

## Supporting Information

### **Revealing Size Dependent Structural Transitions in Supported Gold Nanoparticles in Hydrogen at Atmospheric Pressure**

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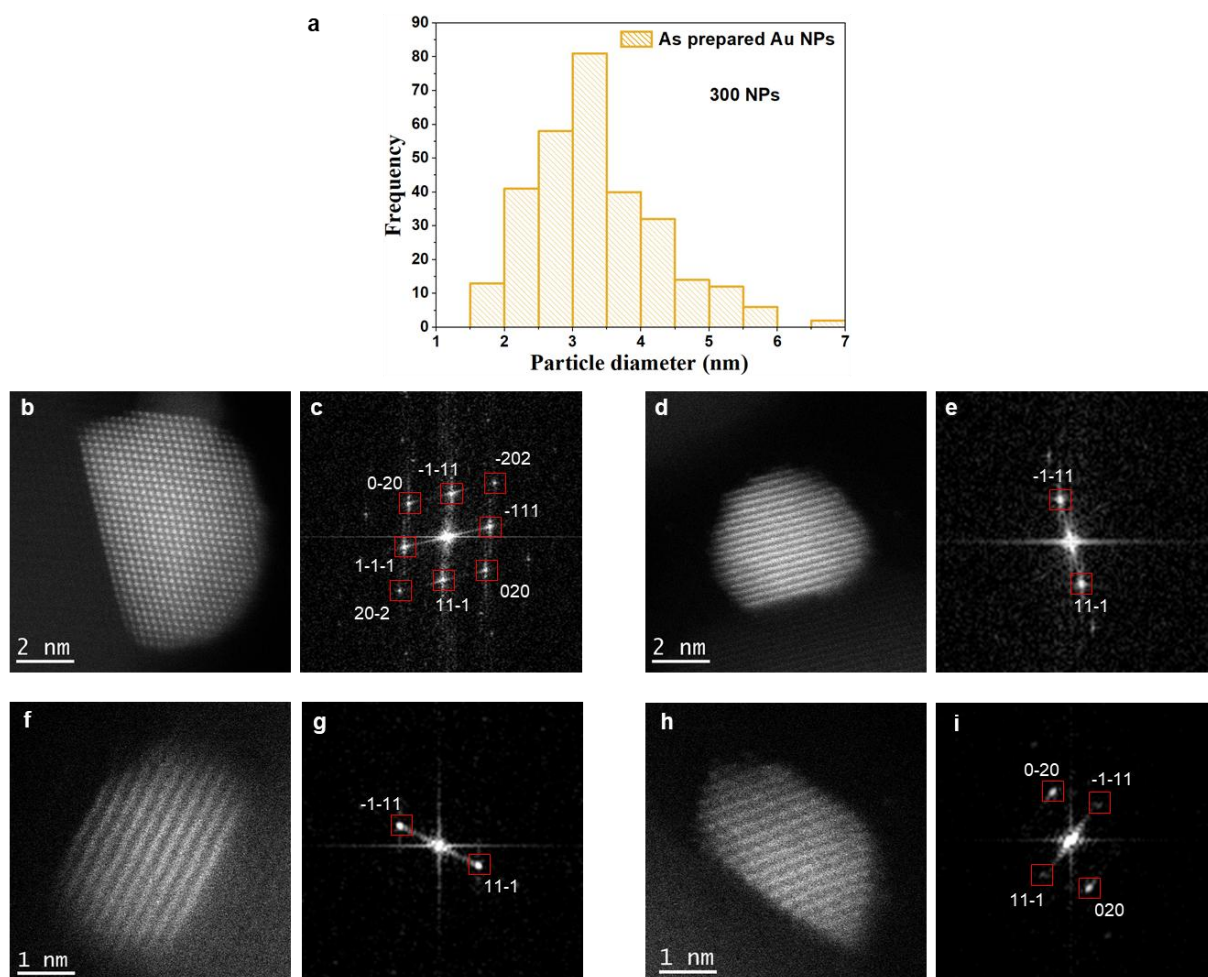
#### **I. Supporting Figures S1 – S6**

##### **Figure S1. Size distribution and crystalline structure of the as-prepared Au NP**

Particle size distribution was obtained by measuring the diameter of 300 as-prepared Au NPs from their 2D projection in medium-magnification HAADF STEM images acquired under vacuum. For TEM imaging, the as-prepared sample was first dispersed in deionized water by sonication. Then, the suspension of nanoparticles was drop-casted (7 drops of 3 µl) onto a

standard TEM copper grid. As the NPs are non-spherical, particle diameter was estimated by measuring the particle extension along two perpendicular directions in projection and taking the mean value. All size measurements were performed manually within Digital Micrograph™. Particle size varies between 1.5 and 7 nm (Figure S1a). The sizes of all particles presented in the present work refer to their corresponding mean diameters.

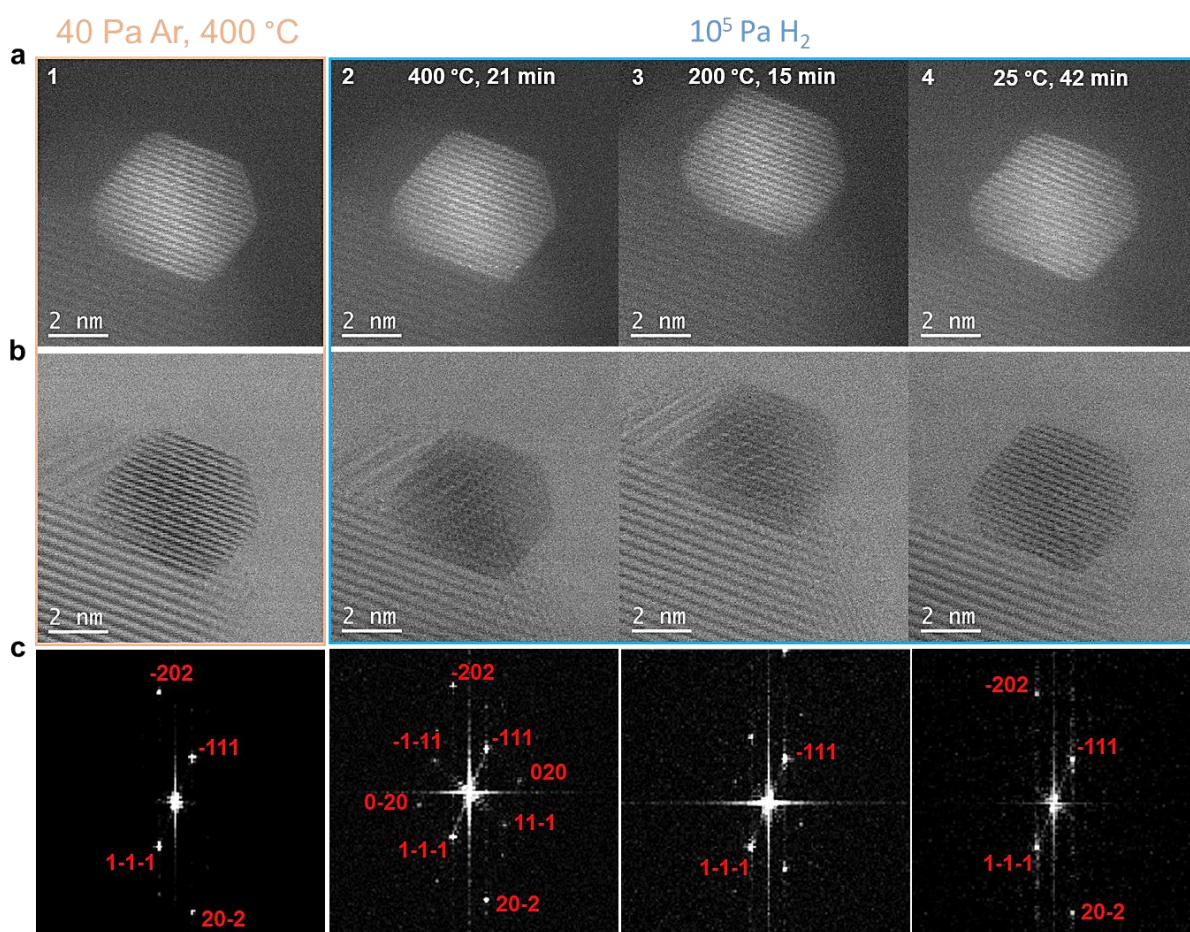
Furthermore, indexation of the fast Fourier transforms (FFT) of atomic scale HAADF STEM images of the as-prepared Au NPs shows that they mostly have fcc atomic packing (Figure S1b-i).



**Figure S1.** Size and structure of the as-prepared gold nanoparticles. a) Particle size in the as-prepared sample. b,d,f,h) Atomically-resolved HAADF STEM images of four Au NPs. c,e,g,i) Indexation of the fast Fourier transforms of the HAADF STEM images.

**Figure S2. Full series of *in situ* STEM images of the ~4.5 nm Au NP in Figure 1a**

The sets of HAADF and BF STEM images presented in (Figure S2a, b) were acquired in parallel. The structure and stability of the particle during hydrogenation was inferred from the indexation of the FFTs of the HAADF STEM images (Figure S2c). In all images, the NP is viewed close to the [101] direction of the fcc structure. Following 21 minutes of hydrogenation at 400 °C, the NP retains its initial fcc structure, truncated octahedral shape and orientation with respect to the support. As the hydrogenation temperature is lowered to 25 °C, no further structural evolution is observed.

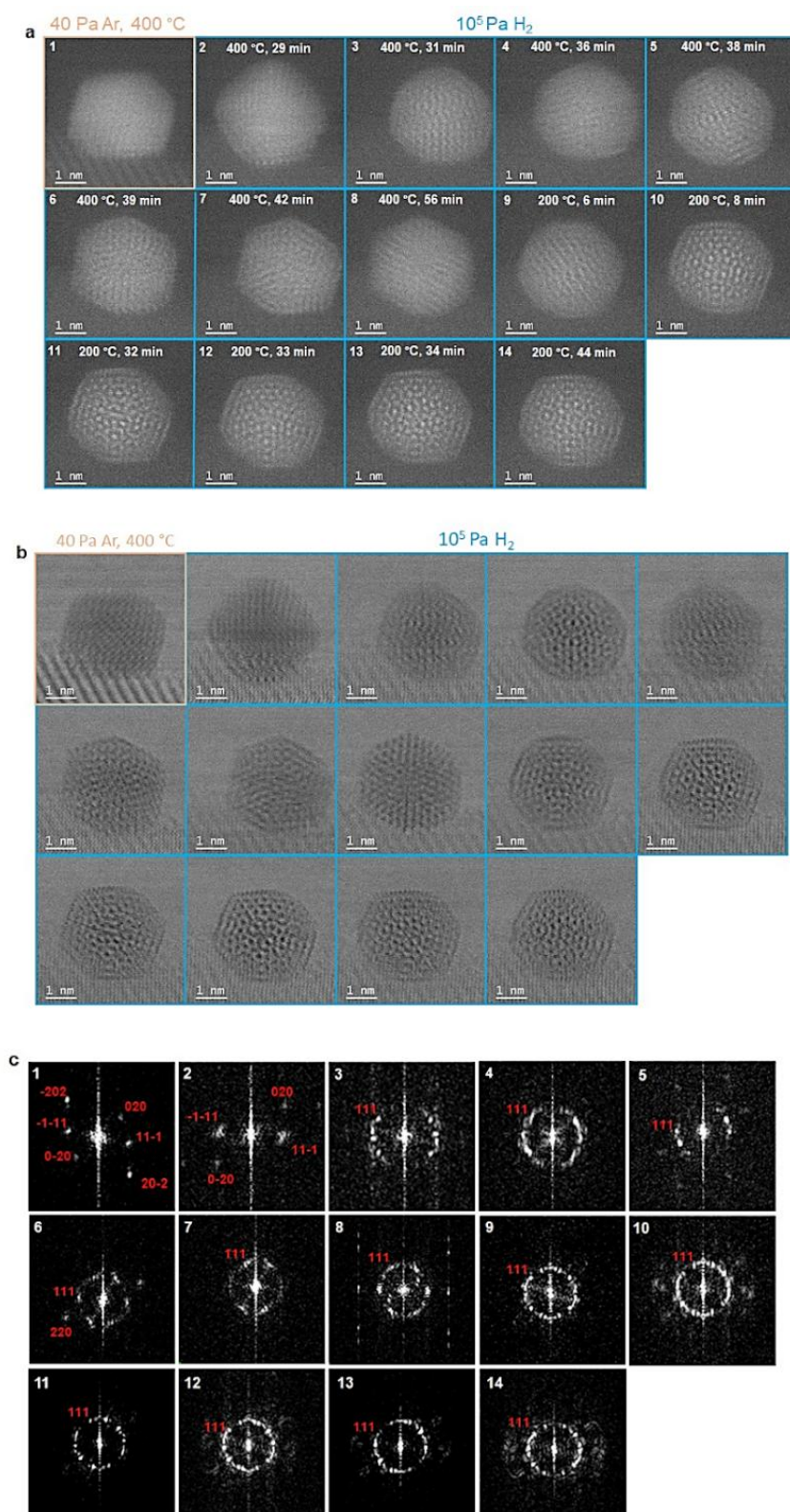


**Figure S2.** Evidence of the structural stability of ~4.5 nm Au NP during H<sub>2</sub> exposure. a) Experimentally HAADF-STEM images captured at 400, 200 and 25 °C. b) Experimental BF-STEM images capture. c) Indexation of the FFTs of the HAADF STEM images showing stable fcc structure.

**Figure S3. Full series of STEM images of the ~3 nm Au NP in Figure 1b**

In contrast with the high structural stability of the previous particle, the crystal structure of this 1 NP drastically evolved as  $10^5$  Pa hydrogen in static condition is introduced in the gas nanoreactor at 400 °C (Figure S3). Analysis of the STEM HAADF and BF contrasts and corresponding FFTs shows the stabilization of a gold icosahedron under hydrogen. The NP continuously rotate on the anatase support at 400 °C. For instance, following 38 minutes of hydrogenation at 400 °C, all experimental data are consistent with an icosahedron oriented along one of its two-fold symmetry axes. This rotation is nearly suppressed once the temperature is reduced to 200 °C. At the latter, the icosahedron is stabilized closed to one of its five-fold symmetry axis with indexation of the FFTs of the BF STEM images indicating that the icosahedral packing of atoms is slightly distorted.



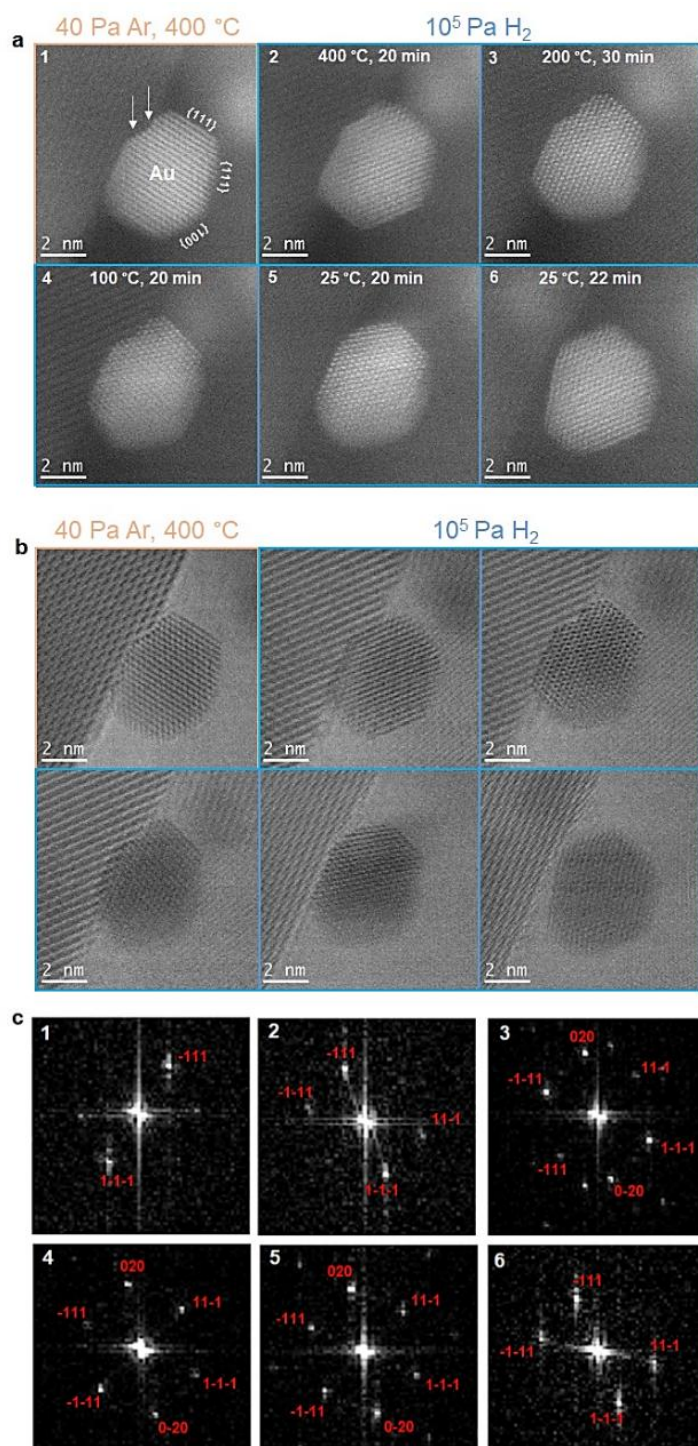


**Figure S3.** Evidence of a structural evolution of ~3 nm Au NP during H<sub>2</sub> exposure. a) Experimental HAADF STEM images captured at 400 and 200 °C. b) Corresponding experimental BF STEM images captured in parallel. c) Indexation of the fast Fourier transforms of the BF STEM images clearly shows the change in particle structure under H<sub>2</sub> with loss of the initial fcc structure.

**Figure S4.** In situ STEM monitoring of a second Au NP beyond 4 nm

It should be noted that Au NPs beyond 4 nm are not all unreactive towards H<sub>2</sub> exposure as exemplified in Figure S4 where *in situ* STEM images of a ~4.8 nm Au NP reveal a continuous

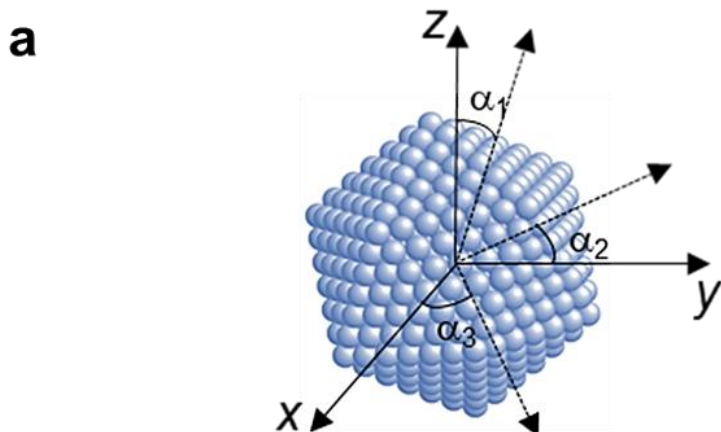
restructuration of the particle surface during cooling. Surface restructuration is initiated here probably because the Au facets, being initially atomically rougher than in the Au NP of Figure 1a, exhibit higher number of low-coordinated Au sites that can bind hydrogen molecules. However, as in Figure 1a, we observe no change in the NP core crystalline structure during surface restructuration, i.e., it remains fcc.



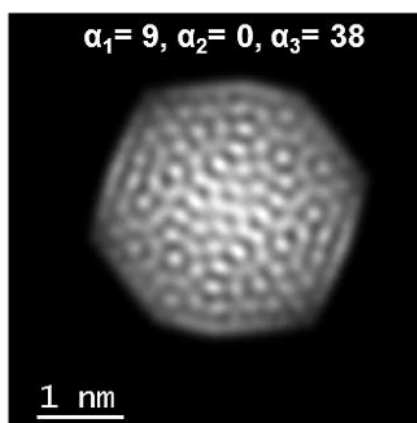
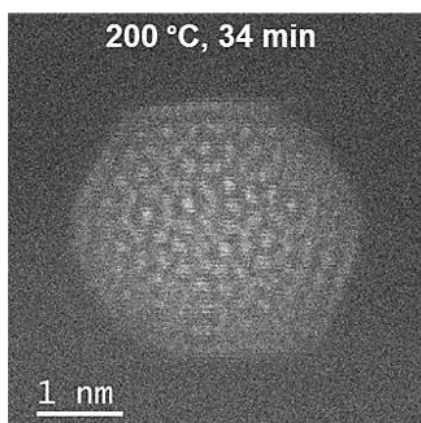
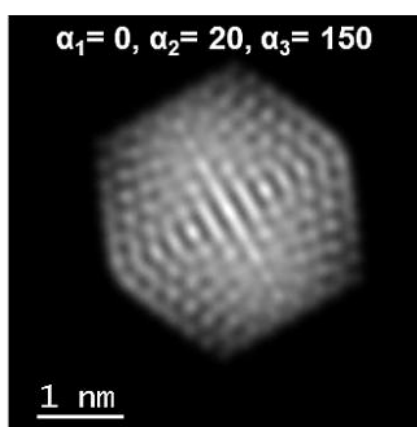
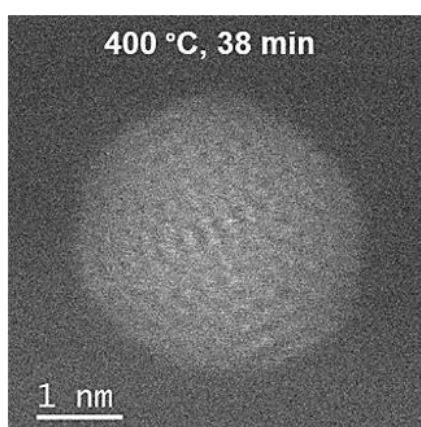
**Figure S4.** Confirmation of the structural stability of small Au NP (4.8 nm) during H<sub>2</sub> exposure. a) Experimental HAADF-STEM images of a 4.8 nm Au NP captured at 400, 200, 100 and 25 °C. b) Experimental BF-STEM images captured in parallel. c) Indexation of the fast Fourier transforms of the HAADF STEM images shows again the preservation of fcc structure as hydrogenation proceeds to 25 °C. Again, the fcc NP is always close to its [101] zone axis (FFT in c).

**Figure S5. Kinematic HAADF STEM monitoring of a 931-atom icosahedron in vacuum**

In these simulations, the electron beam is incident along the Z direction (Figure S5). The particle can be tilted in any direction with respect to the incoming electrons via azimuthal and polar angles  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  (Figure S5a). STEM simulations along the two- and five-fold symmetry axes of the icosahedron shows that the experimentally-observed STEM contrasts under  $H_2$  in Figure 1b are consistent with an icosahedral structure viewed along different directions during *in situ* observations (Figure S5b).



**b** Experimental image      STEM simulation



**Figure S5.** Evidence of a fcc to icosahedron transition in Fig. S3. a) Geometry of STEM simulation. The electron beam is incident along the Z direction and the particle can be tilted in any direction with respect to the incoming electrons via angles  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$ . b) Comparison of experimental HAADF-STEM images captured at 400 and 200 °C in  $10^5$  Pa  $H_2$  of the supported Au NP in Fig. 1b and of the kinematic STEM simulations of  $Au_{931}$  icosahedron in vacuum viewed close to its 2-fold (top) and a five-fold (bottom) axes.

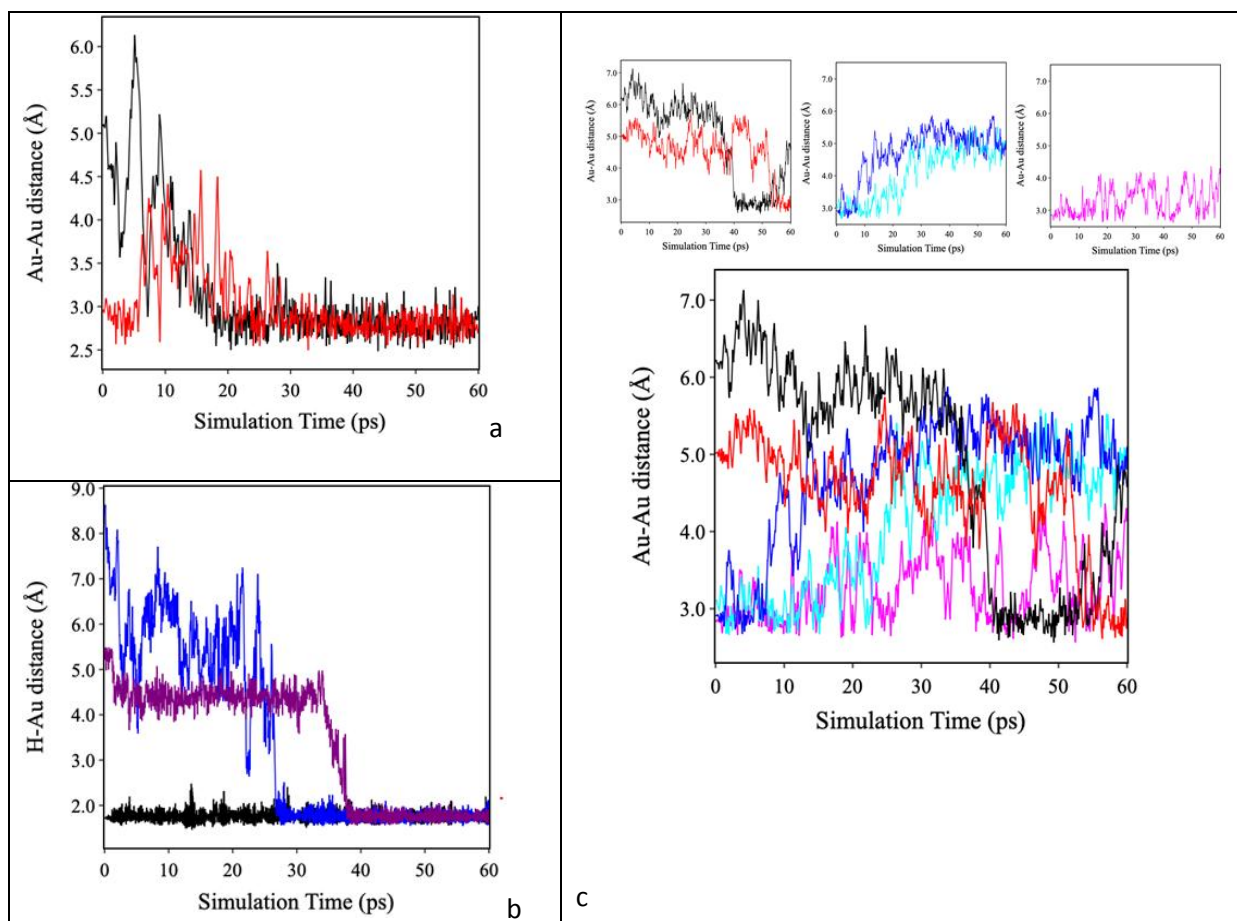
**Figure S6. Dynamic behavior of individual atoms during the simulation time of**

**T0h\_Au<sub>201</sub>H<sub>122</sub> at 500 K**

In order to examine the strong fluctuation of gold NP during simulation time span, the evolution of bond distances of chosen Au-Au and Au-H pair atoms are followed. In Figure S6a, the bond distance  $d_{Au-Au}$  between two pairs of Au atoms (red and black curves) chosen



from the crowned structure (the outer shell surface) are reported. This figure shows bond formation ( $d_{\text{Au-Au}} < 3 \text{ \AA}$ ) and bond breaking ( $d_{\text{Au-Au}} > 3 \text{ \AA}$ ) occurring during equilibration time. After 20-ps simulation, the  $d_{\text{Au-Au}}$  stabilizes at  $2.80 \text{ \AA}$  (bond retention). The Figure S6b, shows the evolutions of Au-H bond distances of three chosen Au-H pair atoms. This Figure evidences the strong mobility of some hydrogen atoms (pink and blue curves). After 40 ps time span simulation, the  $d_{\text{Au-H}}$  bonds remain maintained at  $1.77 \text{ \AA}$ . Figure S6c shows the evolution of  $d_{\text{Au-Au}}$  bonds of five chosen Au pair atoms from the core, i.e. from the inner shell and the center of the simulated gold NP. The Figure evidences the strong and continuous fluctuation of these pairs during the whole simulation time.



**Figure S6.** Breaking and formation of bonds in gold NP. The plots show the time evolution of the distances between several couples of bonded atoms: a) Au-Au and b) Au-H from the crown lines formed at the surface and c) Au-Au from the core (the inner-shell and the center atoms). The pair atoms were chosen to show examples of bond breaking, bond formation and bond retention during dynamic simulation of  $\text{TOh\_Au}_{201}\text{H}_{122}$  at 500K.

## II. Supporting Video Captions S1-S2

**Video S1.** *In situ* STEM video recording of the fluctuating structure of the gold NP in **Figure 1c** during exposure to hydrogen.

Note that, in contrast with the Au NPs in figure 1a (fcc structure - 4.5 nm size) and 1b (icosahedral-like structure - 3 nm size) which were relatively stable on the titania support under hydrogen at 200°C, the morphology and structure of the non-fcc Au NPs shown in figure 1c was found to continuously evolve with high dynamics in similar gas conditions. As it can be seen in video (S1), this imaged NP is highly mobile that it was impossible to obtain the atomic resolution at 200 °C. When the temperature was reduced to 175 °C, we were able to slow down the dynamics of the transformations enough to resolve from time to time the continues evolving structure and morphology. In addition, this particle is designated as a “non-fcc structure with unidentified symmetry” based on the analysis of both orientation and spacing of the fringe contrasts visible in its HAADF images. During the follow-up of the nanoparticle, none of the identified atomically-resolved structures of the particle were compatible with a long-range face-centered cubic lattice symmetry. Instead, the nanoparticle present short-range order with strong variations in both orientation and spacing (from 2.2 Å to 2.8 Å instead of 2.35Å of the Au(111) lattice) of the observed fringes within individual snapshots and between structural isomers.

**Video S2.** MD simulation of TOh\_Au<sub>201</sub>H<sub>122</sub> at 500K over 60 ps.