

Copper Assisted Symmetry and Size Control of Gold Nanobars

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EXPERIMENTAL

Chemicals. Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) ($\geq 99.9\%$), Copper (II) chloride (CuCl_2) ($\geq 99.999\%$), sodium borohydride (NaBH_4) ($\geq 99.9\%$), and L-ascorbic acid (AA) ($\geq 99.9\%$) were purchased from Sigma-Aldrich. Hexadecyltrimethylammonium bromide (CTAB) (98%) was purchased from Ajax Finechem. Ultrapure water (milli-Q) was used for the preparation of all solutions. All glassware used for the syntheses were cleaned using aqua regia prior to use.

Synthesis of gold seeds. Aqueous solutions of CTAB (1.875 mL, 0.20 M), and HAuCl_4 (0.025 mL, 0.050 M) were diluted with milli-Q water (2.83 mL). NaBH_4 solution (0.30 mL, 0.010 M) was then quickly added into the above mixture under vigorous stirring and stirring was continued for 10 minutes. The resulting seed dispersion was kept in a water bath at $28 \pm 1^\circ\text{C}$ for 40 min prior to further use.

Synthesis of Cu^{2+} -assisted gold nanobars. The seed dispersion was diluted 10 times with milli-Q water. Aqueous solutions of CTAB (1.00 mL, 0.20 M) and HAuCl_4 (0.10 mL, 0.050 M) were diluted with milli-Q water (11.38 mL). The solution was thoroughly stirred and allowed to sit for 5 minutes. An aqueous solution of ascorbic acid (1.50 mL, 0.10 M) was then added and the solution was mixed thoroughly. After 5 minutes, an aqueous solution of CuCl_2 (20 μL , 25 μL , 27 μL , 30 μL , 40 μL , 0.010 M) was added, and the resulting solution was mixed thoroughly and allowed to sit for 1 minute. Finally, the diluted seed dispersion (25 μL) was added with thorough mixing. The final dispersion was kept in the water bath at $28 \pm 1^\circ\text{C}$ for 48 hours.

Synthesis of gold nanocubes in the absence of Cu^{2+} ions. The seed dispersion was diluted 10 times with milli-Q water. Aqueous solutions of CTAB (1.00 mL, 0.20 M) and HAuCl_4 (0.10 mL, 0.050 M) were diluted with milli-Q water (11.38 mL). The solution was thoroughly stirred and allowed to sit for 5 minutes. An aqueous solution of ascorbic acid (1.50 mL, 0.10 M) was then added and the solution was mixed thoroughly. The diluted seed dispersion (25 μL) was added with thorough mixing. The final dispersion was kept in the water bath at $28 \pm 1^\circ\text{C}$ for 48 hours.

Preparation of TEM specimens. Ultrathin carbon (or graphene) coated Cu TEM grids were plasma cleaned in H_2/O_2 for 30 seconds before use. Dispersions of the final particles (48 hours) were centrifuged before deposition, while samples taken early in the colloid growth were directly deposited onto the grids. A sample of the colloid was taken and immediately dropped onto the TEM grid. The grid was left 5 minutes (or 15 seconds for the preparation of nanoparticles samples at the early stages of growth). The grid was immersed in spectroscopic grade ethanol for 20 min to remove excess CTAB. SiN3 support film was used for EDX mapping.

TEM characterizations. Electron microscopy was carried out on a FEI Tecnai G2 T20 Twin TEM (@ 200 kV) and a FEI Tecnai G2 F20 S-Twin TEM (@ 200 kV) for yield and shape measurements, and on a FEI Titan³ 80-300 kV FEGTEM equipped with both probe and imaging spherical aberration correctors for (S)TEM imaging at atomic resolution and EDX mapping (all imaging was carried out at 300 kV with a 15 mrad probe-forming aperture).

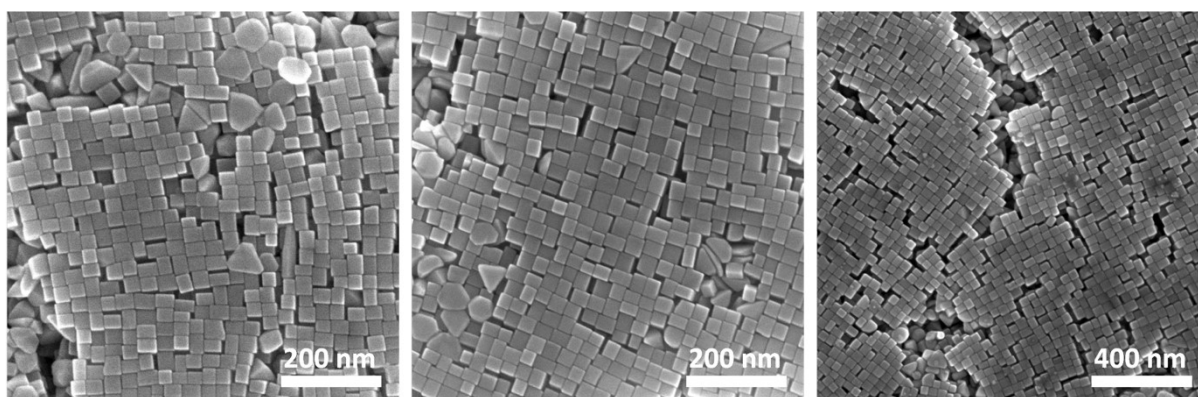


Figure S1. Large-scale SEM images of gold nanocubes synthesized in the presence of Cu additives (19.2 μ M concentration). We note the size statistics were measured for nanocrystals well-dispersed on TEM grids to avoid any small bias from selective stacking in the multiple layers shown here.

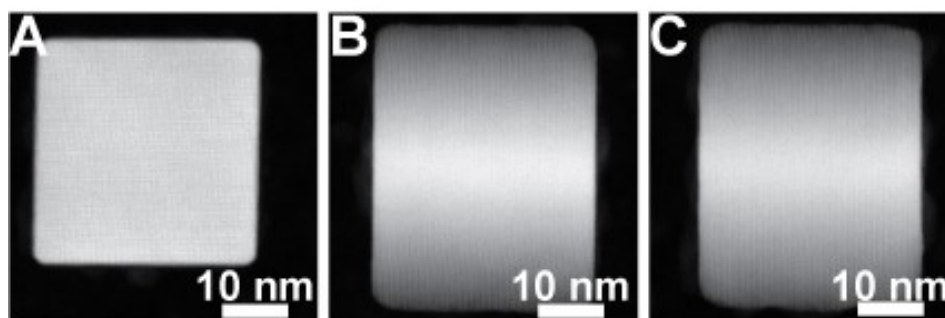


Figure S2. (A-C) HAADF-STEM images of a representative gold nanocube synthesized in the presence of Cu²⁺ additives (19.2 μ M concentration) viewed along $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 0\bar{1}1 \rangle$ directions. Edge lengths measurements ($a = 29.3$ nm, $b = 29.6$ nm, $c = 33.4$ nm) confirms the nanobar has an aspect ratio $\neq 1$, even though it has a square projection in the $\langle 001 \rangle$ zone axis and could be mistaken for a nanocube in this projection.

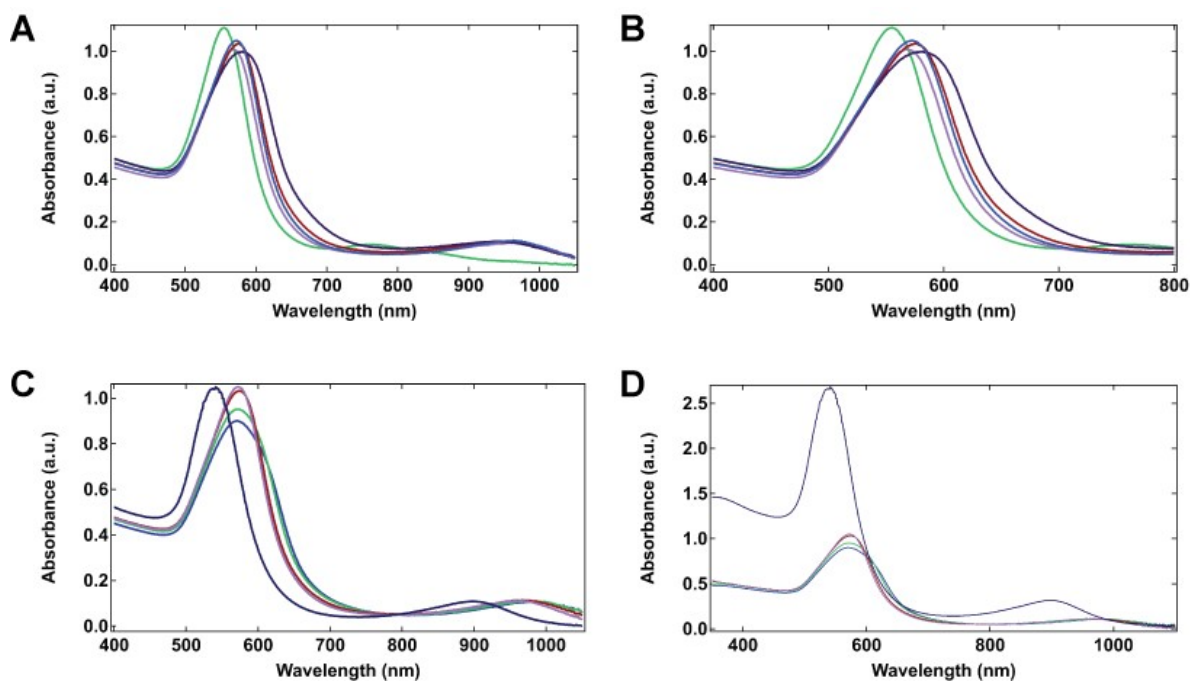


Figure S3. UV-vis spectra (A) Visible-NIR absorption spectra of nanobars grown with various concentrations of Cu^{2+} in the growth solution; 14.3 μM (green), 17.8 μM (purple), 19.2 μM (blue), 21.4 μM (red) and 24.9 μM (dark violet). (B) Visible absorption spectra of nanobars grown with various concentrations of Cu^{2+} in the growth solution; 14.3 μM (green), 17.8 μM (purple), 19.2 μM (blue), 21.4 μM (red) and 24.9 μM (dark violet). (C) Normalized visible-NIR absorption spectra of nanobars grown in the presence of 19.2 μM Cu^{2+} at 15 minutes (blue), 45 minutes (green), 24 hours (red), 48 hours (purple) and 72 hours (dark-blue). (D) Visible-NIR absorption spectra of nanobars grown in the presence of 19.2 μM Cu^{2+} at 15 minutes (blue), 45 minutes (green), 24 hours (red), 48 hours (purple) and 72 hours (dark blue).

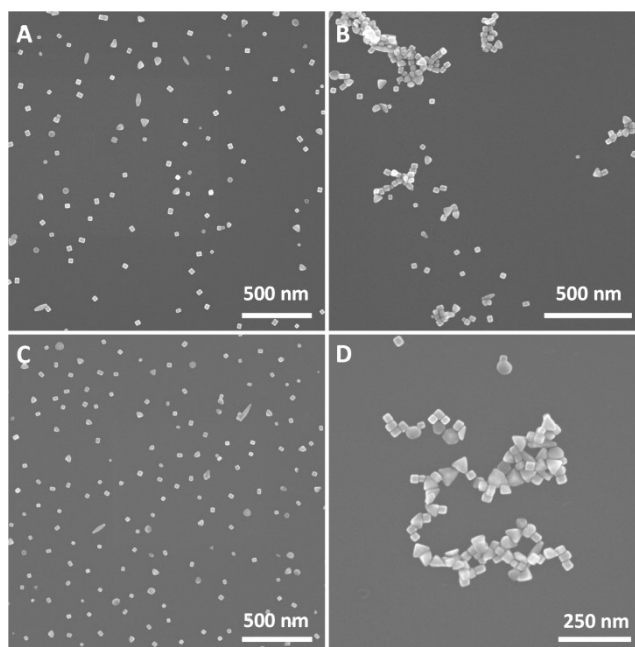


Figure S4. SEM images as a function of Cu^{2+} concentration: (A) 14.3 μM , (B) 17.8 μM , (C) 21.4 μM , (D) 24.9 μM .

Dimension	Size of Nanobars as a function of [Cu ²⁺]				
	14.3 μM	17.8 μM	19.2 μM	21.4 μM	24.9 μM
Length	36 ± 5 nm	36 ± 4 nm	37 ± 5 nm	35 ± 4 nm	33 ± 4 nm
Width	32 ± 4 nm	30 ± 3 nm	31 ± 4 nm	30 ± 3 nm	28 ± 3 nm
Aspect Ratios	1.1 ± 0.1	1.2 ± 0.1	1.2 ± 0.2	1.2 ± 0.1	1.2 ± 0.1
Number of Particle analyzed	151	132	122	332	70

Table S1. Size statistics of the gold nanocuboids by Cu²⁺-assisted synthesis at various Cu²⁺ concentrations.

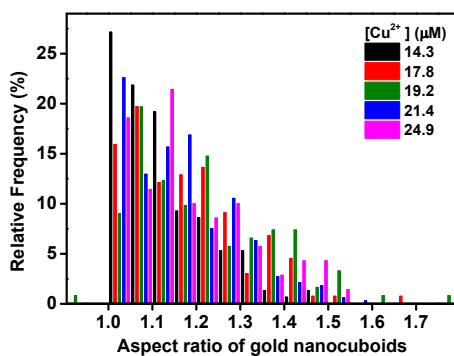


Figure S5. Statistical analyses on the aspect ratios of gold nanobars by Cu²⁺-assisted synthesis at various Cu²⁺ concentrations.

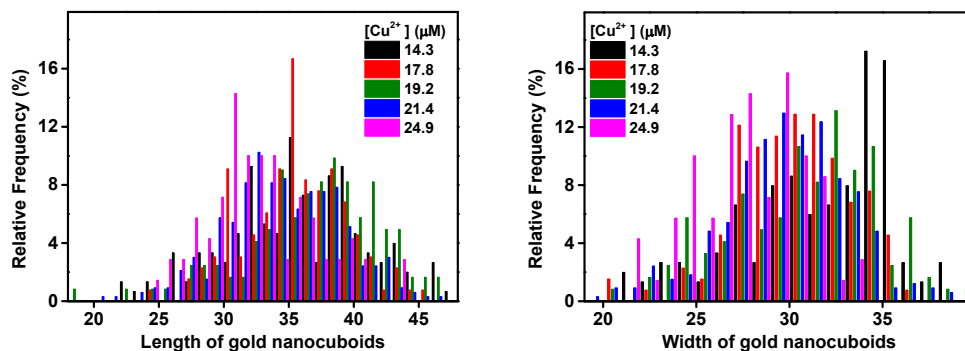


Figure S6. Statistical analyses on the length and width of the gold nanobars by Cu²⁺-assisted synthesis at various Cu²⁺ concentrations.

Shape	Shape yield as a function of $[\text{Cu}^{2+}]$				
	14.3 μM	17.8 μM	19.2 μM	21.4 μM	24.9 μM
Nanobars	70% (170)	71% (244)	88% (862)	70% (275)	56% (114)
RBP	13% (40)	17% (68)	7% (73)	15% (68)	28% (63)
Rod-like	3% (8)	3% (9)	1% (10)	2% (9)	3% (6)
Others	14% (34)	9% (31)	4% (40)	13% (50)	13% (26)
Total number of Particles analyzed	244	343	975	393	203

Table S2. Shape yield statistics as a function of Cu^{2+} concentration in Cu^{2+} -assisted synthesis of gold nanobars.

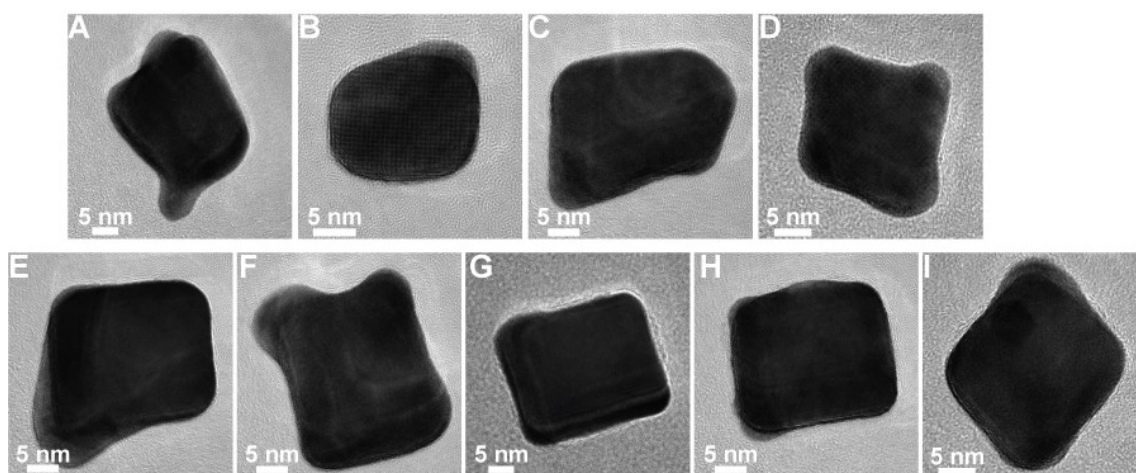


Figure S7. TEM images of Cu^{2+} -assisted gold nanoparticles oriented in $\langle 001 \rangle$ zone axis, sampled at different growth times: (A-D) 1 min, (E-I) 3 min.

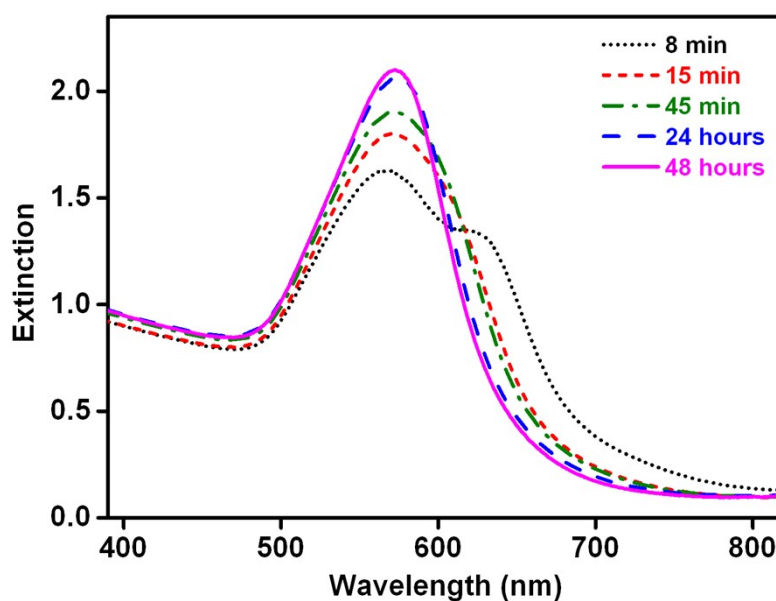


Figure S8. Time-dependent UV-Vis extinction spectra of gold nanobar growth with $[\text{Cu}^{2+}] = 19.2 \mu\text{M}$. The LSPR maxima are 567, 570, 572, 574, and 573 nm for 8 min, 15 min, 45 min, 24 hours, and 48 hours respectively.

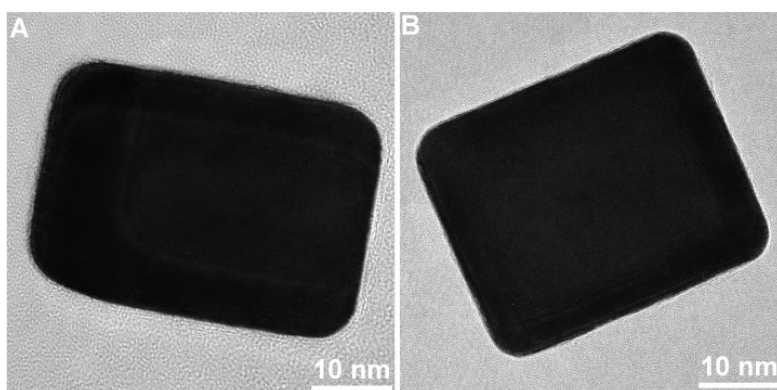


Figure S9. Representative TEM image of Au nanocubes at growth times: (A) 12 minute and (B) 48 hours. Shape/size comparison of many particles can be found in Figure 3C (12 min) and Figure 1B (48 hours), which is consistent with the single particle comparison here.

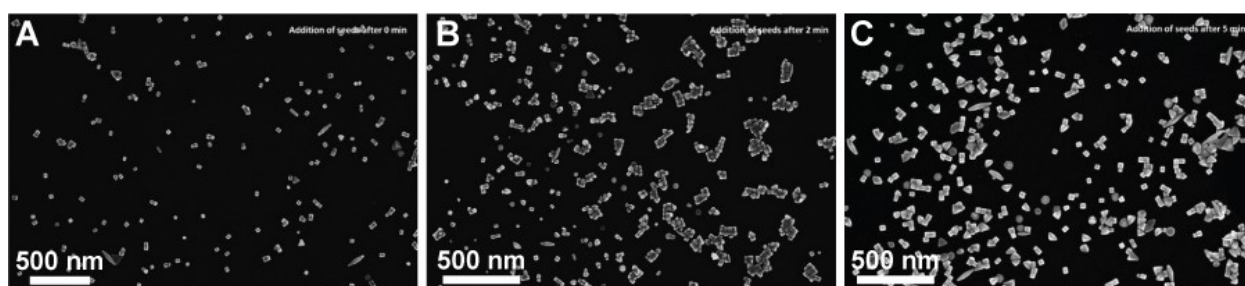


Figure S10. Scanning electron microscopy images of Cu^{2+} -assisted gold nanoparticles when adding seed solution into the growth solution at: (A) 0, (B) 2 and (C) 5 min after the addition of Cu additives.

Shape yield	0 min	2 min	5 min
Bars	85%	71%	64%
Other shapes	15%	29%	36%

Table S3. Statistical shape yield analysis of Cu^{2+} -assisted gold nanoparticles when adding seed solution into the growth solution at 0, 2, 5 min after the addition of Cu additives. In each group of synthesis, more than 700 nanoparticles were examined to determine the shape yield.

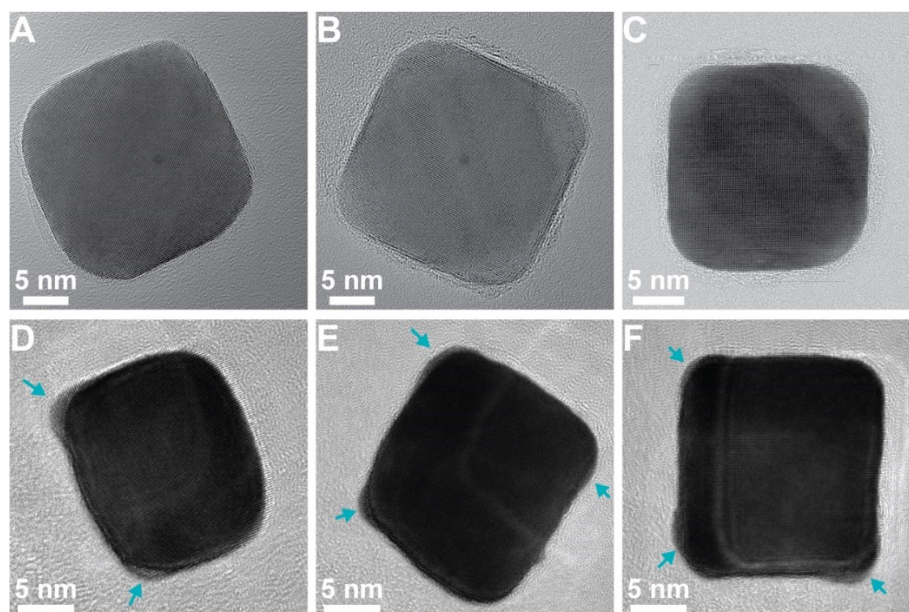


Figure S11. (A-C) TEM images of representative gold nanocubes synthesized in the absence of Cu^{2+} additives. It is sampled from the product at an early growth stage where the shape transition from quasi-spheres to cuboids occurs (1 min growth of seeds in the growth solution). It shows the transition size at 23-25 nm. (D-F) TEM images of representative gold nanocubes synthesized in Cu^{2+} additives under similar growth time of seeds in the growth solution (i.e. 1 min).

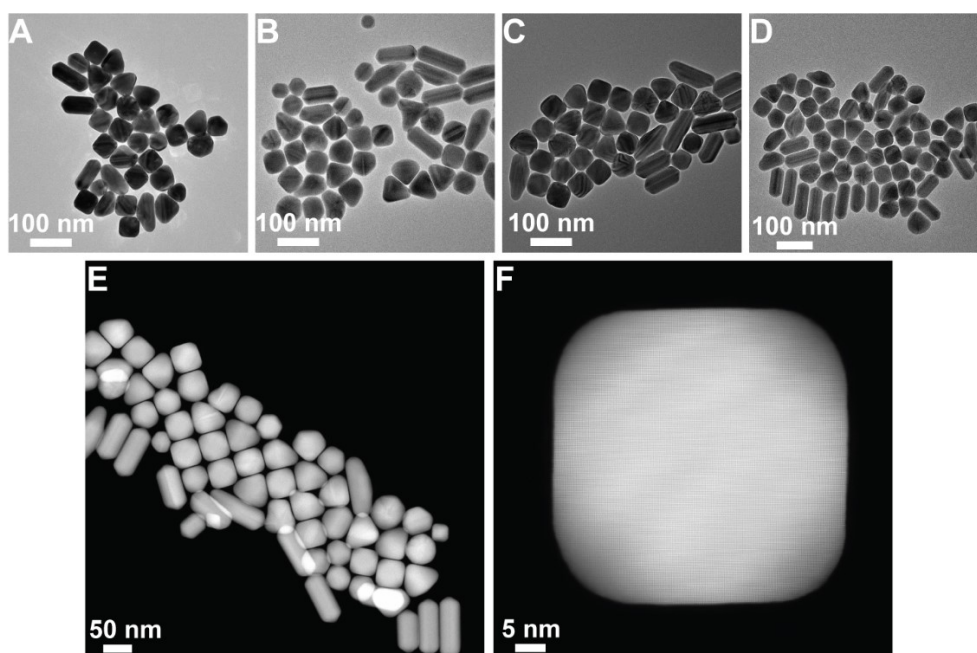


Figure S12. Gold nanocubes synthesized under identical conditions but in the absence of copper additives. (A-E) overview HAADF-STEM image (F) HAADF-STEM image of a $\langle 001 \rangle$ orientated gold nanocube.