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Electronic Supplementary Information (ESI)

Unexpected Refacetting of Palladium Nanoparticles under Atmospheric N_2 Condition

Xun Zhang,‡[a] Jun Meng,‡[bc] Beien Zhu,*[b] Wentao Yuan,[a] Hangsheng Yang,[a] Ze Zhang,[a] Yi Gao*[b] and Yong Wang*[a]

[a] State Key Laboratory of Silicon Materials and Center of Electron Microscopy, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

[b] Division of Interfacial Water and Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

[c] University of Chinese Academy of Sciences, Beijing 100049, China

‡These two authors contributed equally to this work.

Corresponding Authors:

yongwang@zju.edu.cn

zhubeien@sinap.ac.cn

gaoyi@sinap.ac.cn

Contents of Supplementary Information:

1. Materials and Methods

1-1. Preparation of Pd Nanoparticles

Pd NPs with were synthesized and dispersed in water. 57 mg of Na_2PdCl_4 (Aladdin) precursors were reduced in 11 ml aqueous solution, which contained 60 mg of L-ascorbic acid. (AA, Sinopharm Chemical Reagent Co. Ltd.) To control the particle size and morphologies, 105 mg of poly (vinyl pyrrolidone) (PVP, $M_w \approx 55\,000$, Aldrich) and 600 mg of KBr (Sinopharm Chemical Reagent Co. Ltd.) were mixed into the solution aforehand, serving as the stabilizer and capping agent respectively.[1] After heating at 80 ^{o}C for 3 hours, the products were washed over 5 times by centrifugal cleaning and collected. Eventually, the Pd NPs were drop-casted onto a heating chip with SiN_x film and annealed in air at 200 ^{o}C for 30 min. We confirm that the Pd NPs were not oxidized from the TEM observations. The TEM image of the aquired Pd NPs is displayed in Fig. S1, showing NPs ranging from 15 nm to 50 nm with irregular shapes.

1-2. In situ TEM Characterizations

In situ observations were carried out in a field emission TEM (Titan 60-300, FEI company), operating at 300 kV. The gas cell holder (Climate S3, DENSsolutions Company) and its gas supply system make our experiments available under atmospheric pressure environment. The holder was designed by MEMS-based micro-chips.[2] It contains a nanoreactor composed of two chips functionalized with 30 nm thick electron-transparent SiN_x windows. Molybdenum (Mo) spiral under the SiN_x membrane is chosen as the heating module and conducting materials on heating chip. The prepared rounded Pd NPs were studied both in vacuum and in 1 bar N_2 (99.999%) at 200 ^{o}C.

1-3. Computational Details

The (4×4) and the (1×1) slab models are built for each facet to calculate the adsorption energy of a single gas molecule and the lateral interaction between the adsorbates. The (4×4) slab model is a supercell which contains 16 unit cells (16 surface atoms). It is used to simulate the situation of very low adsorption coverage. The (1×1) slab model is a unit cell which contains only one surface atom. We use it to simulate the case of maximum adsorption coverage of gas molecule.

2. Supporting Figures and Table

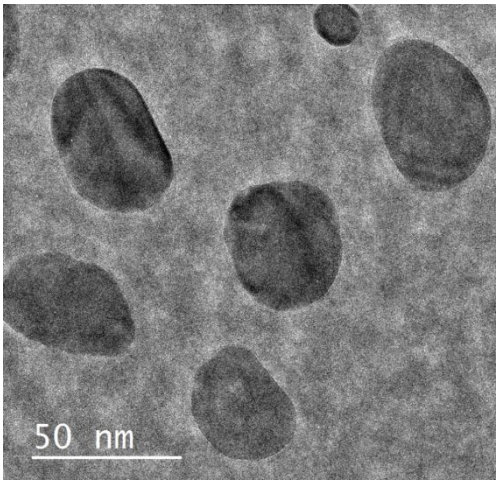

Fig. S1 TEM image of the as prepared Pd NPs showing irregular shapes. The particle sizes change from 15 nm to 50 nm.

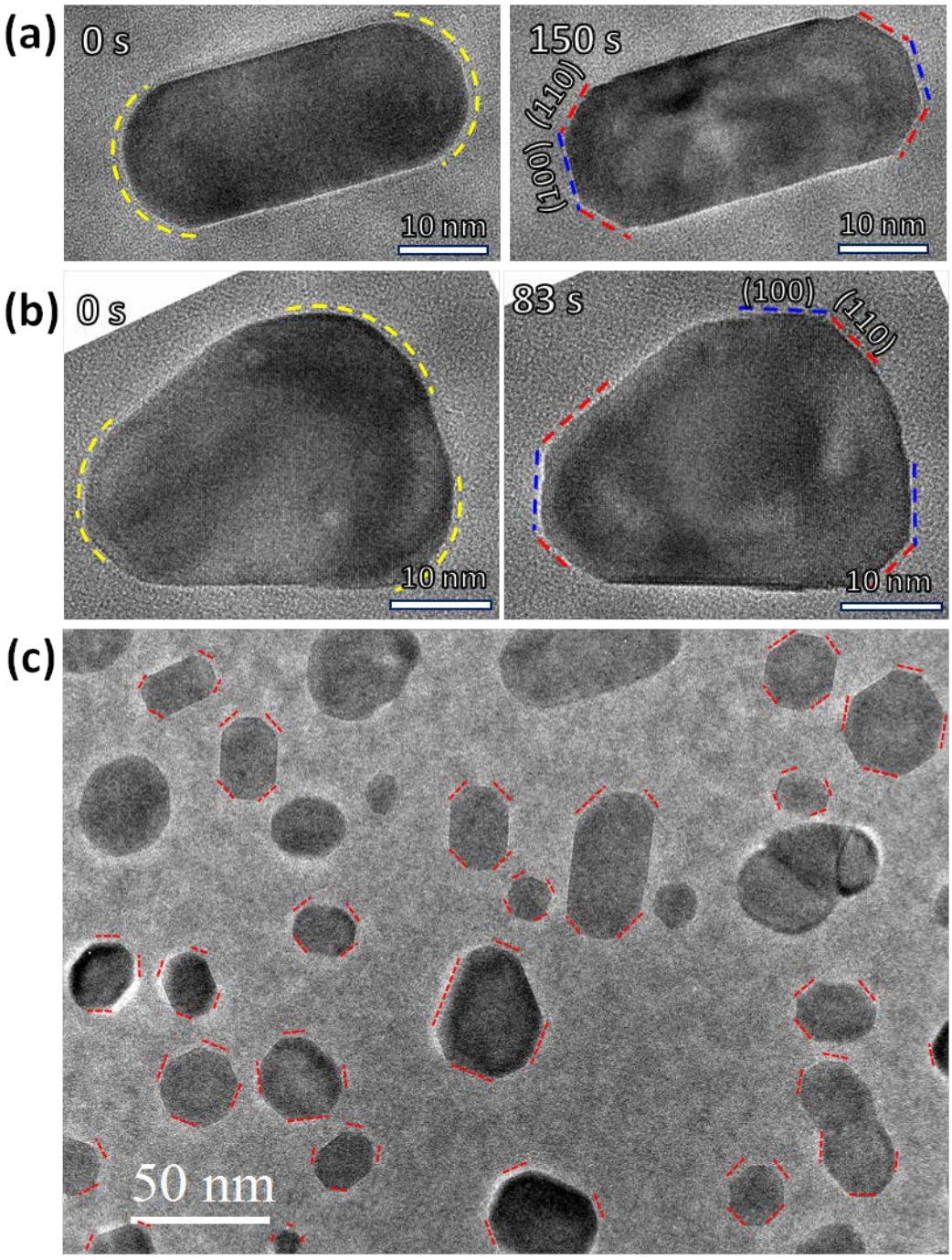

Fig. S2 (a, b) Other examples of Pd surface refacetting when exposed to 1 bar N_2 at 200 °C. (c) TEM image of Pd NPs under 1 bar N_2 at 200 °C indicates that the refacetting process occur homogeneously on nearly all the particles. The red lines correspond to Pd {110} facets.

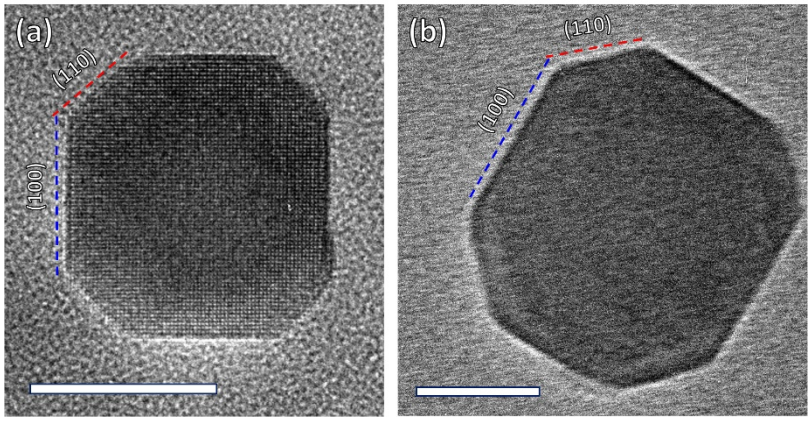

Fig. S3 TEM images show the snapshots of two refacetted Pd NPs under 1 bar N_2 at 200 ^{o}C, which was not exposed to electron beam irradiation before. It indicated that the electron beam is not ans essential requirement for the refacetting. Scale bar: 10 nm.

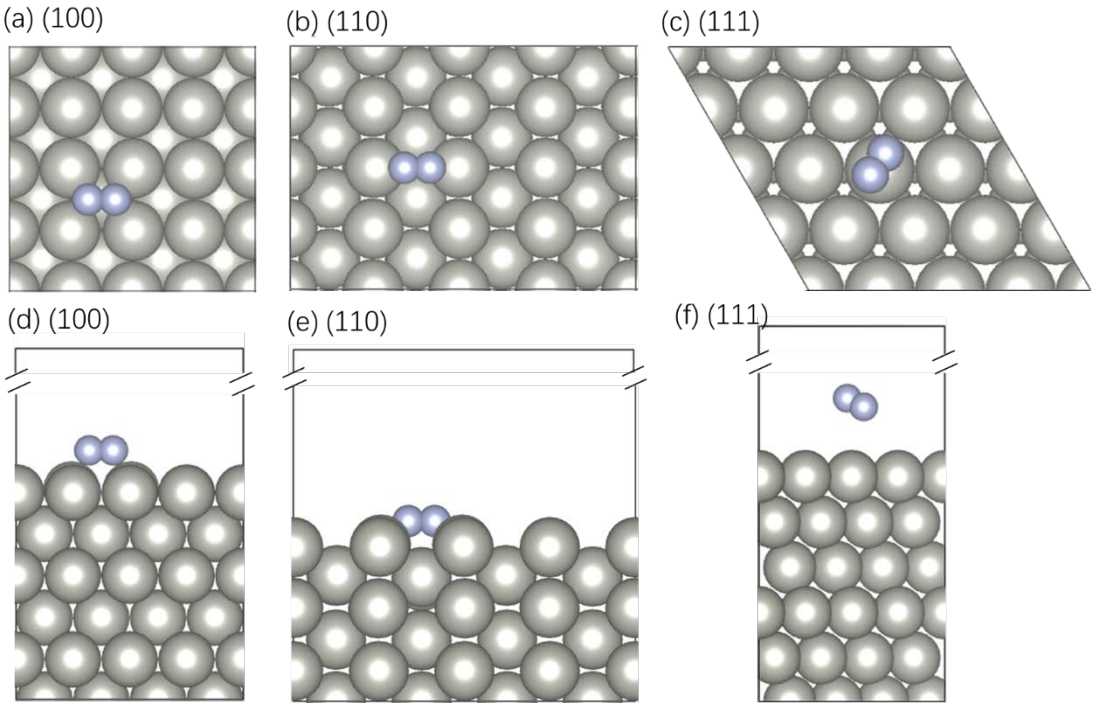

Fig. S4 The most stable adsorption configurations of the N_2 on the (4×4) slab models Pd (100), (110), and (111) facets from the top view (a-c) and the side view (d-f). The grey ball represents Pd and the bule ball represents N.

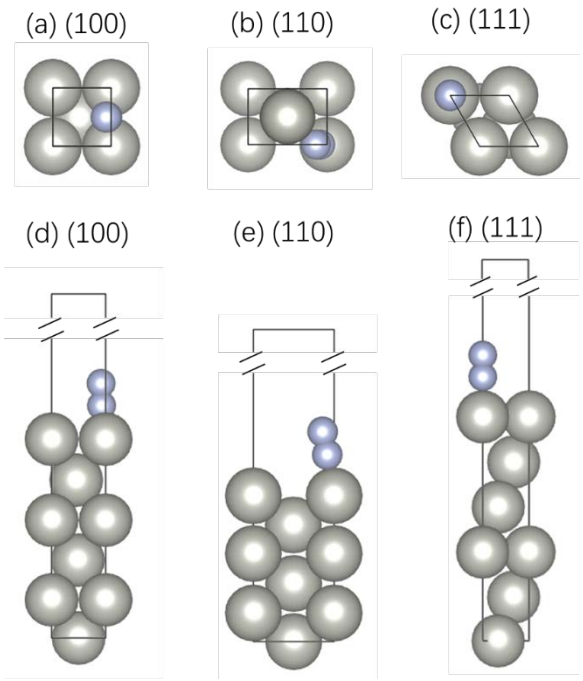

Fig. S5 The most stable adsorption configurations of the N_2 on the (1×1) slab models of Pd (100), (110), and (111) facet from the top view (a-c) and the side view (d-f). The grey ball represents Pd and the bule ball represents N.

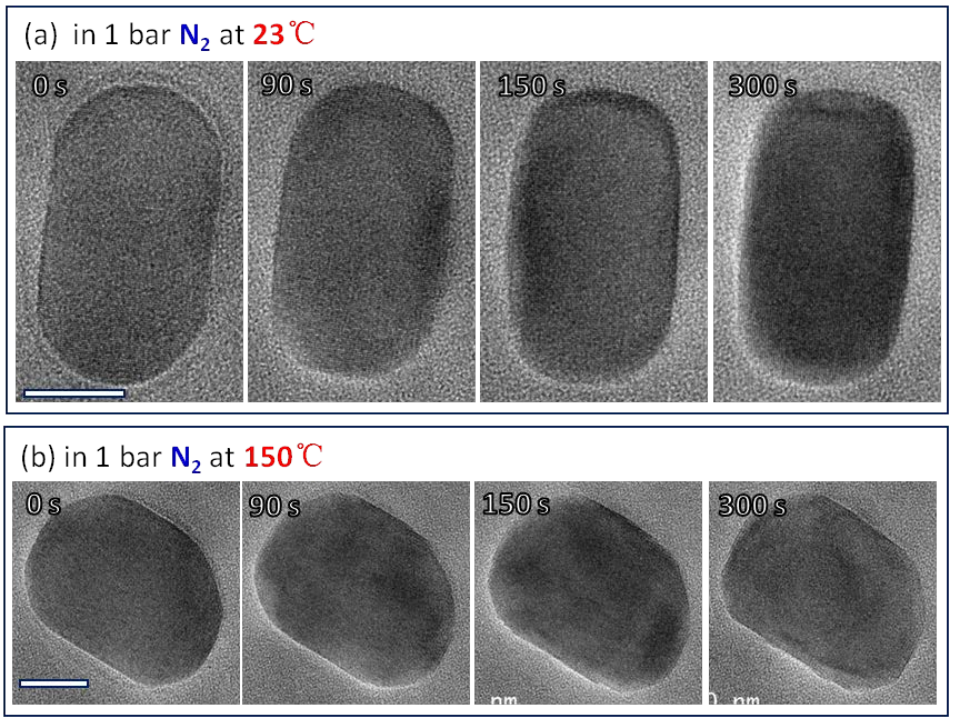

Fig. S6 When the as prepared Pd NPs were heated in 1 bar N_2 at 23°C and at 150 °C, no obvious refacetting of the NPs could be observed. Scale bar: 10 nm.

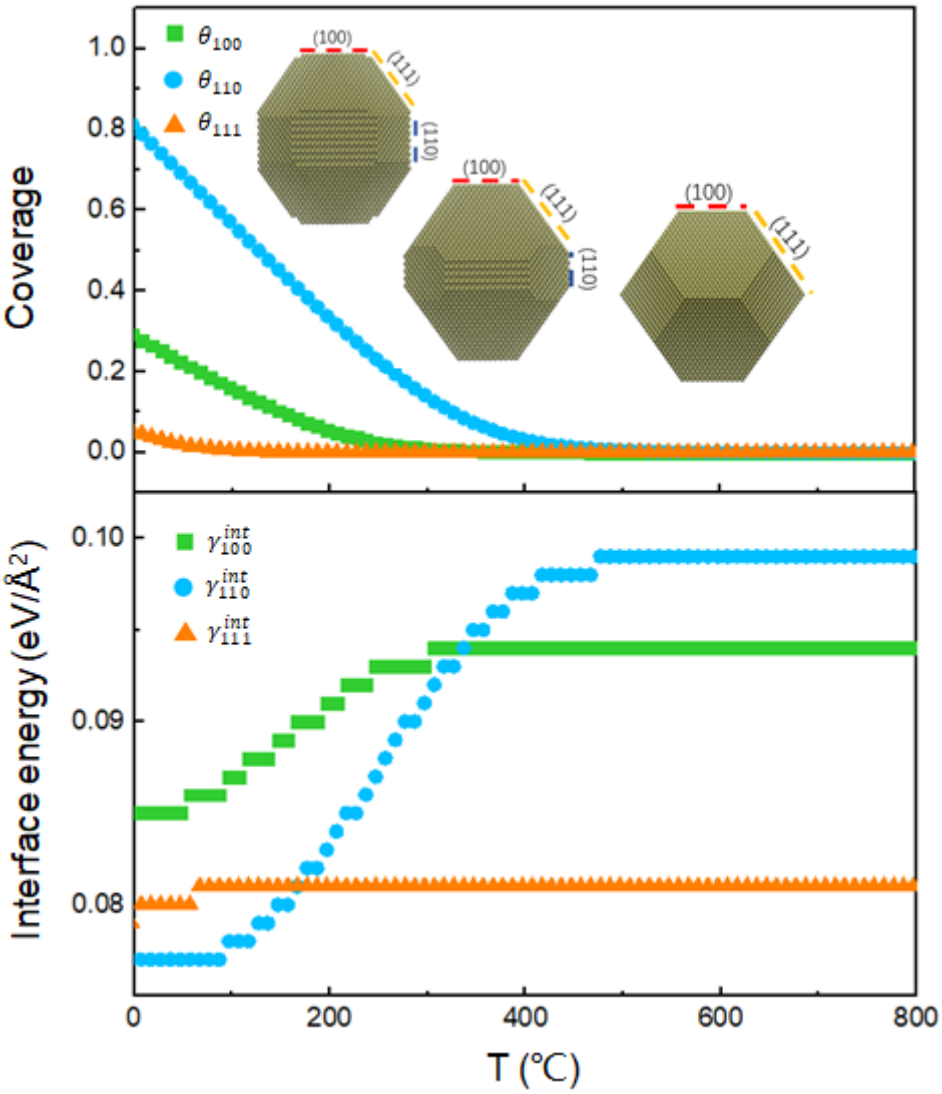

Fig. S7. Theoretical calculated N_2 adsorption coverage and Pd interface energy at 1bar N_2 pressure and at different temperature. The insert images show the predicted structure evolution when temperature changes from low to high.

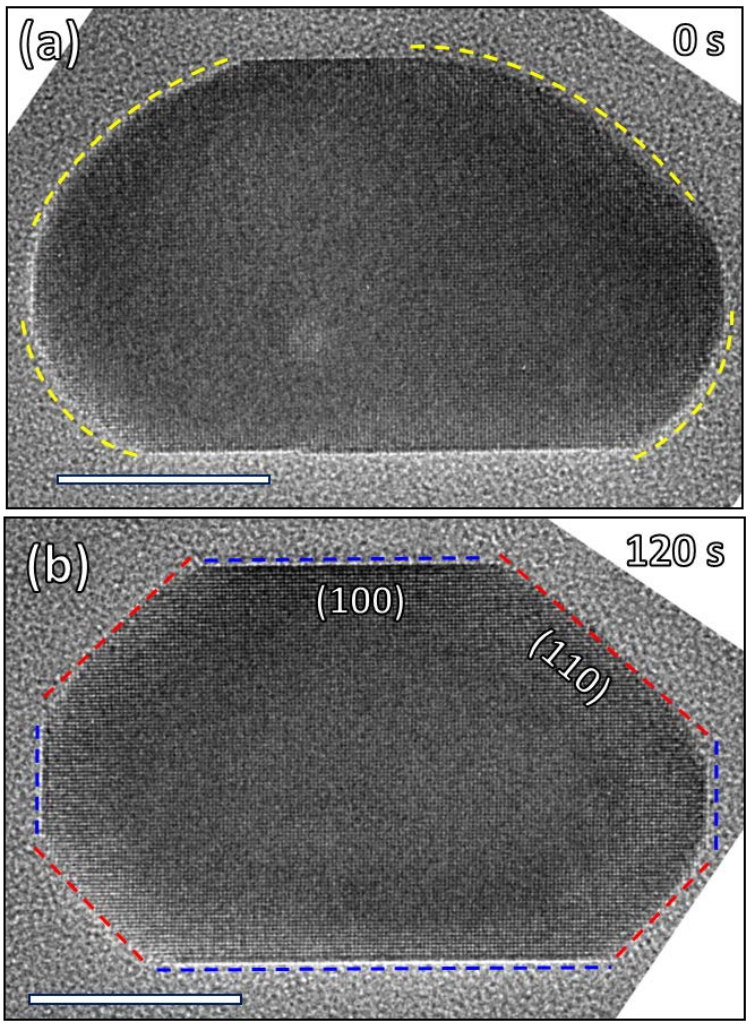

Fig. S8 (a, b) Time resolved TEM images showing Pd surface refacetting when exposed to 1 bar N_2 at 300 °C.

Table S1 The adsorption energies of Ar on the Pd (100), (110), and (111) facets.

Facet	Pd(100)	Pd(110)	Pd(111)
E_{ads} (eV)	-0.01	0.00	-0.01

3. References

[1] M. Jin, H. Liu, H. Zhang, Z. Xie, J. Liu and Y. Xia, *Nano Res.*, 2011, **4**, 83.

[2] J. F. Creemer, S. Helveg, G. H. Hoveling, S. Ullmann, A. M. Molenbroek, P. M. Sarro and H. W. Zandbergen, *Ultramicroscopy*, 2008, **108**, 993.

4. Caption for Movie

Movie S1. The *in situ* shape evolution of two of the Pd NPs at 200 ^{o}C in 1 bar N_2 projected along the [001] direction (4 times faster).