Supplementary Information

Direct atomic imaging and density functional theory study of the $Au_{24}Pd_1$ cluster catalyst

A. Bruma,[1] F. Negreiros,[2] S. Xie,[3,#] T. Tsukuda,[3,+] R. L. Johnston,[4] A. Fortunelli,[2,§] and Z. Y. Li[1,†]

[1] Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham, B152TT, UK

[2] CNR-IPCF, Istituto per i Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche, Via G. Moruzzi 1, 56124, Pisa, Italy

[3] Catalysis Research Center, Hokkaido University, Nishi 10, Kita 21, Sapporo 001-0021, Japan

[4] School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

Correspondence authors:

[§] alessandro.fortunelli@cnr.it

[†] z.li@bham.ac.uk

Present address:

[#] Department of Chemistry, Fudan University, 220 Handan Rd, Shanghai, 200433, China

[+] Department of Chemistry, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo, 113-0033, Japan.

S1. The effect of the electron beam irradiation of $Au_{24}Pd_1$ clusters

For high electron beam dose at 3.3×10^3 electrons/Å^2, the cluster has a high degree of fluctuation under the electron beam. Figure S1 (a) shows a series of images taken at this dosage. It is observed that the number of atoms present in the immediate vicinity of nanoclusters also increases, due to the momentum transfer between the finely-focused electron beam and the cluster. By plotting the relative HAADF-STEM intensity integrated over the cluster (excluding the single atoms nearby) as a function of image sequence number, it is observed that there is a gradual decrease of the intensity over 100 frames (acquired in 5 minutes). However, when the electron dose was halved at 1.66×10^3 electrons/Å^2, the cluster fluxionality is suppressed considerably, as seen from Figure S1 (b). It is also evident that the signal to noise ratio was reduced considerably, which make the atomic structure imaging a challenging task. All images analysed and presented in the main paper of this manuscript were taken at a beam current of 129 μA. They are all first-passing images.

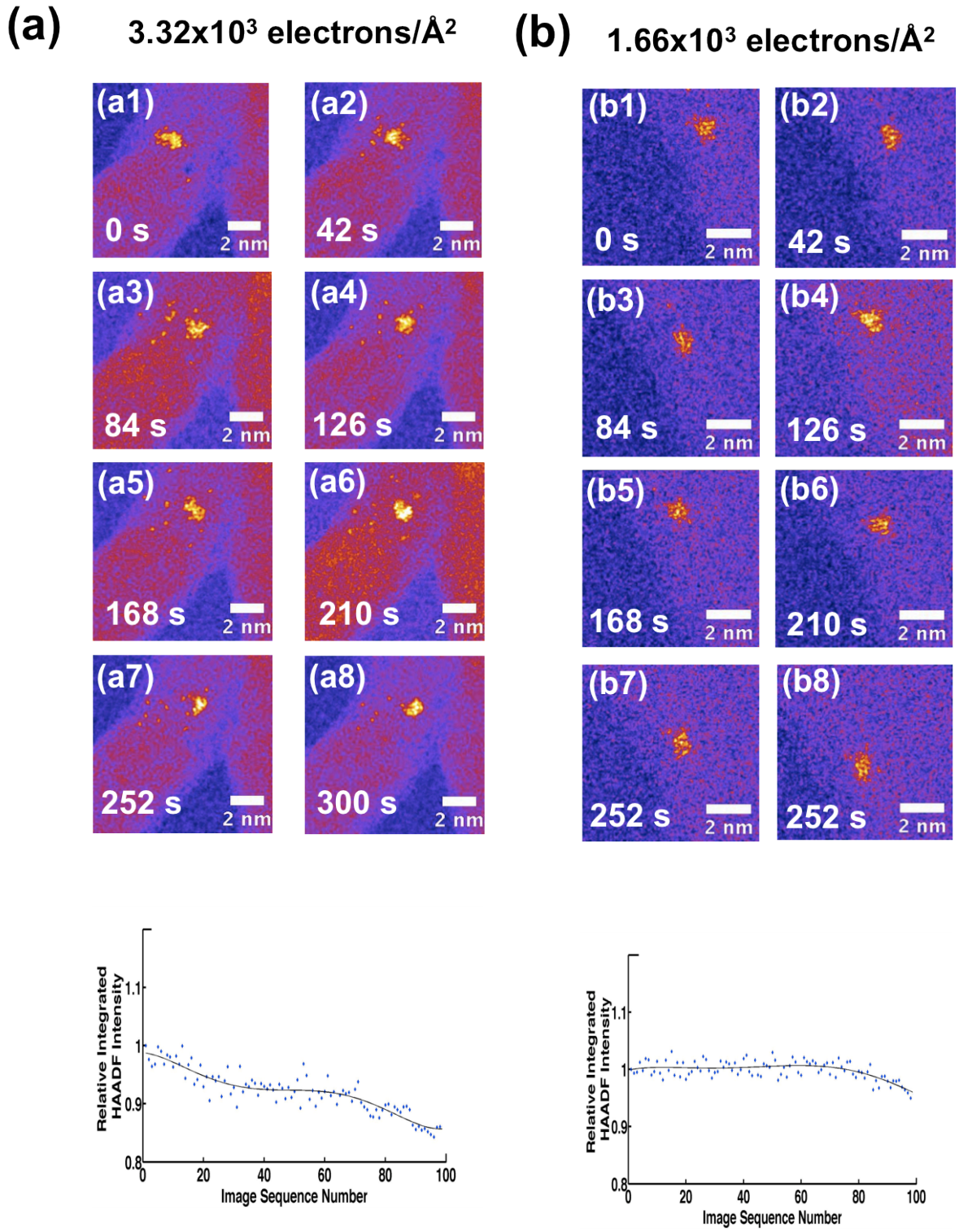

Figure S1. (a) Serial acquisition analysis for an electron dose of 3.32x10^3 electrons/Å^2; (b) Serial acquisition image for an electron dose of 1.66x10^3 electrons/Å^2. Also shown are the analyses of the variation of relative HAADF-STEM integrated Intensities as a function of image sequence number.

S2. Structural motifs calculated using the Gupta empirical potential.

Calculations have been made using the Birmingham Cluster Genetic Algorithm (BCGA) [1] coupled with Gupta empirical potentials to model the inter-atomic interactions. The three sets of parameters, DFT-fit, Exp-fit and Average are described in Ref. [2]. As seen in Figure S2, the isomers tend to have an elongated poly-icosahedron shape, where Au occupies shell positions and the Pd dopant occupies an off-centred, core position. All the isomers have two inner sites, a motif that has been predicted by the DF/BH algorithm (see main paper text) as being higher in energy than the putative global minimum clusters, underlying that the search for global minimum clusters needs for more-sophisticated, first principle calculations.

Finally, we stress that atomic charges are not experimental observables and depend on the charge decomposition scheme one is adopting. In the present case, the Löwdin projection onto occupied atomic orbitals which is implemented in the pwSCF code privileges an analysis of the inner atomic regions with respect to the inter-atomic metallic bond regions. These atomic regions however are of direct interest as they should be connected with theoretical descriptors such as the center of the d-band and experimental quantities such as XPS chemical shifts.

References:

[1] Johnston, R. L., *Dalton Trans.*, 4193 (2003).
[2] Ismail, R., Johnston, R. L., *Phys. Chem. Chem. Phys*, **12**, 8607 (2010).

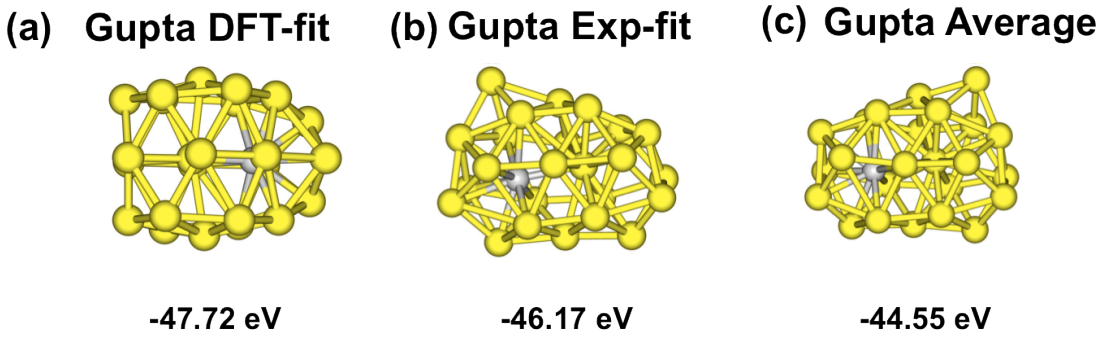

Figure S2. Three isomers found with the Gupta empirical potential with different parametrizations: (a) DFT-fit, (b) Exp-fit and (c) Average. The binding energies have been also included.