Supplementary information

Cu segregation in Au-Cu nanoparticles exposed to hydrogen atmospheric pressure: how is fcc symmetry maintained?

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Au-Cu NP under Ar showing facetted shape

Indexed STEM-BF image of Au-Cu NP under Ar show {100} and {111} facets.

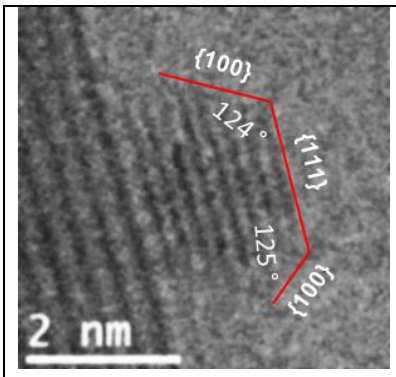

Figure S1|. Faceted nanoparticle shape under Ar at 400 °C revealed by manual adjustment of the brightness and contrast of the raw STEM BF in figure 2B.a using Digital Micrograph software. Indexing of the edge-on facets by angle measurement on the projected image shows that the particle shape is bound mainly by (100) and (111) facets.

AIMD simulation of TOh_Au_{201} at 500K:

In order to check the effect of the applied temperature on the shape and the symmetry of Au NPs, AIMD simulation was performed on bar TOh_Au_{201} at 500K for t=20 ps. In **Figure S2 (A) and S2 (B)**. the radial distribution functions between Au-Au pairs and the probability distribution functions of the Au atoms relative to the center of mass are presented, respectively. The figures compare the initial TOh_Au_{201} structure calculated from DFT (red line) and the final structure obtained after AIMD simulation of 20 ps (blue line). The results show a maintained radial distribution during time simulation with a first neighbor peaks of “Au-Au” distance, located at 2.85 Å. Besides, it can be seen from the distribution function that fcc structure remain preserved within the simulation time span as manifested by the 3 groups of well-defined fcc-signature peaks (**Figure S2 B**). These peaks correspond to the distances of the atoms in the fcc core (located at 2.9 Å), the inner-shell of NP (located at 3.9 ~ 6.5 Å) and the outer-shell (located at 7.2 ~ 9 Å). Thus, despite a few slightly scattered distributions, the peaks remain restrained to their corresponding centers at 500 K confirming the absence of temperature effect.

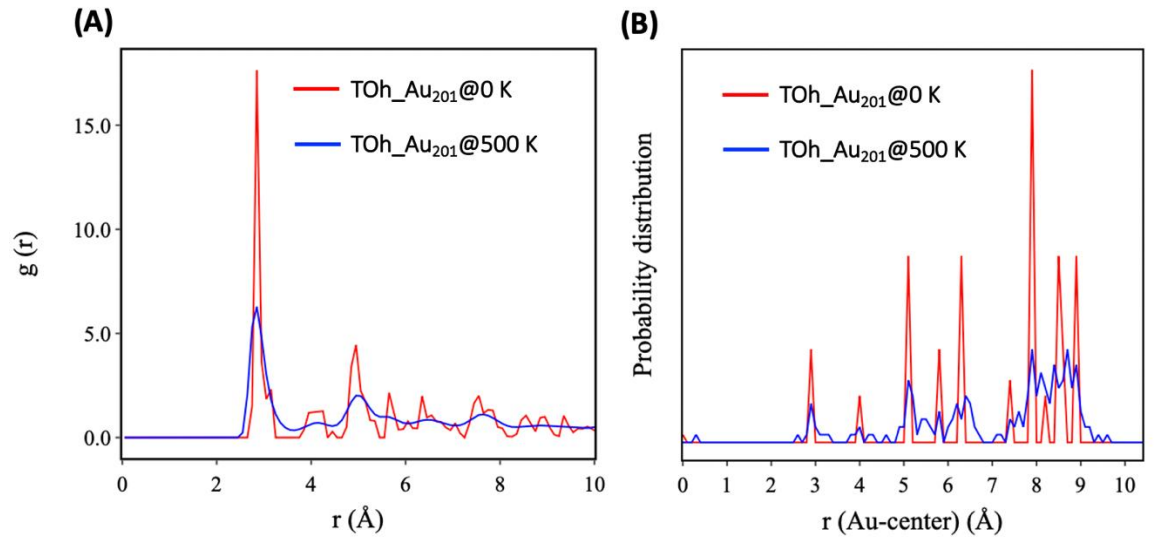

Figure S2|. *Ab-initio* molecular dynamics (AIMD) simulations of TOh_Au_{201} (under vacuum) at 500 K. (A) Radial distribution functions of initial TOh_Au_{201} structure (red line) and the final structure (blue line) between Au-Au pairs. (B) The probability distribution functions of the Au atoms relative to the center of mass between the initial structure (red line), and the final structure (blue line).

Hydrogen adsorption energies on TOh_Au_{201} and TOh_Au_{101}-Cu_{100} model NPs

Table S1|. Calculated adsorption energies of hydrogen atoms on the modeled bare (TOh_Au_{201}) gold and (TOh_$Au_{101}Cu_{100}$) and gold copper NPs.

Configuration	Eads (eV/H atom)
TOh_Au_{201} model NPs	0.08

TOh_$Au_{101}Cu_{100}$ model NPs	
conf1-H	-0.21
conf2-H	0.03
conf3-H	0.015
conf4-H	0.042
conf5-H	0.107
conf6-H	0.010

Video S1: AIMD simulation at 500K of Au-Cu NP (conf_7) in presence of 1ML adsorbed atomic hydrogen for time simulation of 20 ps. The Cu and Au atoms are represented by blue and yellow balls. The small white balls indicate adsorbed hydrogen atoms. For clarity, a Cu atom segregating from the subsurface towards the surface is colored in red while an Au atom segregating from the surface towards the subsurface is colored in green.

Video S2: AIMD simulation at 500K of Au-Cu NP (conf_7) in presence of 1ML adsorbed atomic hydrogen for time simulation of 20 ps. The Cu and Au atoms are represented by blue and yellow balls. The small white balls indicate adsorbed hydrogen atoms. For clarity, Cu atoms forming one H-Cu-H-Cu chain are colored in red.