

## Supplementary material

### Size-dependent Hydrogen trapping in Palladium nanoparticles

Wang Liu<sup>1</sup>, Yann Magnin<sup>2,3</sup>, Daniel Förster<sup>4,5</sup>, Julie Bourgon<sup>1</sup>, Thomas Len<sup>6</sup>, Franck Morfin<sup>6</sup>, Laurent Piccolo<sup>6</sup>, Hakim Amara<sup>4,7\*</sup>, Claudia Zlotea<sup>1\*</sup>

<sup>1</sup>*Université Paris Est, Institut de Chimie et des Matériaux Paris-Est (UMR7182), CNRS, UPEC, 2-8 rue Henri Dunant, 94320 Thiais, France*

<sup>2</sup>*Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

<sup>3</sup>*Consultant, Total@Saclay NanoInnov, 2 boulevard Thomas Gobert, 91120 Palaiseau Cedex, France*

<sup>4</sup>*Laboratoire d'Etude des Microstructures, ONERA-CNRS, UMR 104, Université Paris Saclay, BP 72, Chatillon Cedex, 92322, France*

<sup>5</sup>*CINaM-UMR 7325, CNRS-Aix Marseille Université, Campus de Luminy-Case 913, 13288, Marseille Cedex 09, France*

<sup>6</sup>*Univ Lyon, Université Claude Bernard - Lyon 1, CNRS, IRCELYON - UMR 5256, 2 Avenue Albert Einstein, 69626 VILLEURBANNE CEDEX, France*

<sup>7</sup>*Laboratoire Matériaux et Phénomènes Quantiques, Université de Paris-CNRS, Case Courrier 7021, F-75205, Paris Cedex 13, France*

\*corresponding authors email: [claudia.zlotea@icmpe.cnrs.fr](mailto:claudia.zlotea@icmpe.cnrs.fr) and [hakim.amara@onera.fr](mailto:hakim.amara@onera.fr)

SI-1: TEM images of Pd nanoparticles with averages sizes: 6.0, 2.0 and 1.4 nm.

SI-2: in situ XRD under vacuum (initial state), under 1 bar H<sub>2</sub> (absorbed state) followed by vacuum (desorbed state) for bulk, 6.0, 2.0 and 1.4 nm Pd at 25 °C.

SI-3: Selected EXAFS refinements.

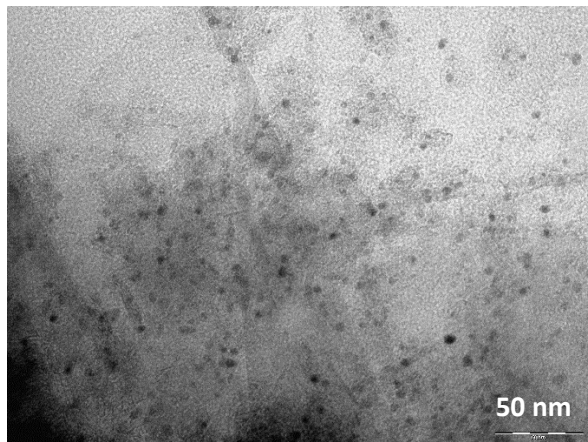
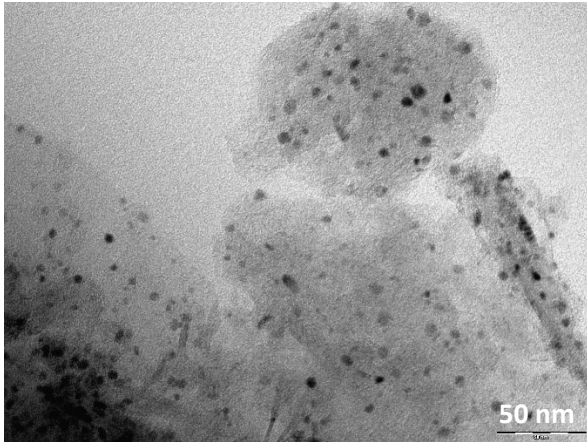
SI-4 : Comparison between the PCI curves (expressed as H/Pd vs. Pressure) and the nearest Pd-Pd distances determined by EXAFS as function of H<sub>2</sub> pressure for bulk, 6.0, 2.0 and 1.4 nm Pd nanoparticles at 25 °C. Full and empty symbols stands for absorption and desorption, respectively.

SI-5: Kinetics of hydrogen desorption for bulk, 6.0, 2.0 and 1.4 nm Pd nanoparticles at 25 °C. The data are recorded during a pressure drop from 50 to 0 mbar H<sub>2</sub> partial pressure in He flow.

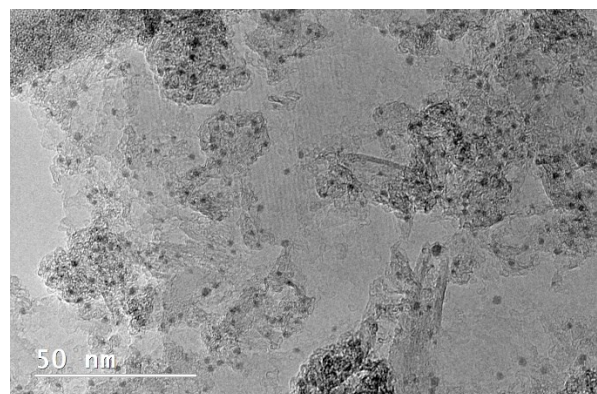
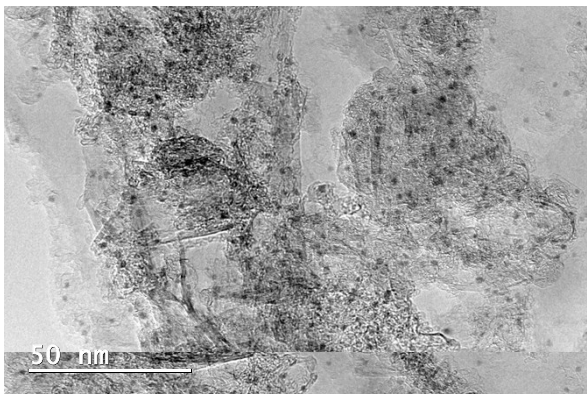
SI-6: TB calculation details and figures.

SI-1: TEM images of Pd nanoparticles with averages sizes: 6.0, 2.0 and 1.4 nm.

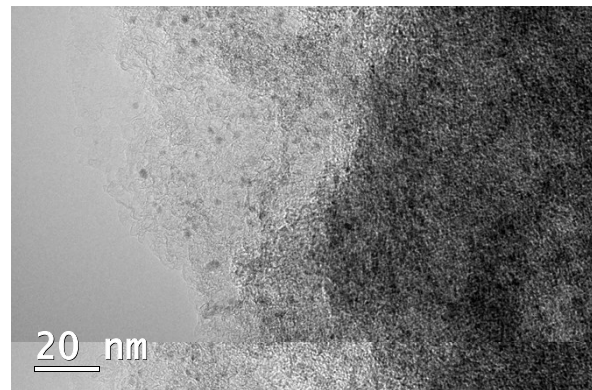
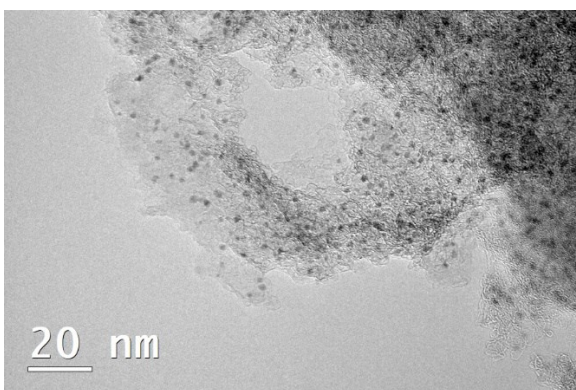
For Pd nanoparticles with 6.0 nm average size:



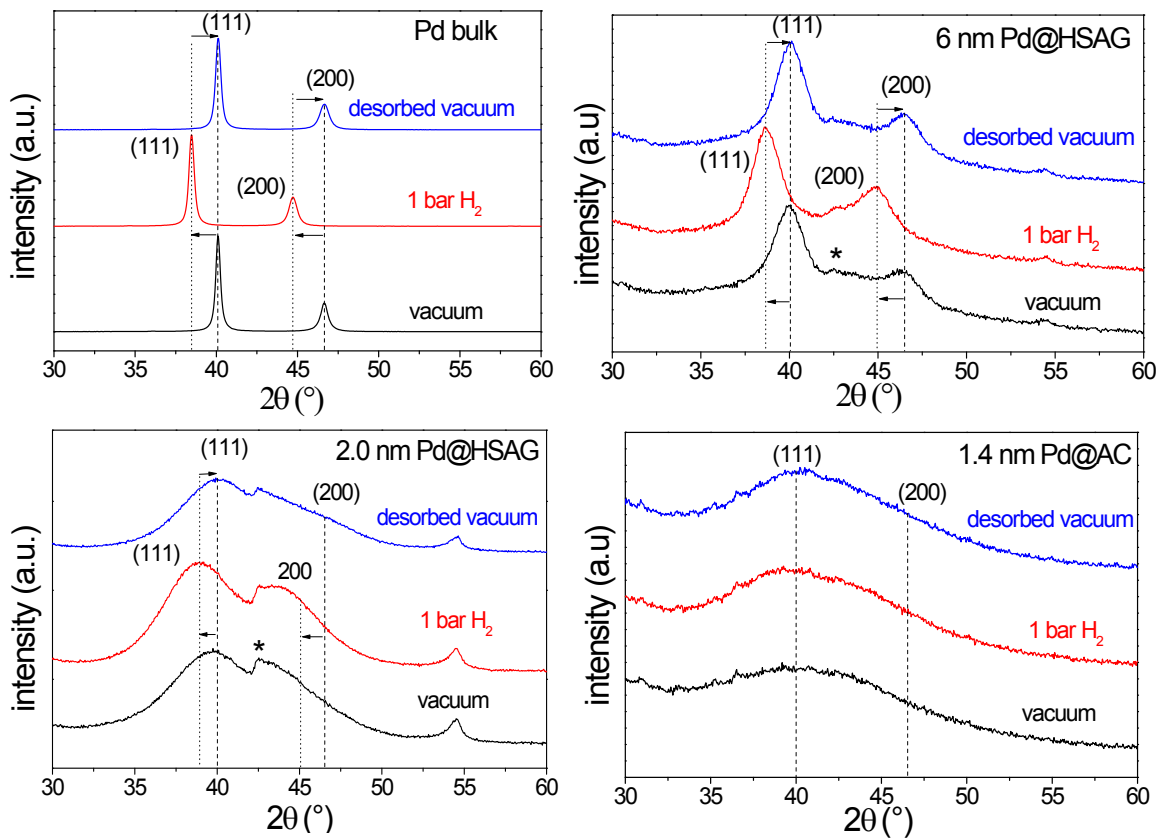
For Pd nanoparticles with 2.0 nm average size:



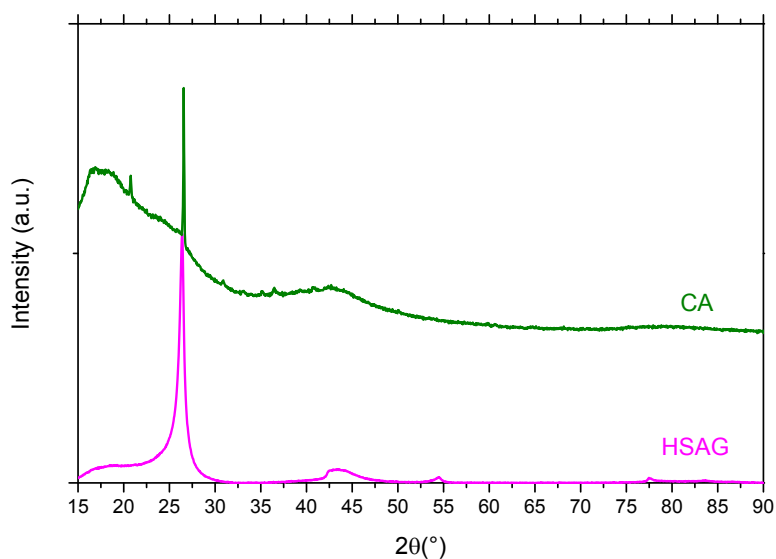
For Pd nanoparticles with 1.4 nm average size:



SI-2: in situ XRD under vacuum (initial state), under 1 bar H<sub>2</sub> (absorbed state) followed by vacuum (desorbed state) for bulk, 6.0, 2.0 and 1.4 nm Pd at 25 °C. XRD patterns of pristine carbon supports (HSAG and CA) are also given.

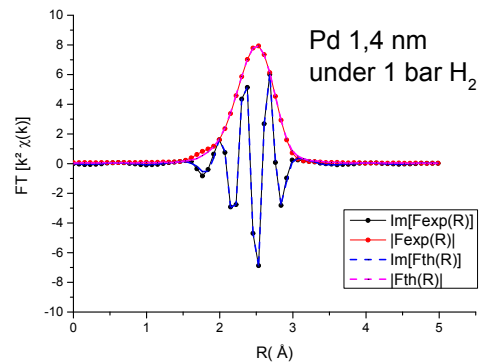
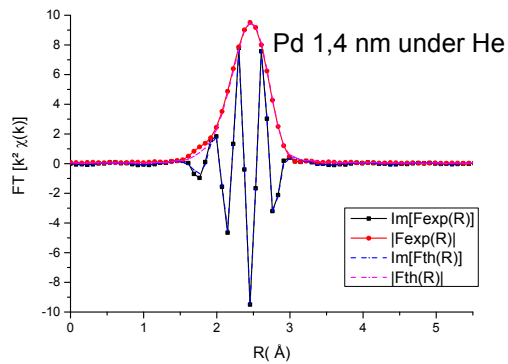


The star marks the graphitic carbon position (HSAG).

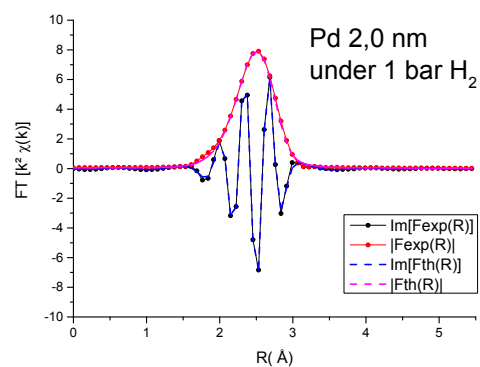
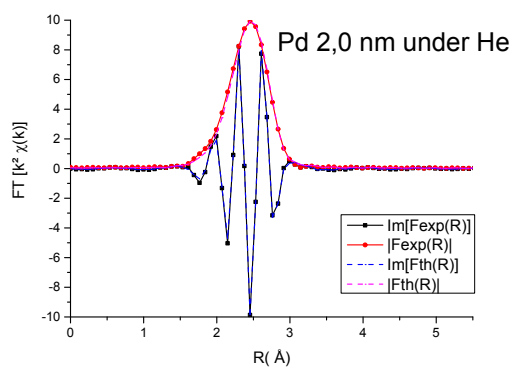


XRD patterns of pristine carbon supports: HSAG (magenta) and CA (green).

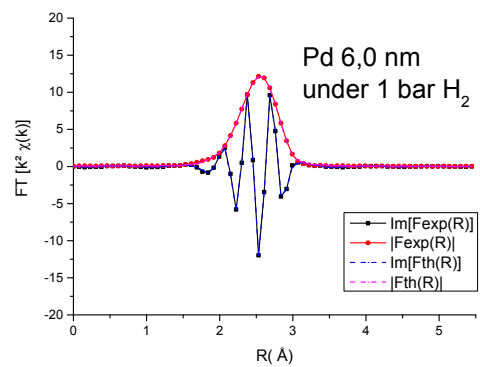
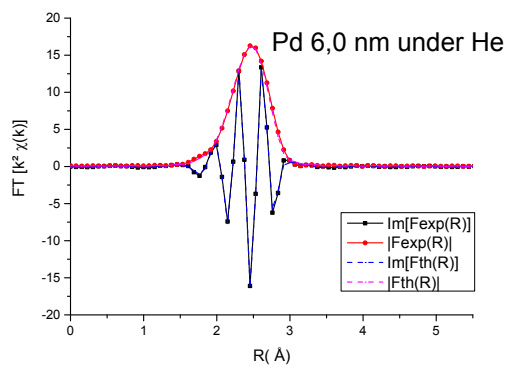
SI-3: Selected EXAFS refinements: experimental curves are represented by points and the corresponding fit by dotted lines.



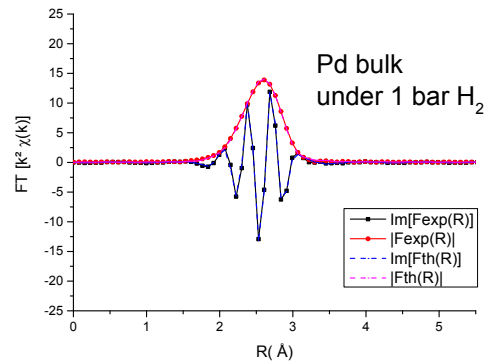
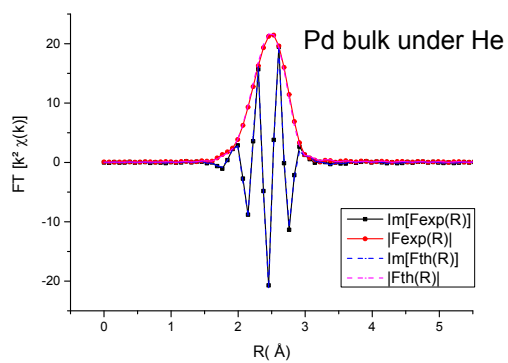
FT [ $k^2\chi(k)$ ] for 1.4 nm Pd under He (left) and 1 bar H<sub>2</sub> (right) at RT.



FT [ $k^2\chi(k)$ ] for 2.0 nm Pd under He (left) and 1 bar H<sub>2</sub> (right) at RT.

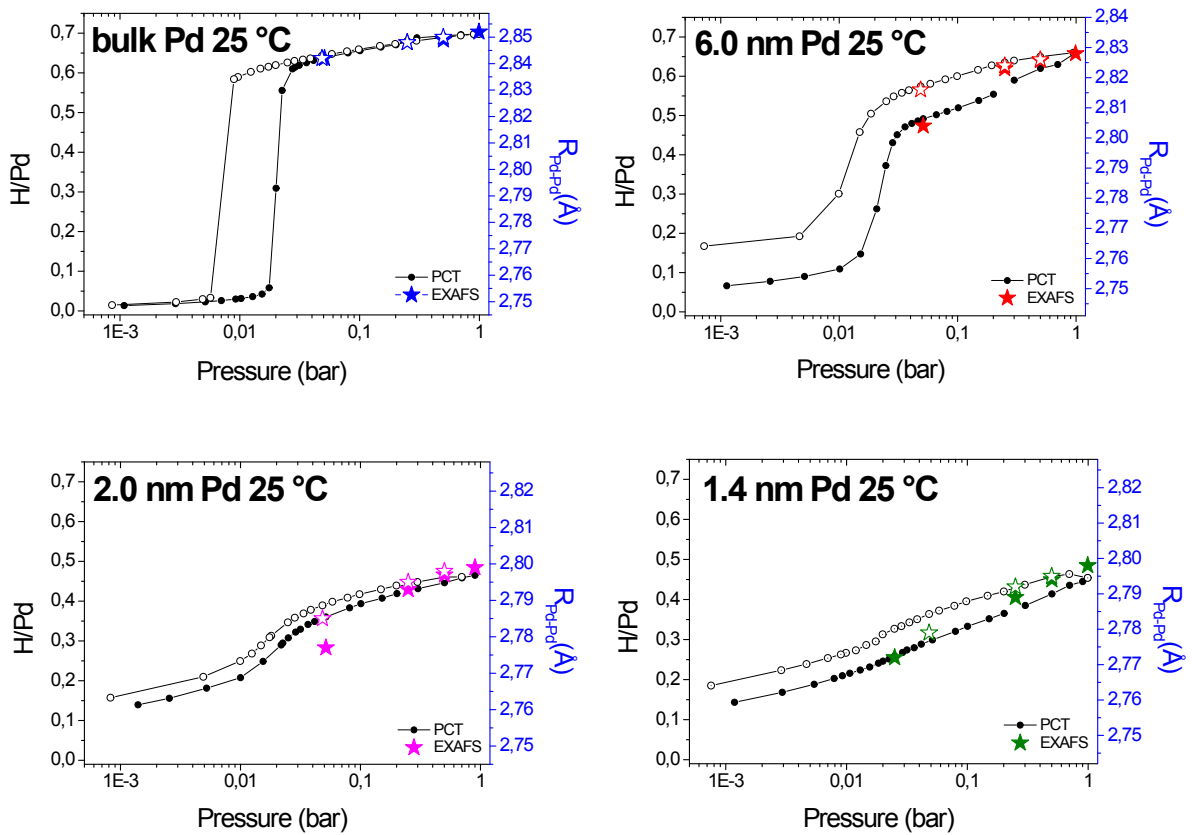


FT [ $k^2\chi(k)$ ] for 6.0 nm Pd under He (left) and 1 bar H<sub>2</sub> (right) at RT.

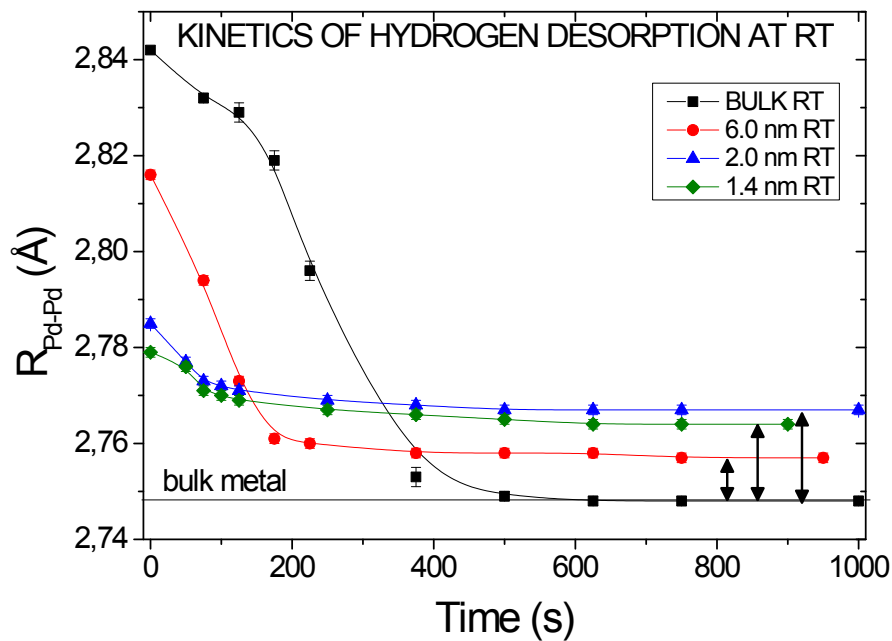


FT [ $k^2\chi(k)$ ] for Pd bulk under He (left) and 1 bar H<sub>2</sub> (right) at RT.

SI-4 : Comparison between the PCI curves (expressed as H/Pd vs. Pressure) and the nearest Pd-Pd distances determined by EXAFS as function of H<sub>2</sub> pressure for bulk, 6.0, 2.0 and 1.4 nm Pd nanoparticles at 25 °C. Full and empty symbols stands for absorption and desorption, respectively.

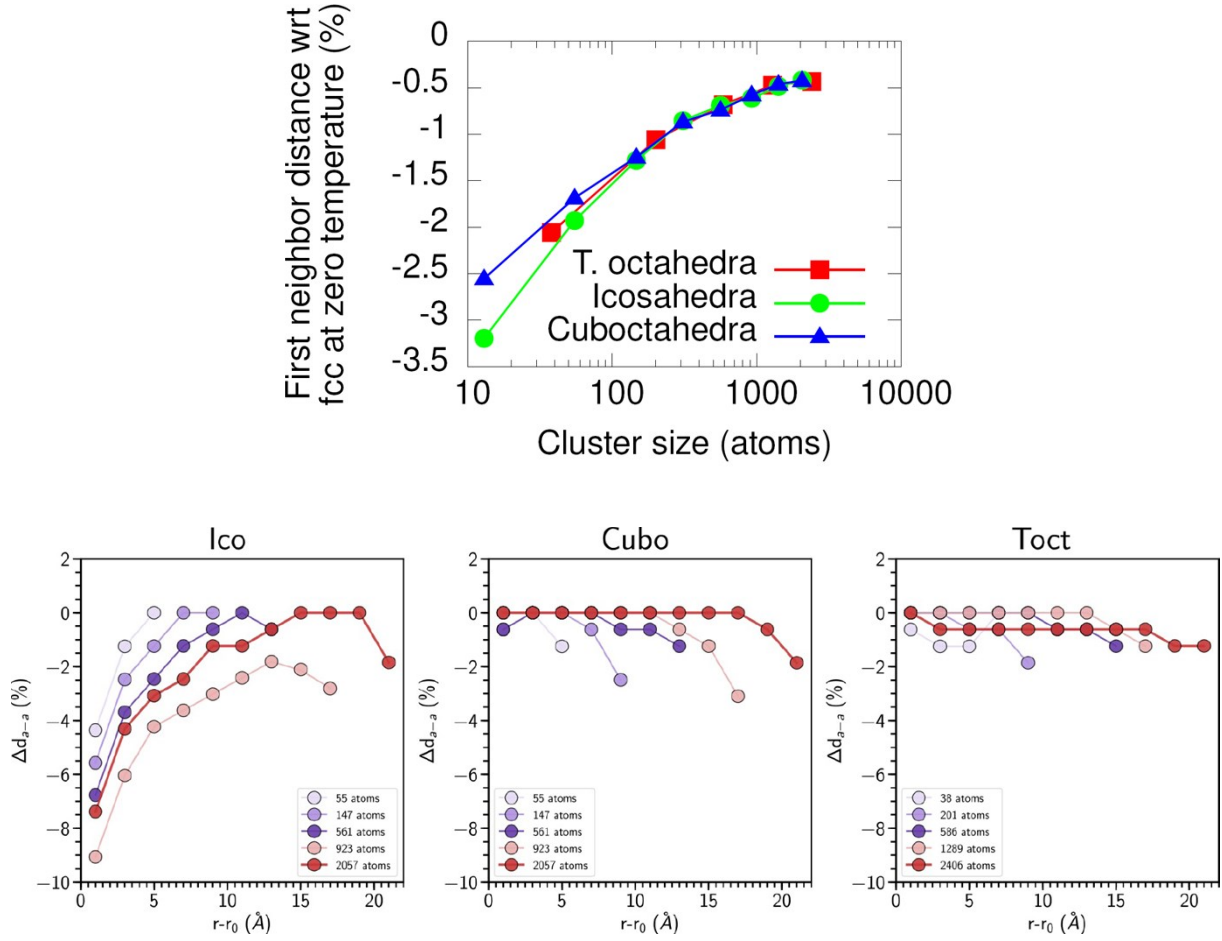


SI-5: Kinetics of hydrogen desorption for bulk, 6.0, 2.0 and 1.4 nm Pd nanoparticles at 25 °C. The data are recorded during a pressure drop from 50 to 0 mbar H<sub>2</sub> partial pressure in He flow.



Bulk Pd has the slowest kinetics for hydrogen desorption and reaches the initial metal value after around 400 s whereas, all nanoparticles attain a stable value of  $R_{Pd-Pd}$  distance in less than 200 s. However, the stabilisation values for all nanoparticles are above the bulk Pd, clearly indicating a H trapping, which is size dependent: the smaller the size, the larger final  $R_{Pd-Pd}$  value. Consequently, this is a clear size effect not a kinetic issue that can be explained by the H trapping inside the lattice of Pd.

SI-6: TB calculation details and figures.



The TB parameters used in this study are fitted to reproduce several bulk physical properties of Pd. They are obtained by fitting on experimental values of the lattice parameter, of the cohesive energy, and of the elastic moduli (bulk modulus and the two shear moduli) for the fcc structure as seen in Table 1.

	a(Å)	Cohesive energy (eV/at)	B (GPa)	$C_{11}$ (GPa)	$C_{12}$ (GPa)	$C_{44}$ (GPa)
Experiments	2.75	-3.90	189	234	176	72
TB model	2.75	-3.90	194	241	170	67

Table 1: Comparison of our TB model with experimental data ([1] see references therein): lattice parameters ( $a$ ), cohesive energies, bulk modulus and elastic moduli ( $C_{ij}$ ).

The analysis of interatomic distances is performed using atomic scale simulations from our TB potential developed to describe Pd-Pd bonds. In order to put an emphasis on a size and shape effects, three

types of NPs (icosahedral, cuboctahedral and truncated octahedron) have been considered containing a number of atoms ranging from few tens to few thousand of atoms. The equilibrium structures are obtained by performing simulated annealing between 300 and 10 K to get a complete relaxation of the NPs.

Fig. SI-5 depicts the variation of the relative contraction of the lattice in Pd nanoparticles as a function of the cluster size. The distance between Pd-Pd atoms clearly decreases with decreasing cluster size, to reach around 2.5-3.5% of contraction for the smallest NP studied in this work. This tendency is in good agreement with previous TB and DFT calculations to deal with Pd [2] and Ag NPs [3], respectively. To go beyond and highlight a shape effect, we now focus on the variation of the first neighbor distances along the radius of the NP for different FCC particles morphologies and various sizes. As seen in Fig. SI-5 2b, two different behaviours can be identified. In case of cuboctahedral and truncated octahedron NPs, the Pd-Pd distances remain almost constant in the core but decreases in a meaningful way close to the surface. This tendency is in agreement with infinite surfaces of transition metals where it has been shown that TB model yields contraction in the interlayer separation of the first two layers as observed experimentally [4, 5]. The same surface contraction is observed for icosahedral NPs. However, due to the presence of a center atom in this particular shape, elastic effects are strongly different and lead to a core under large strain (up to almost 10% for large particles). Obviously, it is tempting to think that the icosahedral shape is not adapted to incorporate H atoms since many interstitial sites are unavailable.

#### References

- [1] M.J. Mehl and D.A. Papaconstantopoulos, 1996, *Phys. Rev. B*, 54, 4519
- [2] W. Qi, B. Huang and M. Wang, *Nanoscale Res. Lett.*, 2009, 4, 269-273
- [3] B. Medasani, Y.H. Park and I. Vasiliev, *Phys. Rev. B*, 2007, 75, 235436.
- [4] M.-C. Desjonquères, *Journal de Physique Lettres*, 1979, 40; L-249
- [5] R. P. Gupta, *Phys. Rev. B.*, 1981, 23, 6265