Supplementary Information

Order-Disorder Phase Transitions in Au-Cu Nanocubes: From Nano-Thermodynamics to Synthesis

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Synthesis of gold-copper nanocubes.

Gold-copper nanocubes were first synthesized chemically by using a solvent-less protocol based on the thermolysis of gold and copper salts transferring the metal ions from the aqueous to the organic phase by using a low surface energy material, 1-dodecanethiol (DDT), as capping and stabilizing agent.* The gold-copper molar ratio was varied to obtain different chemical composition of the cubes by changing the volume of the metal precursor. Succinctly, for nanocubes with composition Au_3Cu, 10 μl of gold (III) chloride trihydrate $HAuCl_4$ (0.07 M) and 10 μl of copper (II) chloride $CuCl_2$ (0.028 M) aqueous solutions were mixed and heated into a 20 ml vial at 150°C to end up only with solid precursors, by dehydrating the solution. Once the solution was dried, 0.2 ml of DDT were added and the mixture was heated up again at 180°C for 2 h. By monitoring the color of the solution, the formation of the nanoparticles was indicated by the apparition of a dark-brown color. The vial was then removed from the heating source and cooled down naturally to room temperature. The produced nanocubes were dispersed in chloroform, purified by precipitation within ethanol and centrifuged at 3000 rpm to remove all the undesirable products. In order to obtain nanocubes with compositions close to the AuCu and $AuCu_3$, the same protocol was followed but increasing the Cu/Au initial molar ratio: 10 μl of $HAuCl_4$ (0.040 M) and 10 μl $CuCl_2$ (0.060 M); and 10 μl of gold (III) $HAuCl_4$ (0.025 M) and 10 μl of $CuCl_2$ (0.080 M) aqueous solutions, respectively. Finally, the gold-copper particles were re-dispersed in chloroform for their subsequent characterization by advanced electron microscopy techniques.

Characterization.

Transmission electron microscopy (TEM) images and nano-beam diffraction patterns were acquired in a JEOL 2010F microscope operating at 200 keV. X-Ray Diffraction measurements were acquired in a Rigaku Ultima IV diffractometer, with Cu Kα radiation. Scanning transmission electron microscopy (STEM) in high angle annular dark field (HAADF) imaging mode were carried out in a JEOL ARM200F aberration-corrected microscope operating at 200 keV and equipped with an energy dispersive spectroscopy (EDS) EDAX Apollo detector.

References

* Larsen, T. H., Sigman, M., Ghezelbash, A., Doty, R. C. & Korgel, B. A. Solventless synthesis of copper sulfide nanorods by thermolysis of a single source thiolate-derived precursor. *J Am Chem Soc* **125**, 5638-5639, (2003).

Figures

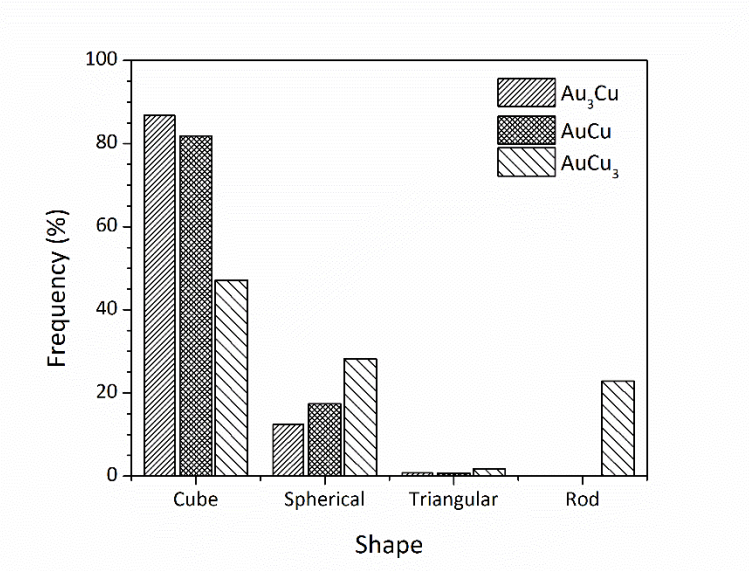

Figure S1. Shape histogram of the nanoparticles synthesized with three different compositions.

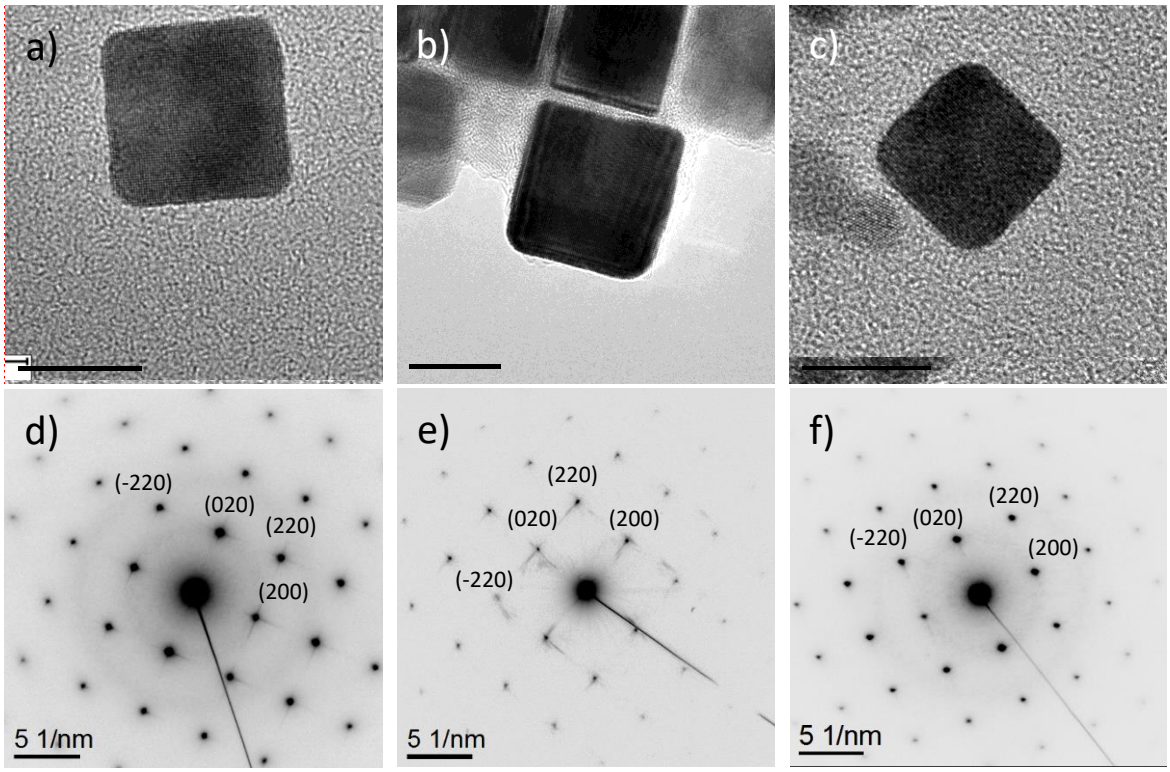

Figure S2. TEM images and nano-beam electron diffraction of the as-synthesized nanocubes showing the typical of the disordered phase of the Au-Cu alloy. The diffraction patterns were indexed as fcc phase viewed along the [001] direction.

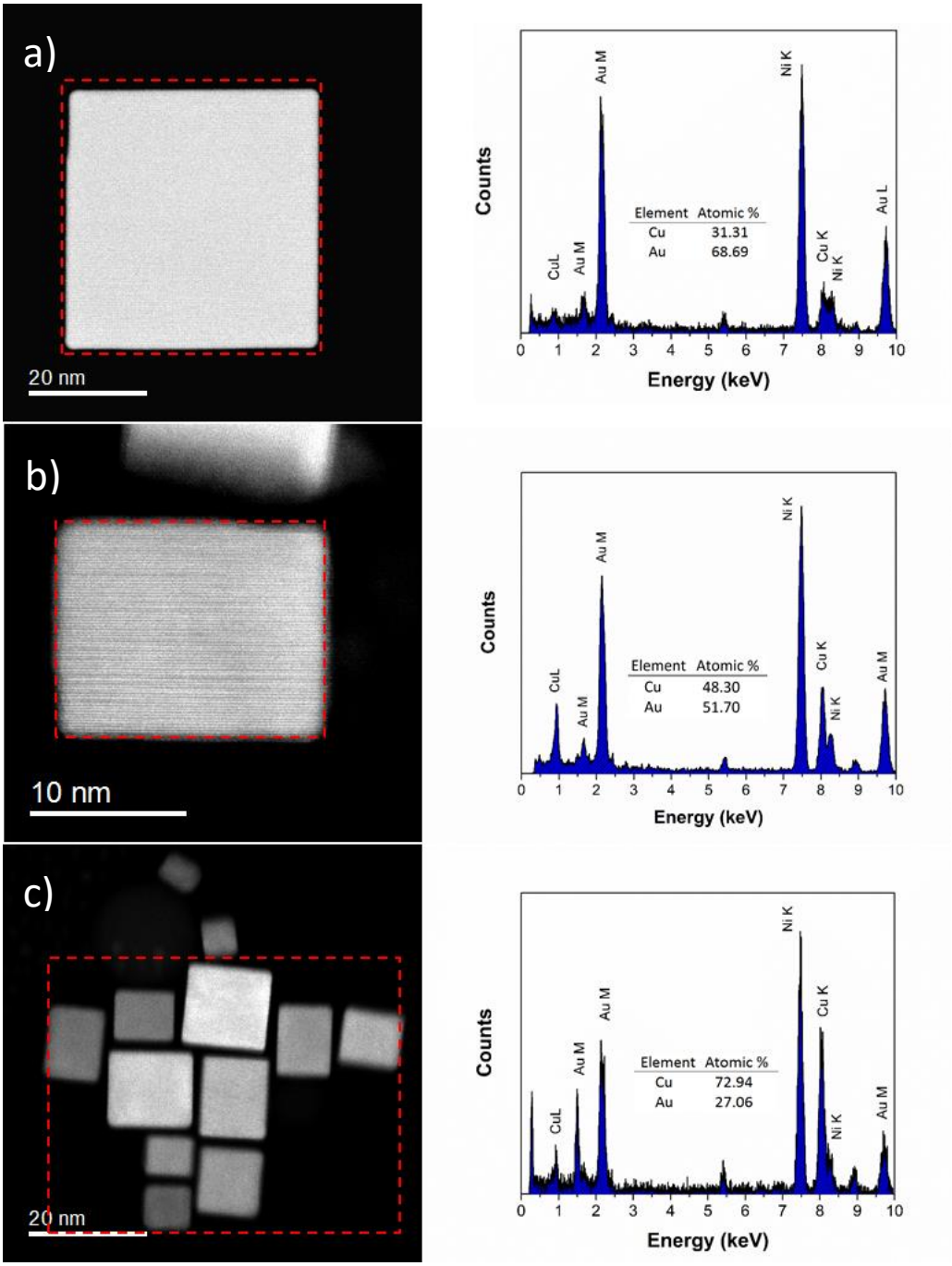

Figure S3. STEM images and EDS spectra of the produced disordered-phase nanocubes near to the composition (a) Au_3Cu, (b) AuCu, and (c) $AuCu_3$.

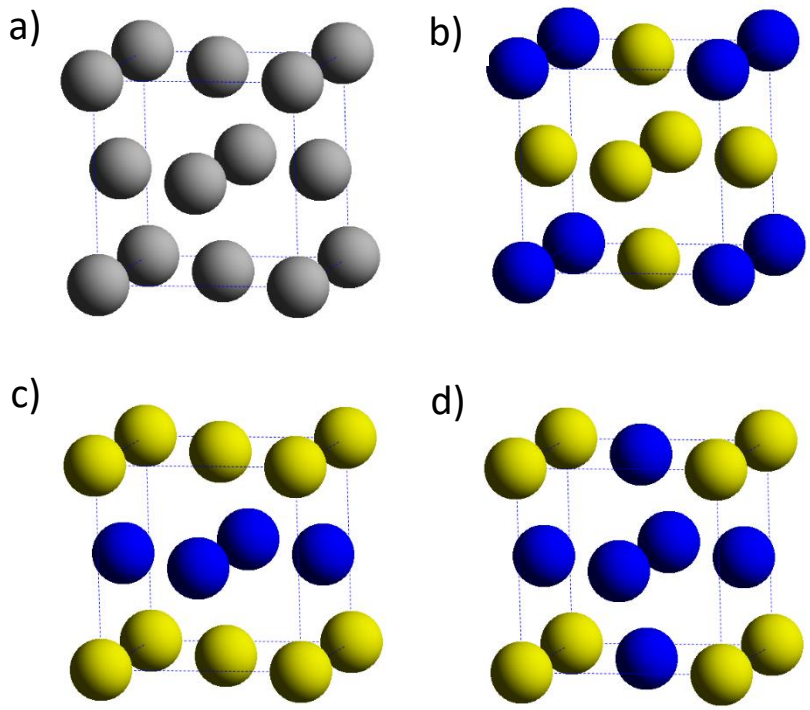

Figure S4. Atomistic models of the structural arrangement of the different gold-copper alloys. (a) Disordered Au_xCu_{1-x} alloy. Gold and copper atoms are randomly accommodate in a face-centered cubic cell. Ordered (b) Au_3Cu, (c) AuCu, and (d) $AuCu_3$ alloys. Gold and copper atoms (yellow and blue, receptively) accommodate in specific positions of the cell giving rise to a layered arrangement.

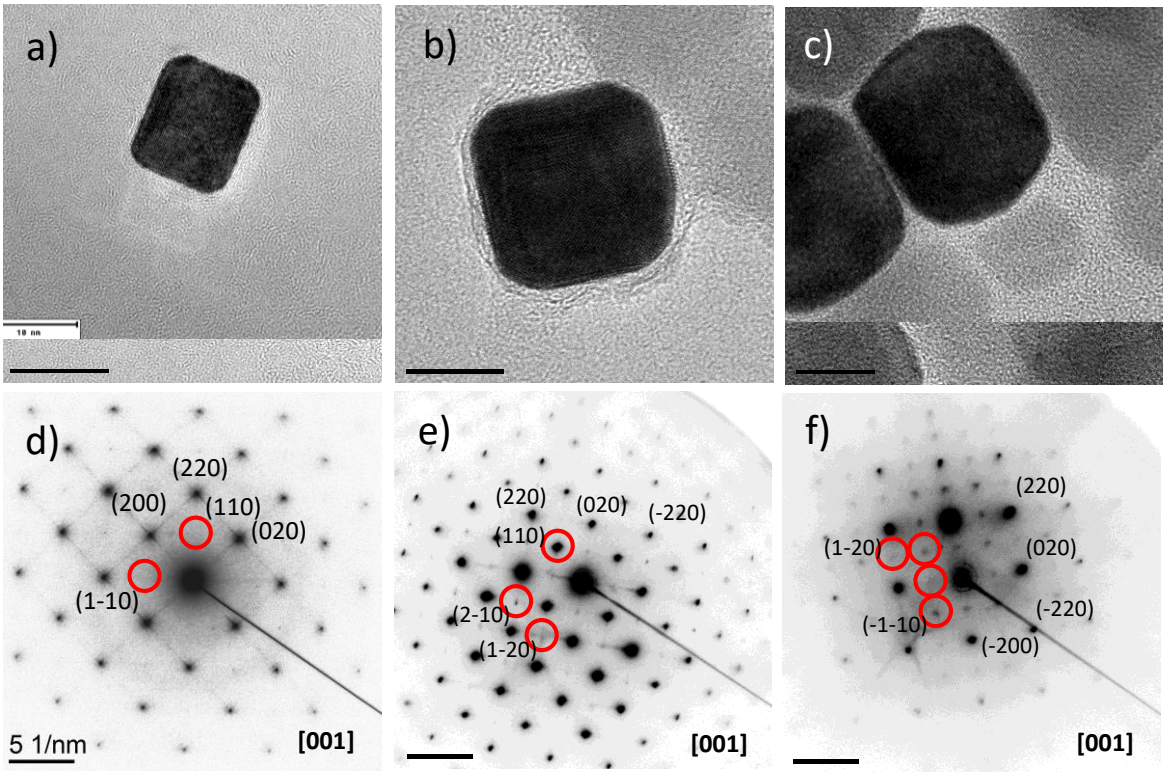

Figure S5. TEM images and nano-diffraction patterns of single nanocubes showing ordered structure (highlighted by red circles indicating superlattice reflections) after heating treatment. (a,d) Au_{rich}-Cu cubes heated at 120°C; (b,e) Au-Cu cubes heated at 300°C; and (c,f) Au-Cu_{rich} cubes heated at 270°C. All particles were aligned parallel to the [001] axis zone for an suitable comparison.

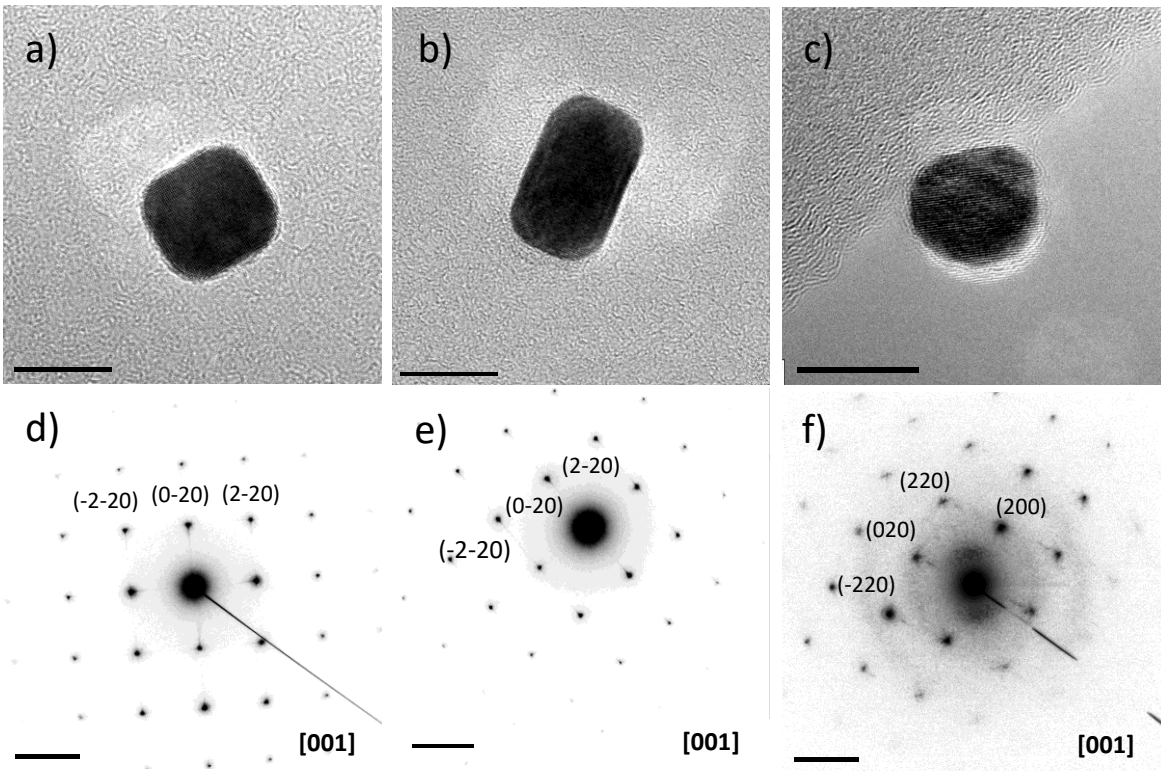

Figure S6. TEM images and nano-diffraction patterns of single nanocubes showing disordered structure after heating treatment. (a,d) Au_{rich}-Cu cubes heated at 200°C; (b,e) Au-Cu cubes heated at 200°C; and (c,f) Au-Cu_{rich} cubes heated at 350°C. All particles were aligned parallel to the [001] axis zone for an suitable comparison.

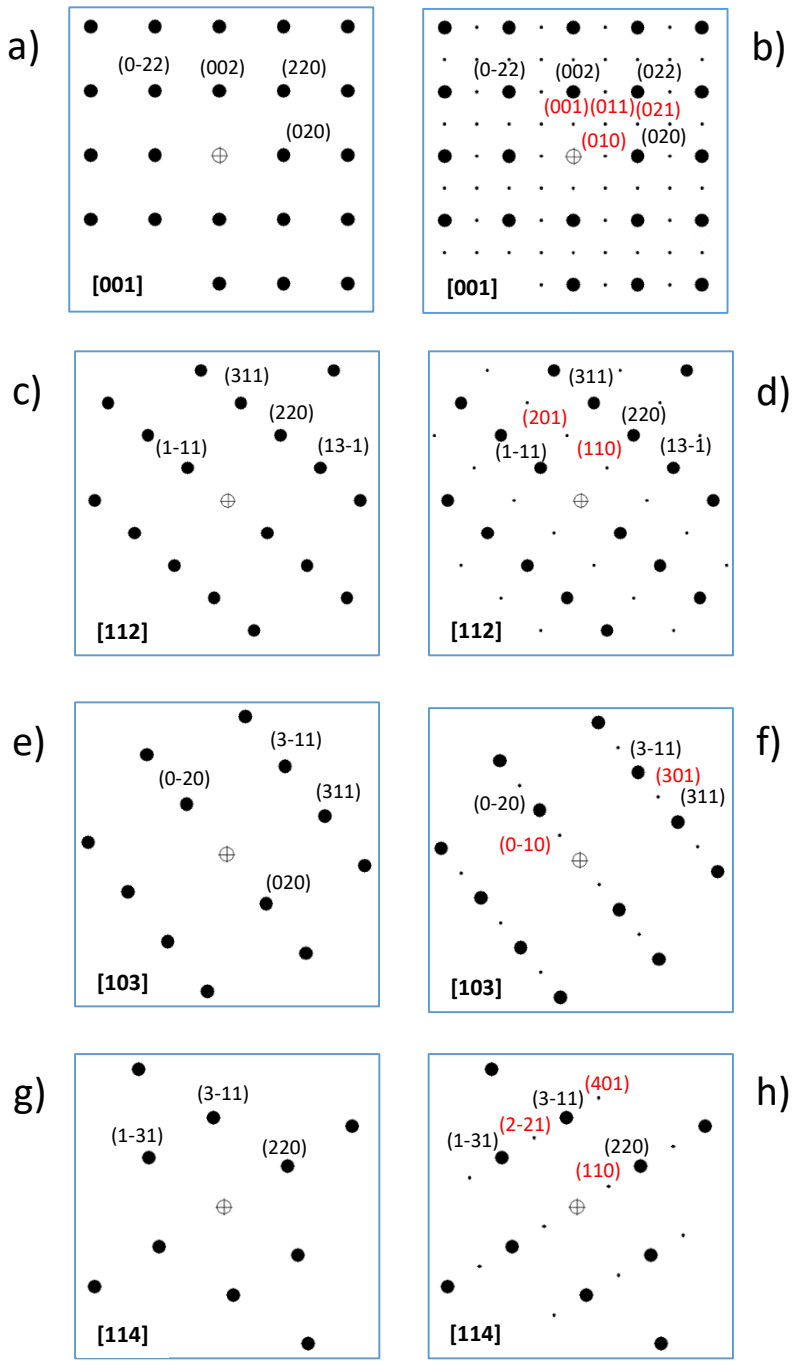

Figure S7. Sketched comparison between electron diffraction patterns of disordered fcc (a,c,e,g) and ordered $L1_2$ (b,d,f,h) structures viewed at different axis zones. The superlattice reflections are labeled in red color.

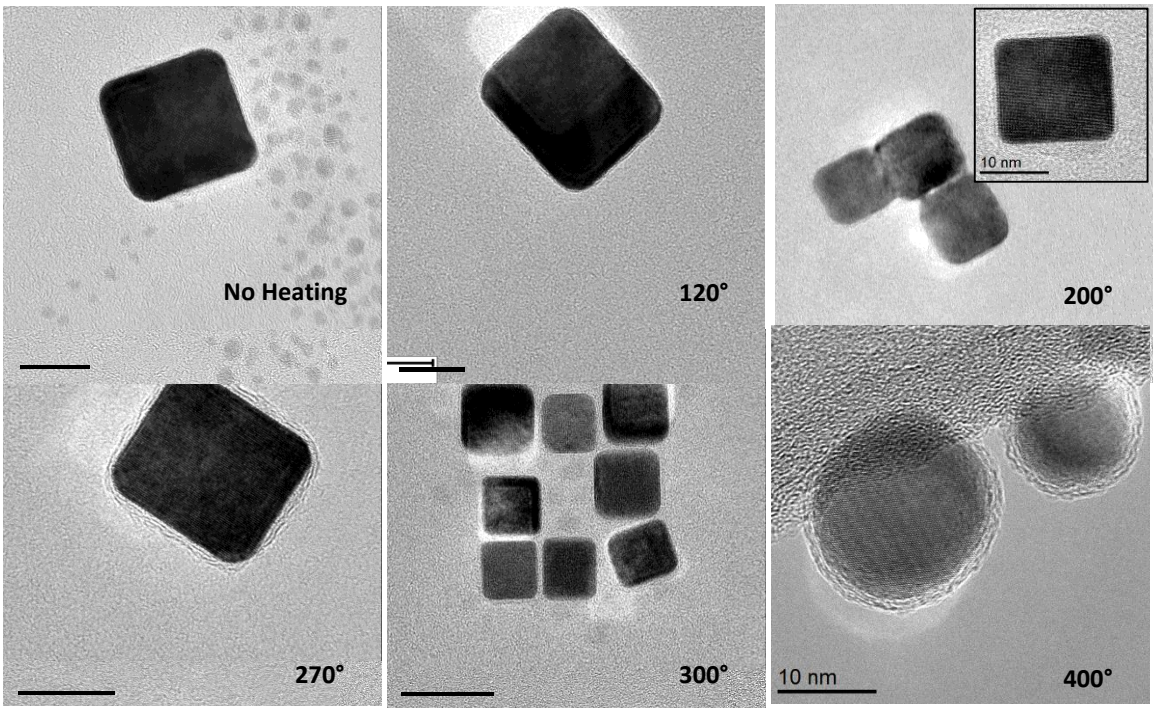

Figure S8. TEM images of the shape evolution of the synthesized Au_{rich}-Cu nanocubes after heating treatment at different temperatures. It can be observed that the cubic shape is maintained above 300°C. At 400°C a drastic change from cubes to spherical particles occurred.