Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Thermal behaviour of $Pd@SiO_2$ nanostructures in various gas environments: a combined 3D and in-situ TEM approach

Walid Baaziz,[1]* Mounib Bahri,[1] Anne Sophie Gay,[2] Alexandra Chaumonnot,[2] Denis Uzio,[2] Sébastien Valette,[3] Charles Hirlimann[1] and Ovidiu Ersen[1,4,5,]*

[1] Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504, CNRS - Université de Strasbourg, 23 rue du Lœss BP 43, 67034 Strasbourg cedex 2, France

[2] IFP Énergies Nouvelles (IFPEN) Lyon, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

[3] Centre de Recherche en Acquisition et Traitement de l'Image pour la Santé (CREATIS), UMR 5220 – INSERM U1206, Université Lyon 1 – INSA Lyon - Université Jean Monnet Saint-Etienne, 7 Avenue Jean Capelle O, 69100 Villeurbanne, France

[4] University of Strasbourg Institute for Advanced Studies (USIAS), Strasbourg, France

[5] Institut Universitaire de France (IUF), Paris, France

* corresponding authors

Figure 1 SI. Typical STEM BF images of Pd@SiO_2 particles with in the inset the corresponding STEM-ADF images; the size distribution of Pd particles localized in the core, fitted with a gauss function.

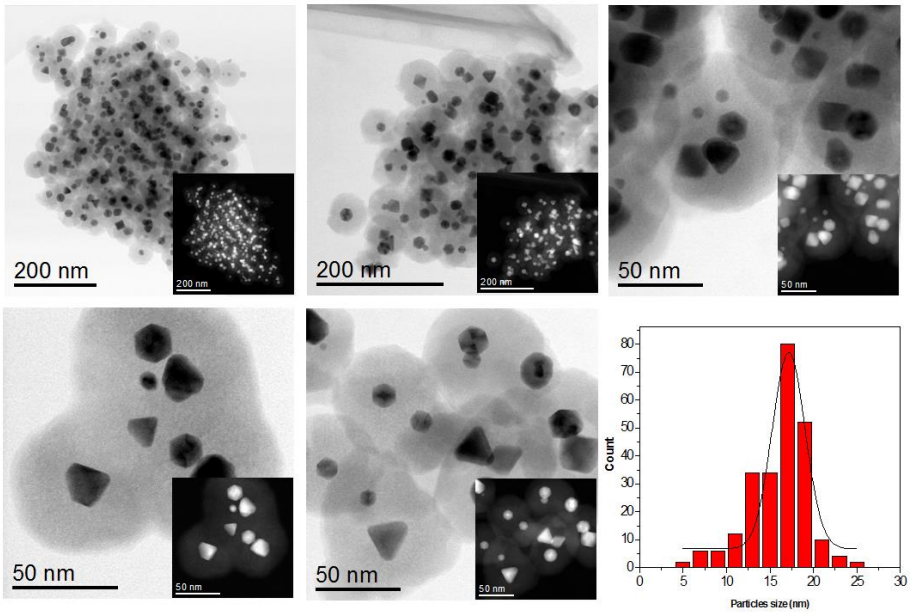

Figure 2 SI. Pd@SiO_2 particles evolution during an *in situ* thermal reduction from 200 °C to 400 °C under H_2 gas at 760 torr: STEM-ADF images of typical regions, in the inset STEM-BF images.

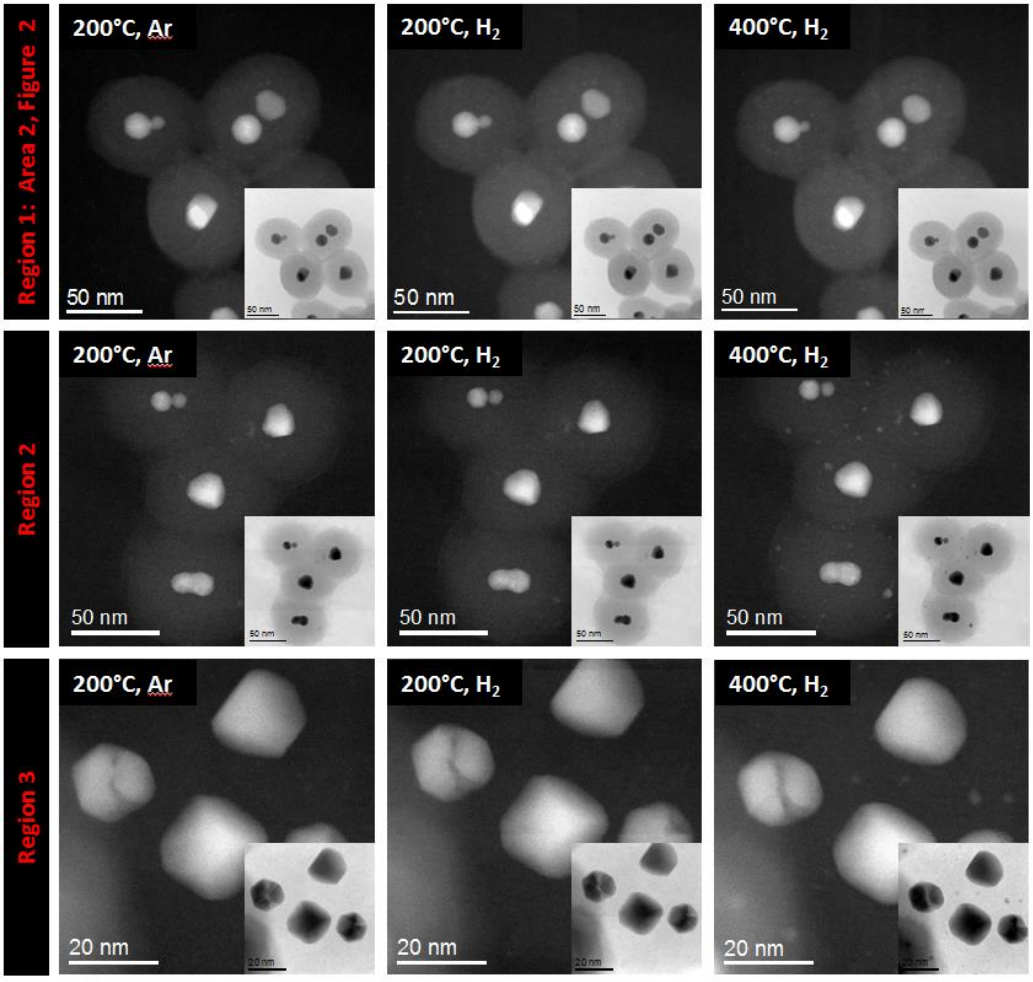

Figure 3 SI. EDX spectra recorded on several areas of silica shell showing the presence of only Si and O peaks, no Pd, K and Cl peaks being observed (Cu and C signals originate from the TEM grid).

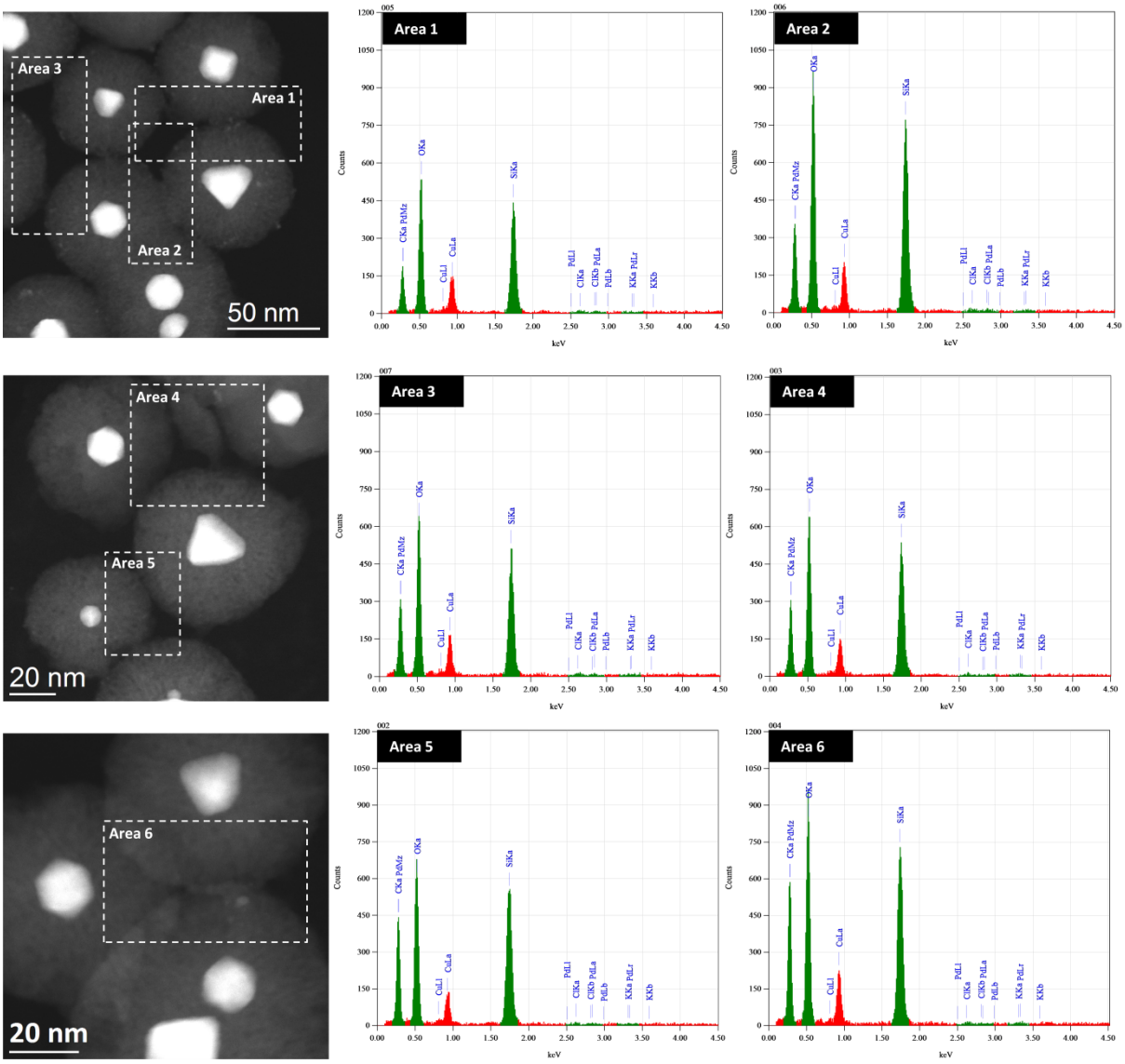

Figure 4 SI. Size of silica shells measured before and after a thermal treatment of the Pd@SiO_2 particles of the areas 1 and 2 presented in Figure 2.

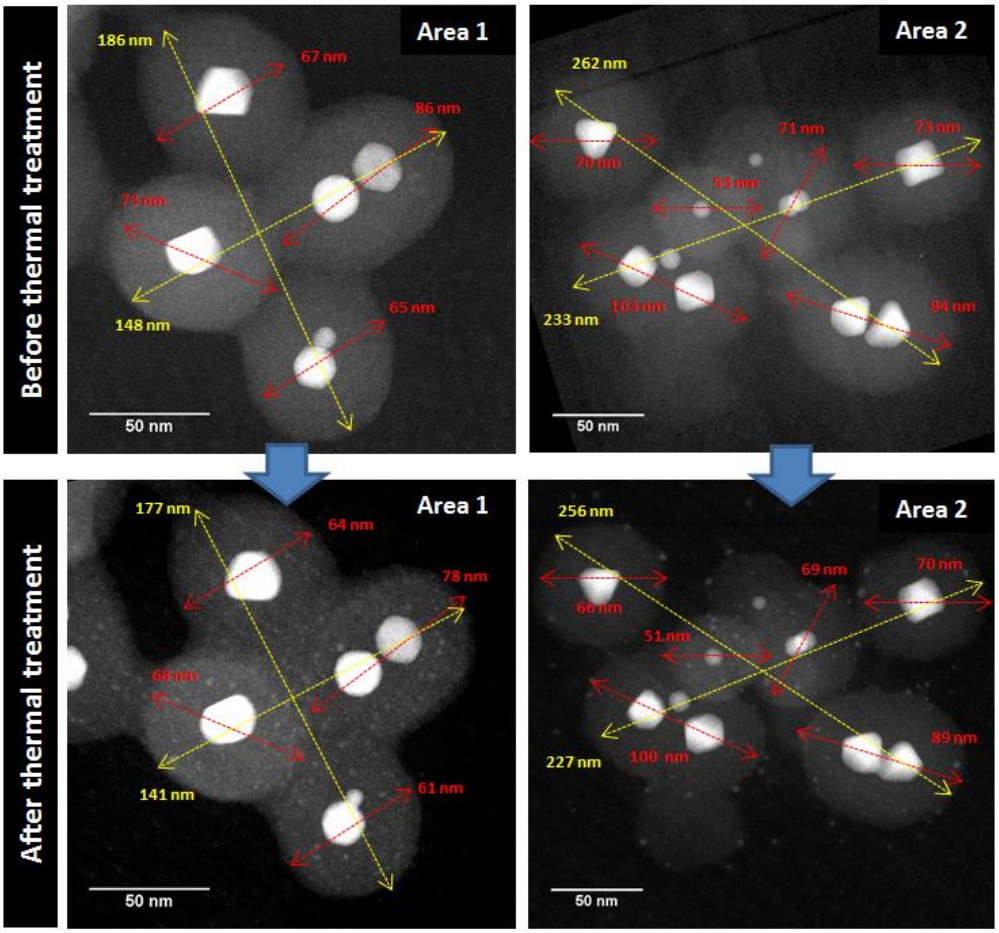

Figure 5 SI. Typical STEM-BF images (inset STEM-ADF images) of Pd@SiO_2 particles in which Pd cores do display a cubic shape before (top) and after (bottom) an *in situ* thermal treatment carried out in the same conditions: 400 °C under H_2 gas at 760 torr. (The images before and after do not correspond to the same areas)

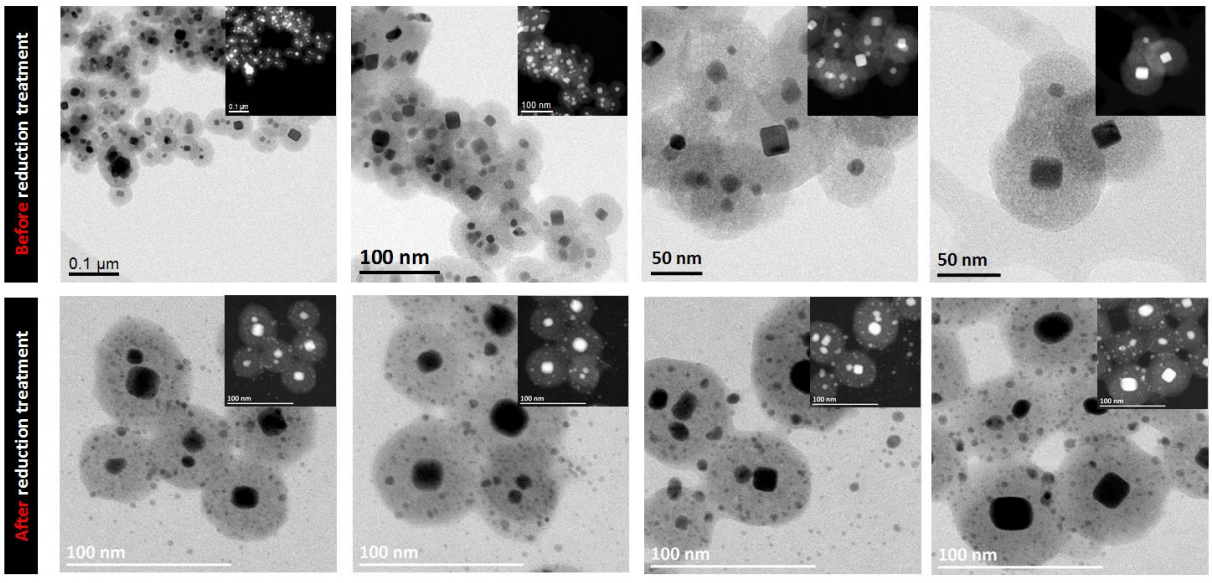

Figure 6 SI. Thermal evolution of Pd@SiO_2 particles under Ar up to 400 °C and under H_2 from 400 °C up to 1000 °C.

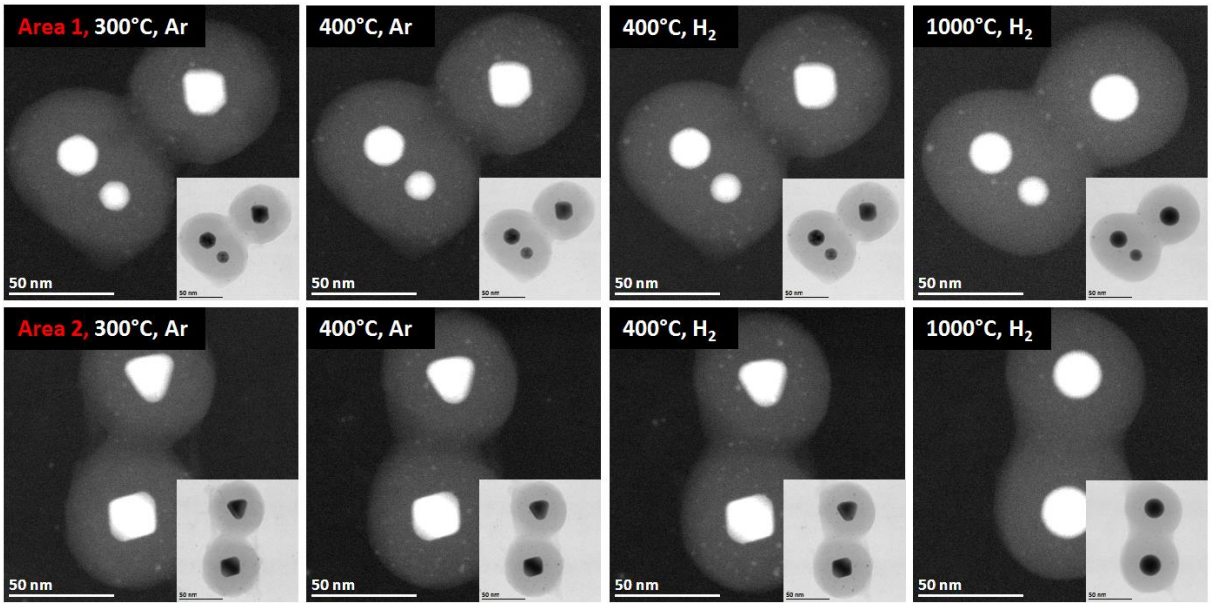

Figure 7 SI. *Top and middle*: STEM-ADF images illustrating the thermal evolution of Pd@SiO_2 particles under air up to 850 °C. *Bottom*, STEM-BF images extracted from the video SI3 recorded between 700 °C and 850 °C under air and showing the diffusion of Pd from the core to the external part of the silica shells.

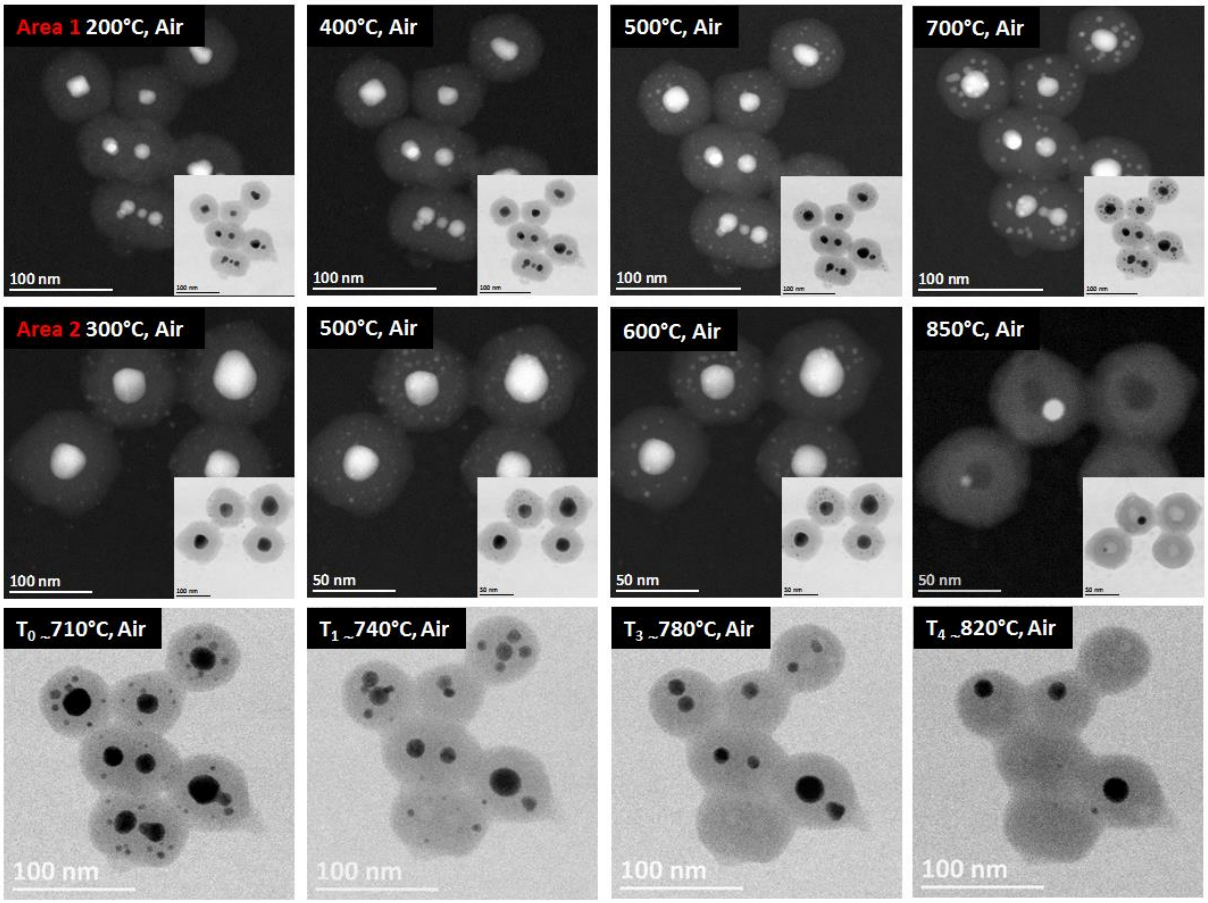

Table 1 SI. 3D surface quantification of the well-defined facets of 2 typical monocrystallines Pd particles with octahedral shape (from the area 1, Figure 4) before and after thermal treatment.(*)

Particle 1		
Facets	Surfaces before thermal treatment (pixel)^2	Surfaces after thermal treatment (pixel)^2
1	553	380
2	578	359
3	722	491
4	757	727
5	1023	853
6	1102	926
7	1321	1182
8	1428	1261
∑	**7484**	**6179**
Particle 2		
Facets	Surfaces before thermal treatment (pixel)^2	Surfaces after thermal treatment (pixel)^2
1	767	360
2	825	432
3	911	666
4	1016	768
5	1362	820
6	1364	907
7	1517	1412
∑	**7762**	**5365**

Table 2 SI. 3D surface quantification of the well-defined facets of a typical Pd MTP with icosahedral shape (Particle 1, Figure 5) before and after thermal treatment.(*)

Facets	Surface before thermal treatment (pixel)^2	Surface after thermal treatment (pixel)^2
1	255	309
2	400	449
3	485	451
4	515	486
5	549	560
6	573	568
7	617	629
8	617	656
9	623	659
10	639	688
11	718	696
12	737	698
13	776	701
14	905	703
15	998	715
∑	**9407**	**8968**

(*) N.B for Table 1 SI and Table 2 SI, the values are given in a random way and do not necessarily correspond to the same surface before and after the thermal treatment. To the sum of these surfaces, we add the surfaces which were not defined as facets and which represent an important deviation to the standard planes.

Movies of 3d models animation	
Movie 1 SI.	3D model of $Pd@SiO_2$ particles before thermal treatment
Movie 2 SI.	3D model of $Pd@SiO_2$ particles after thermal treatment
Movie 3 SI.	3D faceted model of monocrystalline octahedral particle before thermal treatment
Movie 4 SI.	3D faceted model of monocrystalline octahedral particle after thermal treatment
Movie 5 SI.	3D faceted model of MTP icosahedral particle before thermal treatment
Movie 6 SI.	3D faceted model of MTP icosahedral particle after thermal treatment
Movie 7 SI.	Video of the diffusion mechanism of Pd cores between 700°c and 850°C under air