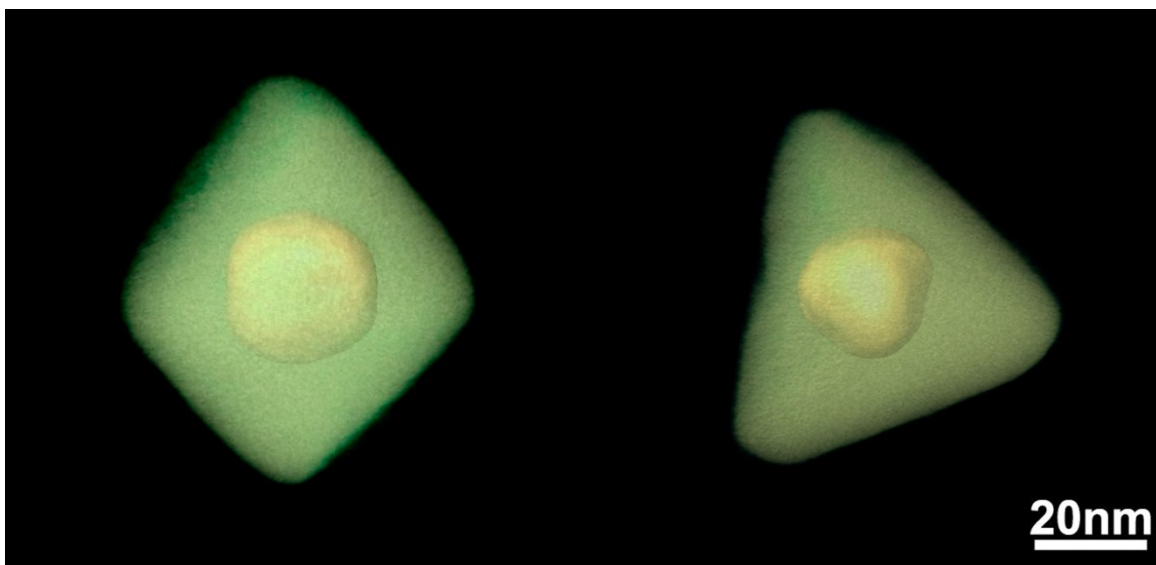


Fig. S4 HAADF-STEM tomography reconstruction images in two different orientations, showing a gold seed embedded within a silver triangular-based nanobipyramid.

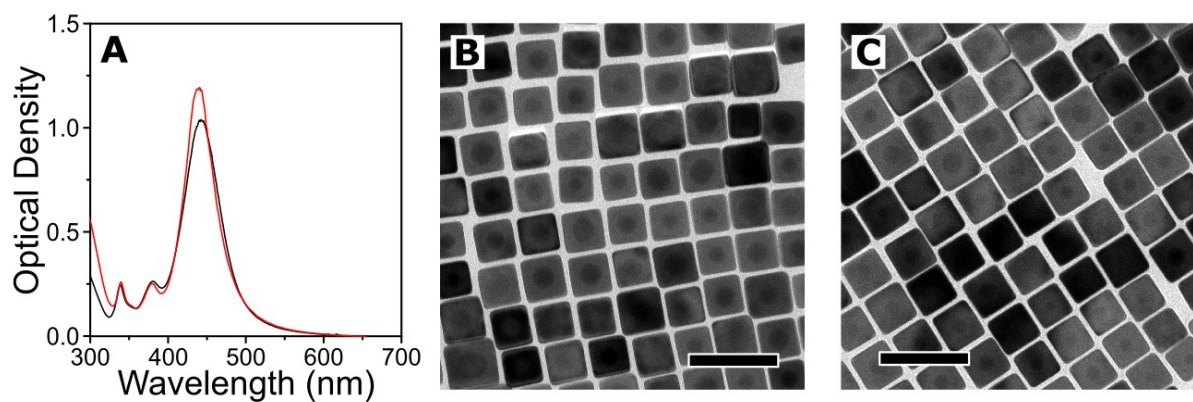


Fig. S5 **A:** UV-vis spectra of 20NR (black line) and 10NR (red line) seeds coated with silver. **B-C:** TEM images of 20NR (**B**) and 10NR (**C**) seeds coated with silver. Scale bars: 100 nm.

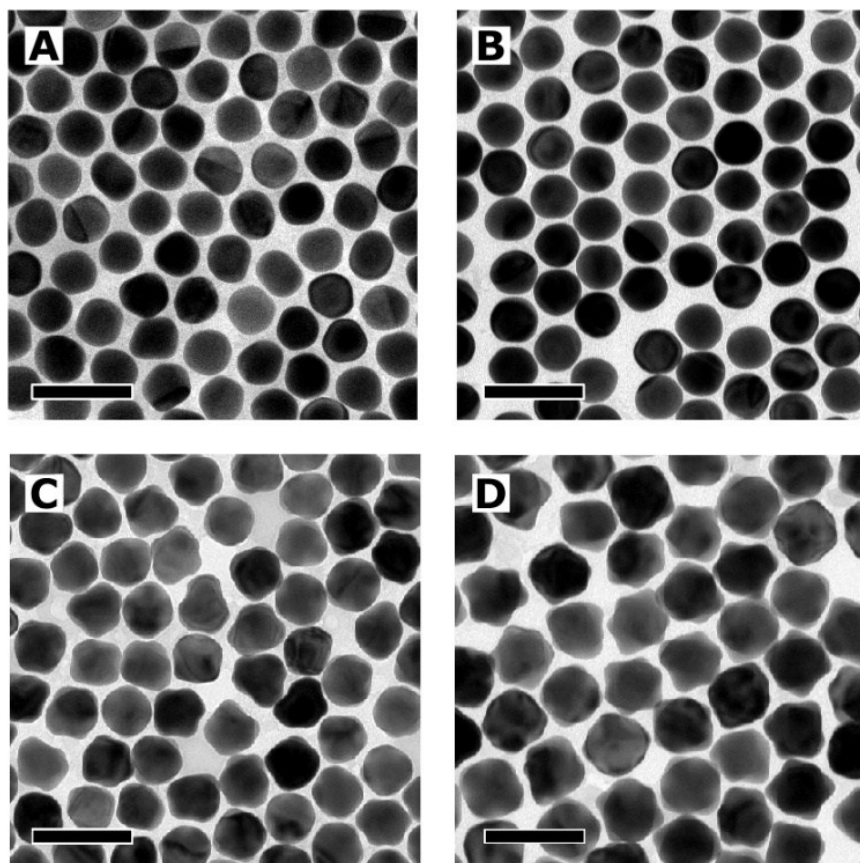


Fig. S6 TEM images of the four seed solutions grown in the absence of iodide. **A:** 10NT, **B:** 20NT, **C:** 10NR, **D:** 20NR. Poorly defined shapes can be appreciated. Scale bars: 100 nm.

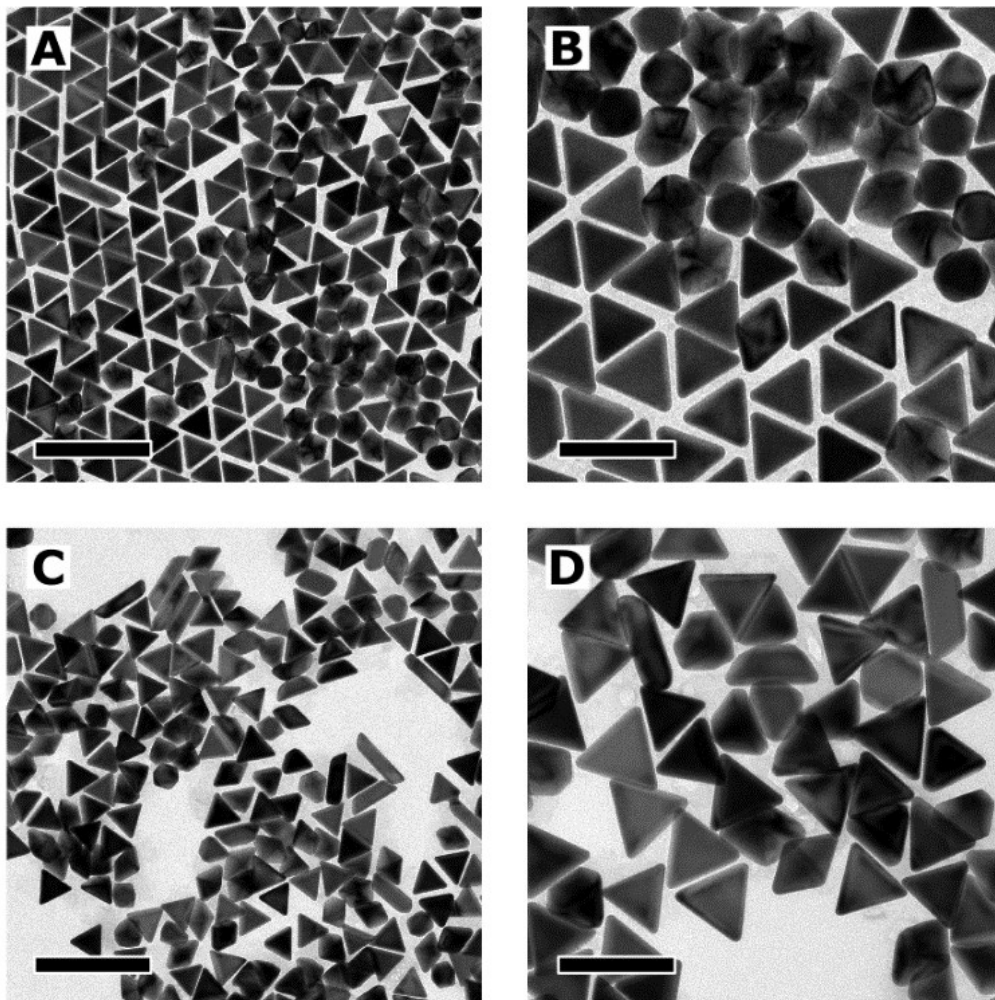


Fig. S7 TEM images at different magnifications of particles grown from 20nm seed solutions, using 500 μ M iodide. **A,B:** 20NT; **C,D:** 20NR. It should be noticed the presence of penta-twinned nanoparticles in 20NT, and the mono-twinned product in 20NR. Scale bars: **A,C:** 200 nm; **B,D:** 100nm.

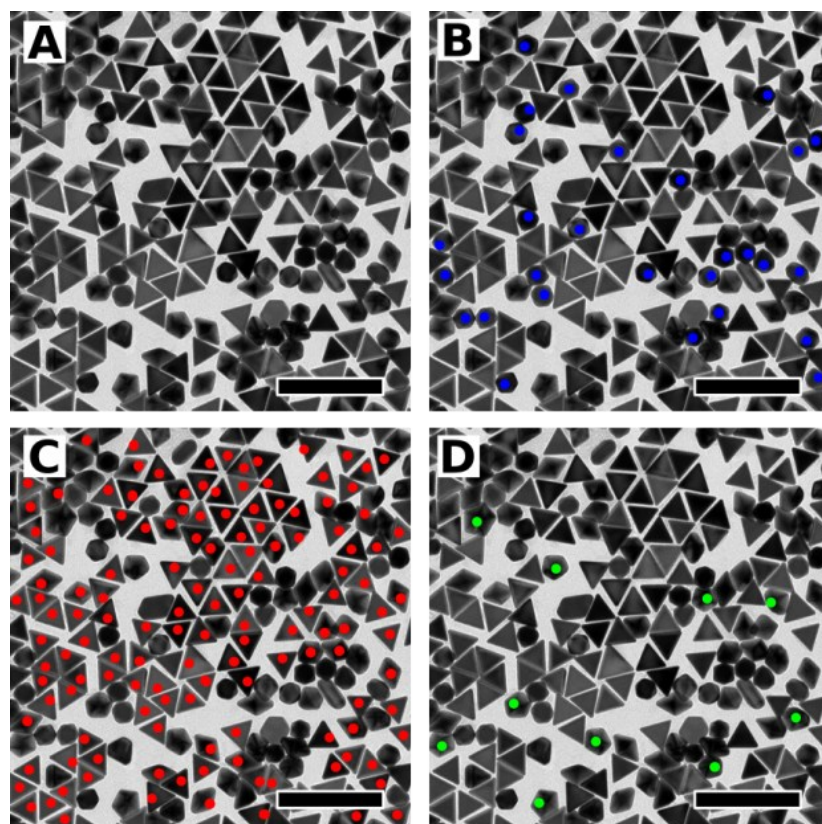


Fig. S8 TEM composition analysis. An example is shown for 20NT grown in the presence of 50 μM iodide, counting the amount of: **B:** single-crystal (nanooctahedra, blue dots); **C:** mono-twinned (nanotriangles and nanobipyramids, red dots); **D:** penta-twinned (decahedra, green dots). **A:** reference picture. Scale bars: 200nm.

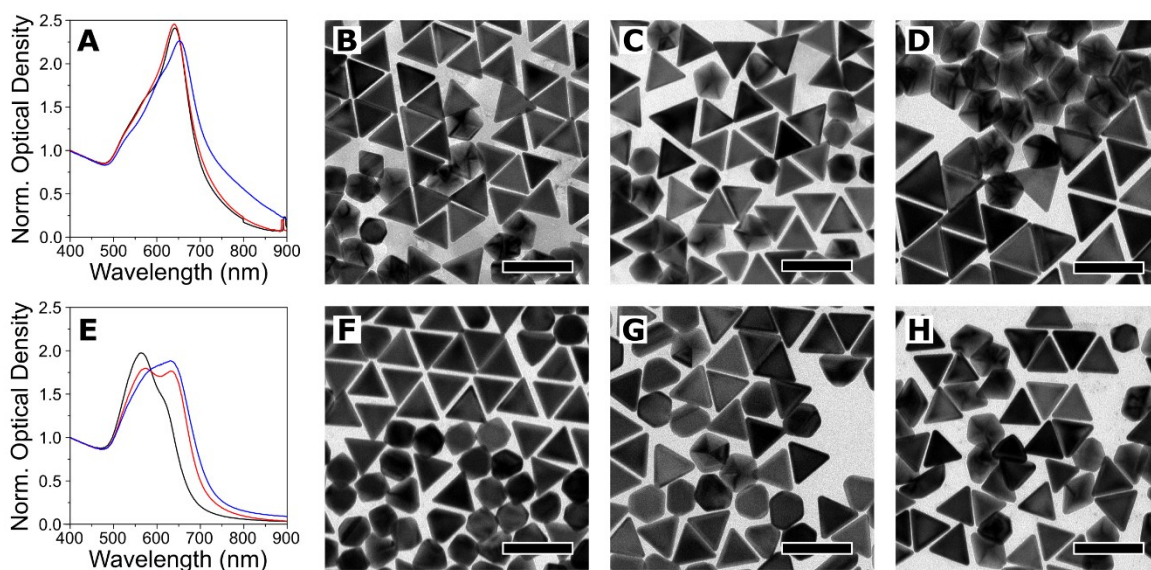


Fig. S9 Left: UV-vis spectra of 12NT (**A**) and 12NR (**E**), grown in the presence of different concentrations of iodide: 50 μM (black), 75 μM (red) and 100 μM (blue). **Right:** TEM analysis of 12NT (**top**) and 12NR (**bottom**) grown with different iodide concentrations: 50 μM (**B,F**), 75 μM (**C,G**) and 100 μM (**D,H**). Scale bars: 100 nm. (Images at different magnifications are shown in **Figures S14-S15**).

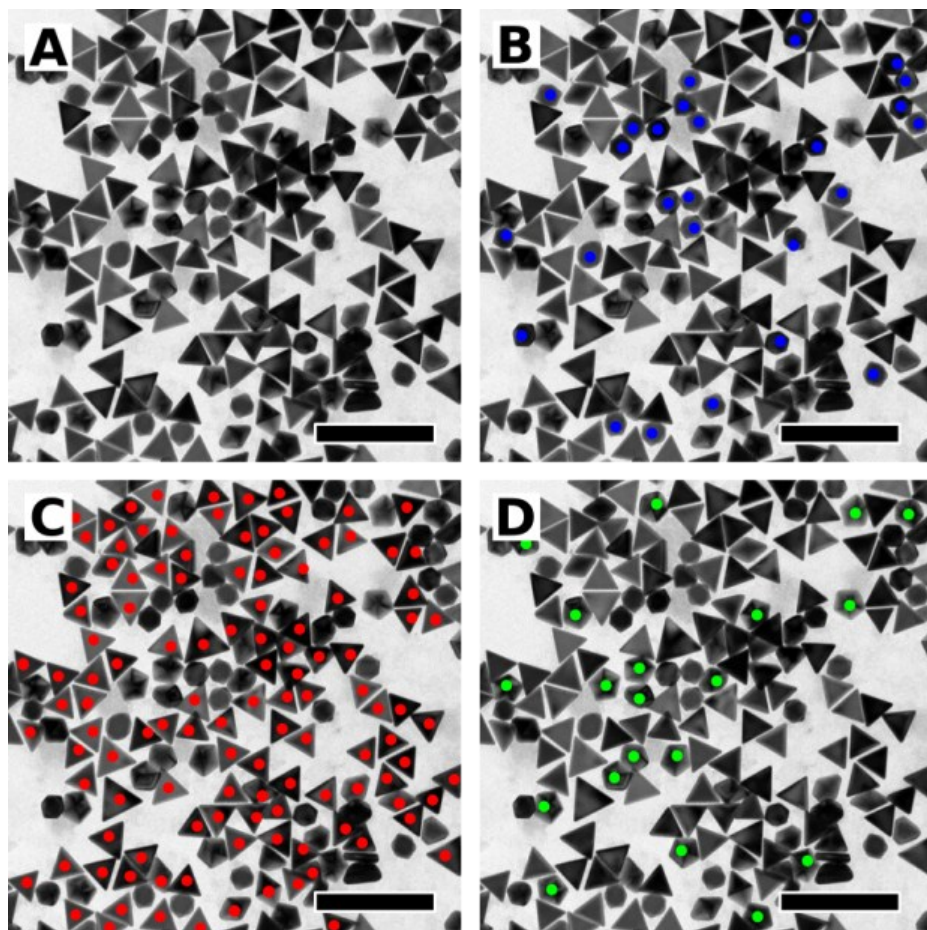


Fig. S10 TEM composition analysis. In this example, we investigated 12NT grown in the presence of 50 μM of iodide, counting the amount of: **B:** single-crystal (nanooctahedra, blue dots), **C:** mono-twinned (nanotriangles and nanobipyramids, red dots), and **D:** penta-twinned (decahedra, green dots). **A:** reference picture. Scale bars 200nm.

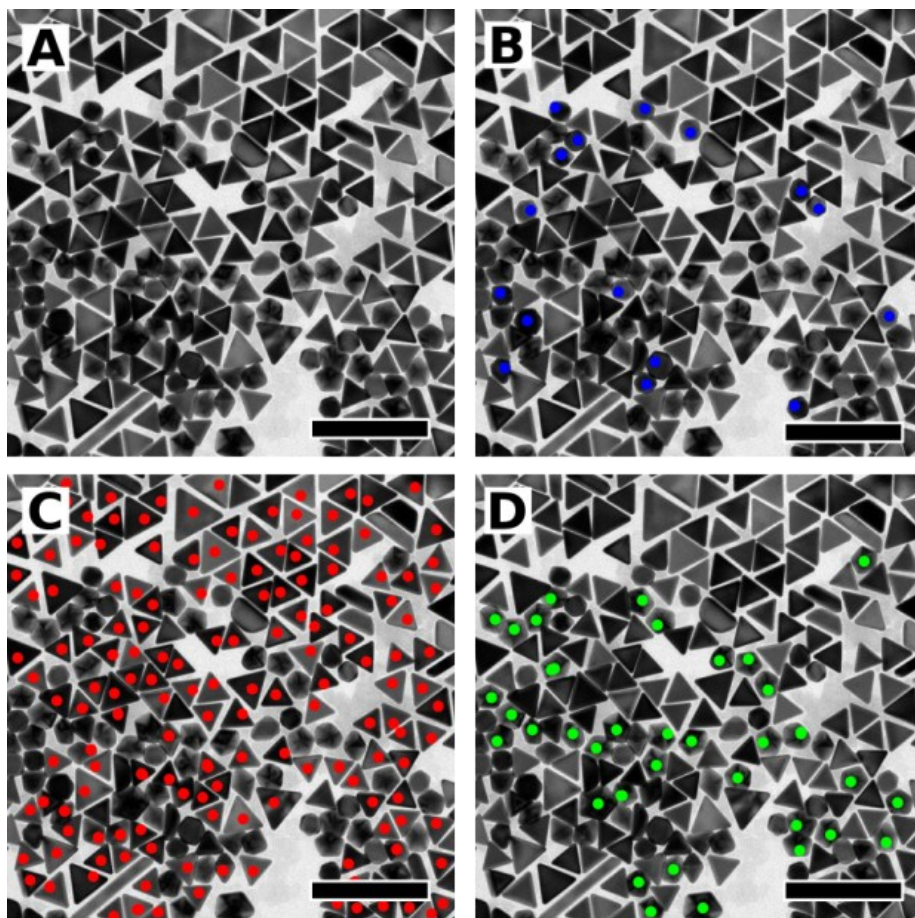


Fig. S11 TEM composition analysis. In this example we investigated 12NT grown in the presence of 500 μM of iodide, counting the amount of: **B:** single-crystal (nanooctahedra, blue dots), **C:** mono-twinned (nanotriangles and nanobipyramids, red dots), and **D:** penta-twinned (decahedra, green dots). **A:** reference picture. Scale bars 200nm.

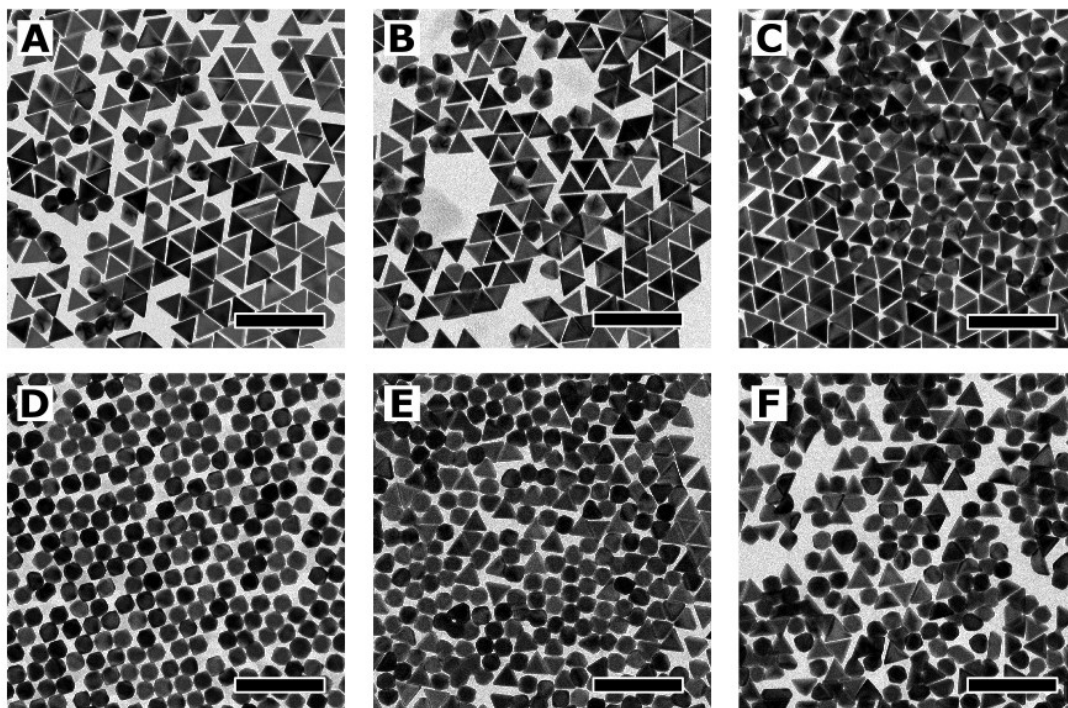


Fig. S12 TEM analysis of 20NT (**Top**) and 20NR (**Bottom**) grown with different concentration of iodide: **A,D**: 50 μM , **B,E**: 75 μM and **C,F**: 100 μM . Scale bars: 200 nm.

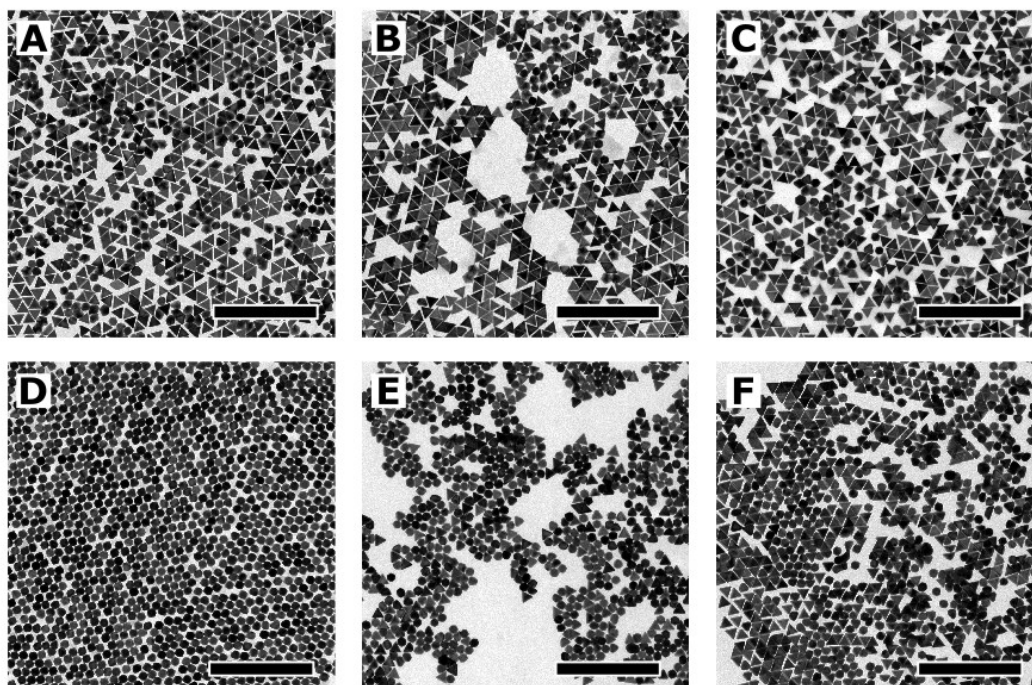


Fig. S13 TEM analysis of 20NT (**Top**) and 20NR (**Bottom**) grown with different concentrations of iodide: **A,D**: 50 μM , **B,E**: 75 μM and **C,F**: 100 μM . Scale bars: 500 nm.

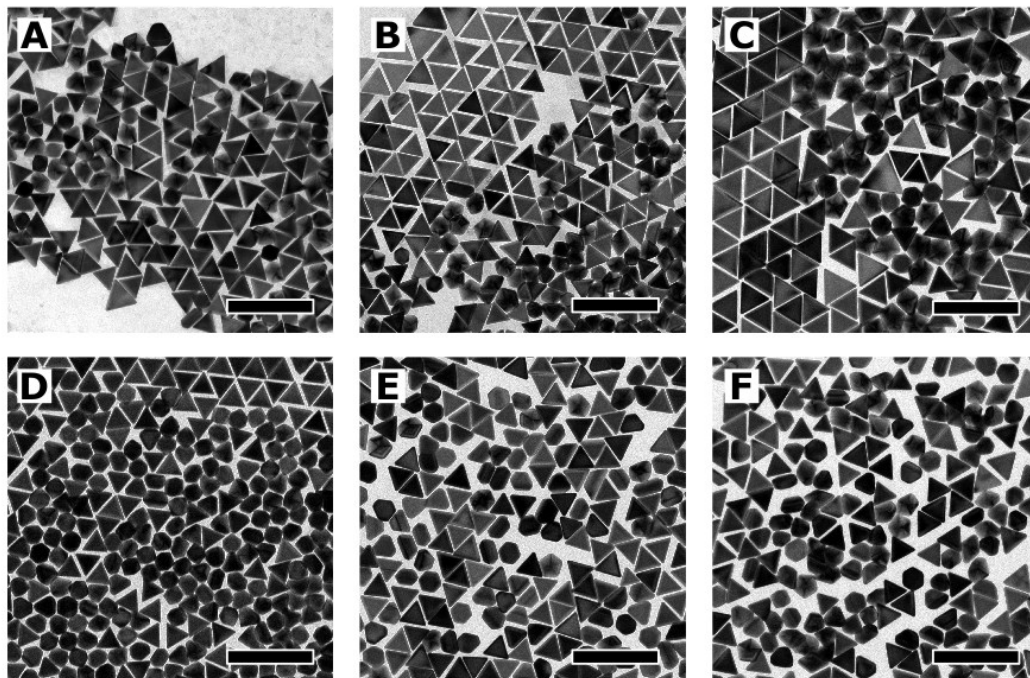


Fig. S14 TEM analysis of 12NT (**Top**) and 12NR (**Bottom**) grown with different concentrations of iodide: **A,D:** 50 μM , **B,E:** 75 μM and **C,F:** 100 μM . Scale bars: 200 nm.

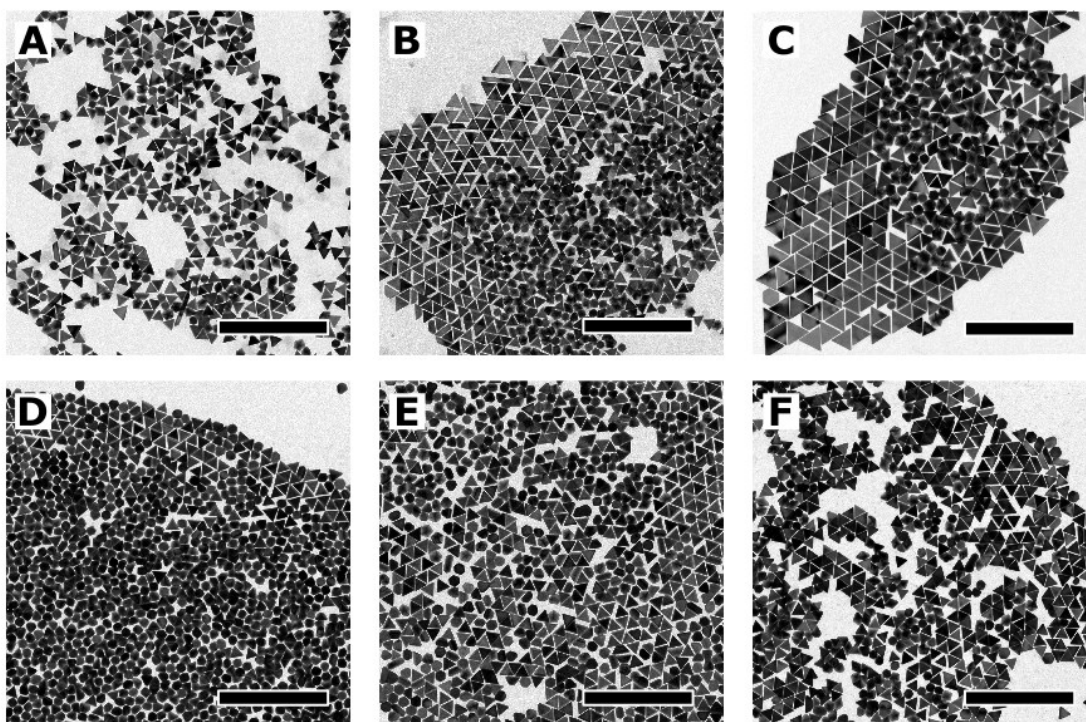


Fig. S15 TEM analysis of 12NT (**Top**) and 12NR (**Bottom**) grown with different concentrations of iodide: **A,D:** 50 μM , **B,E:** 75 μM and **C,F:** 100 μM . Scale bars: 500 nm.

We hypothesize that an increase in the yield of nanotriangles should be achieved by favouring the formation of mono-twinned particles and avoiding the formation multiply twinned products, through a rational selection of the nature of the seeds and growth conditions. The choice of size and crystal habit for the seeds was then made taking into account the following experimental observations: a) bigger seeds are less prone than smaller seeds to form multiply twinned products during growth (even at high iodine concentration, a driving force toward the formation of defects); b) single-crystal seeds can evolve into multiply twinned structures but twinned seeds cannot evolve into single-crystal particles. Therefore, the use of 20 nm mono-twinned seeds appeared to be the most suitable choice to increase the yield in gold nanotriangles. Since the preparation of high-yield mono-twinned seeds is still a challenge, the best option was preparing 20 nm single-crystal gold seeds and increase the iodine concentration (up to 150 μ M) to maximize the amount mono-twinned products during growth.

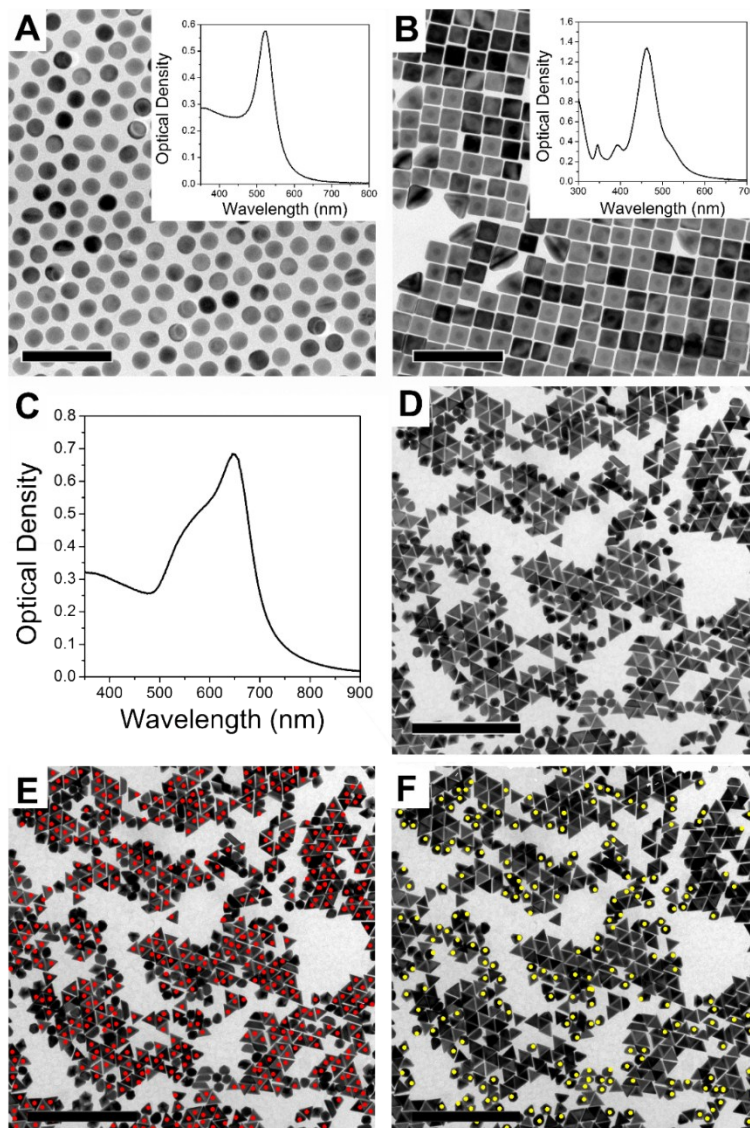


Fig. S16 TEM images and UV-vis spectra (insets) of **A**: 20 nm “standard” gold seeds (20 ± 1 nm) and **B**: the result of silver coating (89% single-crystal, 10% mono-twinned). **C**: UV-vis spectra and **D**: TEM image of gold nanotriangles grown from synthesized 20 nm seeds, in the presence of 150 μ M of iodine. **E,F**: Analysis of **D**, by counting the amount of nanotriangles (**E**, red dots, 70%); nanooctaedra, nanobipyramids and nanodecahedra (**F**, yellow dots). Scale bars: **A**: 100 nm, **B**: 200 nm and **D**, **E**, **F**: 500 nm.

REFERENCES

1. W. Van Aarle, W. J. Palenstijn, J. De Beenhouwer, T. Altantzis, S. Bals, K. J. Batenburg and J. Sijbers, *Ultramicroscopy*, 2015, **157**, 35–47
2. L. Scarabelli, M. Grzelczak and L. M. Liz-Marzán, *Chem. Mater.*, 2013, **25**, 4232–4238.
3. L. Scarabelli, A. Sánchez-Iglesias, J. Pérez-Juste and L. M. Liz-Marzán, *J. Phys. Chem. Lett.*, 2015, **6**, 4270–4279.
4. L. Scarabelli, M. Coronado-Puchau, J. J. Giner-Casares, J. Langer and L. M. Liz-Marzán, *ACS Nano*, 2014, **8**, 5833–5842.
5. Y. Zheng, X. Zhong, Z. Li and Y. Xia, *Part. Part. Syst. Charact.*, 2014, **31**, 266–273.
6. C. Hanske, G. González-Rubio, C. Hamon, P. Formentín, E. Modin, A. Chuvilin, A. Guerrero-Martínez, L. F. Marsal and L. M. Liz-Marzán, *J. Phys. Chem. C*, 2017, **121**, 10899–10906.