Long-range chemical orders in Au-Pd nanoparticles revealed by aberration-corrected electron microscopy†

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Supplementary materials

Unit cells and crystallographic aspects of fcc, $L1_0$ and $L1_2$ structures

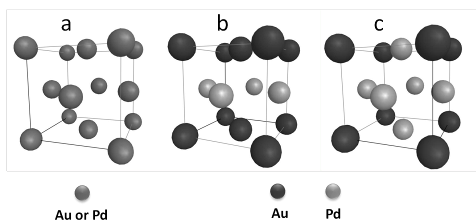

Fig. 1S : Unit cells of (a) disordered face-centered cubic, (b) $L1_0$ tetragonal and (c)$L1_2$ cubic structures

The space groups of face-centered cubic, $L1_2$ and $L1_0$ structures are $Fm\bar{3}m$, $Pm\bar{3}m$ and P4/mmm respectively.

Analysis of composition at single particles level using STEM-EDS

Fig. 2S shows a dark-field image of an assembly of Au-Pd NPs. In inset, the STEM-EDS spectrum from the NP marked 007 is shown. As explained in the main text, the beam is scanned over a rectangular region of the nanoparticle during X-ray counting. This limits electron beam damage and ensures precise determination of the particle composition. The region of NP 007 probed by the electron beam is indicated by a thick black line.

Errors in STEM-EDS measurements has been evaluated by statistical analysis of the EDS spectrum of each single particle as follows. From Cliff-Lorimer equation, the atomic concentrations (C) of Au and Pd are related to the intensities (I) under the Au-$M_{\alpha,\beta}$ and Pd-$L_{\alpha,\beta}$ edges by

$$\frac{C_{Au}}{C_{Pd}} = k\frac{m_{Pd}}{m_{Au}}\frac{I_{Au}}{I_{Pd}} \tag{1}$$

where m_{Au} and m_{Pd} are the atomic masses of Au and Pd respectively. The Cliff-Lorimer factor K has been determined experimentally as described in the main text. Its value is 2.0 ± 0.2. The counting of X-rays obeys Poisson statistics. By approximating the Poisson distribution by Gaussian, the standard deviation of

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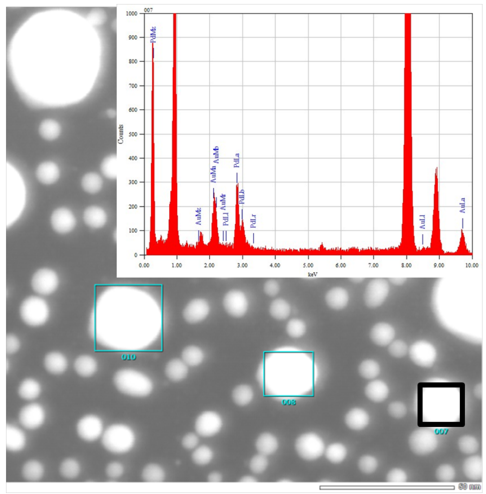

Fig. 2S : (a) A raw STEM-EDS spectrum and (b)the corresponding dark-field image acquired prior to spectrum acquisition.

I counts is equal to $\sqrt{I}$. With the errors on K and $I_{Au(Pd)}$ known, the error on C_{Au} can be calculated by standard error propagation method applied to the Cliff-Lorimer equation. In the present work, uncertainties on elemental composition were in the range 1-3 %.

Size distribution of the nanoparticles in sample B before high-temperature annealing

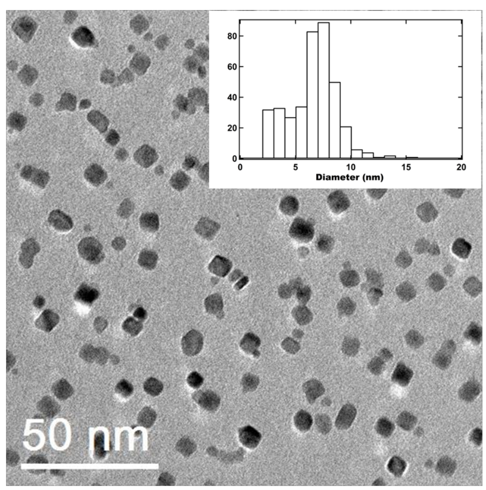

Fig. 3S: Bright-field image of sample B. The size histogram of the NPs is given in insert.

Fig. 3S shows a low magnification transmission electron microscopy (TEM) image of an assembly of carbon-supported as-grown nanoparticles (NPs)in sample B before annealing. The size distribution of the as-grown NPs is shown in inset and is built by analyzing the in-plane diameter of 383 NPs from TEM images similar to the one shown in Fig. 3S. The mean in-plane diameter is 6.5 ± 2.2 nm.