Electronic Supplementary Information (ESI)

In situ TEM studies of Shape Evolution of Pd Nanocrystals under Oxygen and Hydrogen Environment at Atmospheric Pressure

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Contents of Supplementary Information:

Ⅰ.Materials and methods

A. preparation of cubic Pd NCs

The cubic Pd NCs with an average width of 17.5 nm were synthesized by a previously reported method[1]. In a typical synthesis, a combination of 105 mg of poly (vinyl pyrrolidone) (PVP, $M_w \approx 55\ 000$, Aldrich), 60 mg of L-Ascorbic acid (AA, Sinopharm Chemical Reagent Co. Ltd.) and 600 mg of KBr (Sinopharm Chemical Reagent Co. Ltd.) were dissolved into 8 ml of deionized water in a 20 ml vial, with preheating and magnetic stirring in air at 80°C for 10 min (solution 1). A second solution was prepared by dissolving 57 mg of Na_2PdCl_4 (Aladdin) to 3 ml of water (solution 2), and then added to solution 1. The mixed final solution was heated in air under magnetic stirring at 80°C for 3 hours. After cooling to room temperature, the product was separated by centrifugation and washed for more than 5 times with water. Eventually, before in situ observations, the as-prepared Pd NCs were dispersed in water and drop-casted on a silicon nitride (SiN_x) film supported across a heating chip, followed by annealing in air at 100℃, which was supposed to reduce the carbon (PVP) contamination and ensure a better image during TEM observations.

B. In situ TEM observations

In situ observations of the shape evolution of Pd NCs were carried out in a field emission TEM (Tecnai, F20, FEI company), operating at 200 kV. The gas cell holder system (Climate S3, DENSsolutions Company) makes the experiments available under atmospheric pressure environment. The holder contains a nanoreactor closed by two chips functionalized with electron-transparent SiN_x windows.[2, 3] The thickness of the window membrane was about 30 nm for both heating and top chips. Molybdenum (Mo) is chosen as the heating spiral and conducting materials on heating chip. The as prepared Pd NCs were studied at various temperature under 1 bar O_2 (99.999%) and 1 bar H_2 (99.99%), respectively. Noted that our in situ observations are performed in gas environment at 200°C and higher and at such a condition, PVP ligands could be easily decomposed.[4] This is also confirmed by the coalescence of Pd nanocrystals in our experiments.

Ⅱ. Figs. S1-S4:

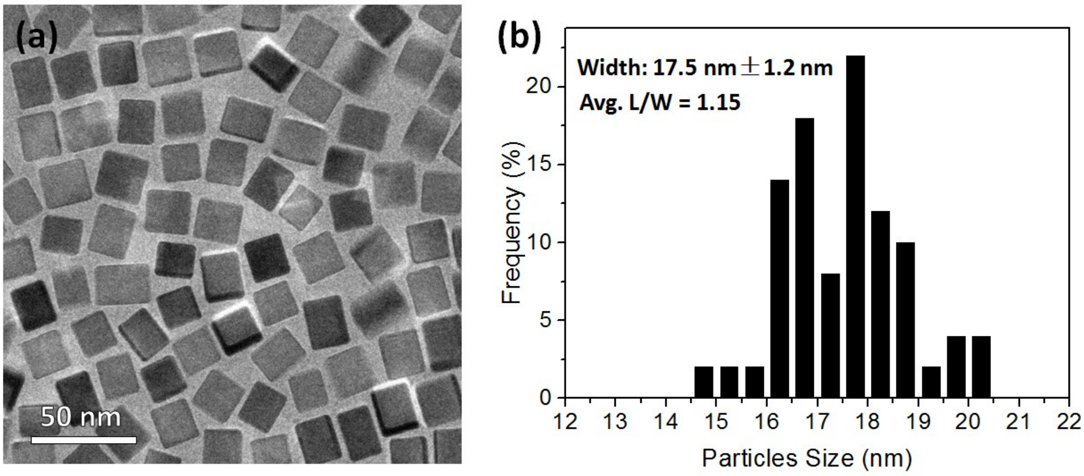

Fig. S1 (a) TEM image of as synthesized Pd NCs and (b) the corresponding histogram of particle size distribution.

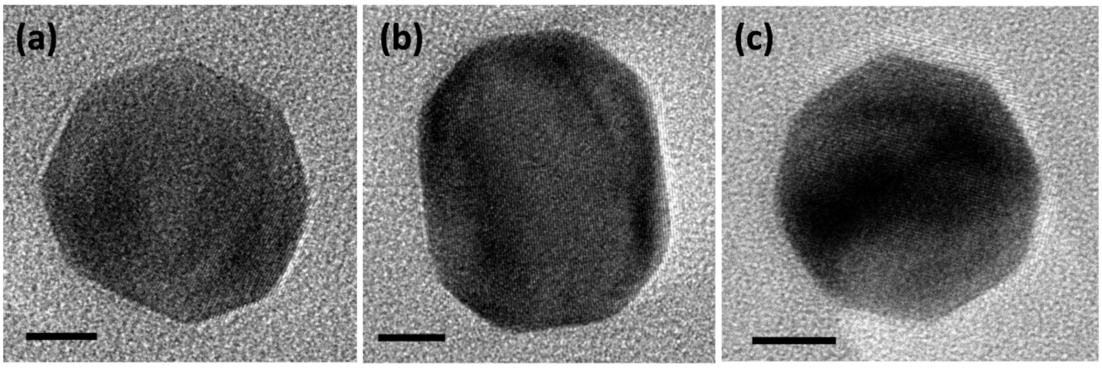

Fig. S2 (a-c) Other examples of shape changed Pd NCs exposed to 1 bar O_2 at 200°C. Scale bar: 5 nm.

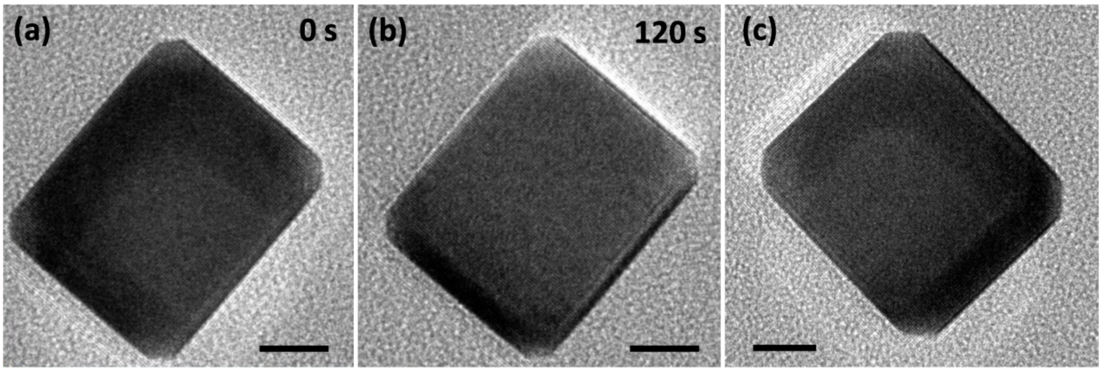

Fig. S3 (a-b) In situ TEM images of a Pd NC under 1 bar H_2 at 200℃ and (c) Pd NC heated at 200-300℃ in 1 bar H_2 for more than 2 hours. No shape changes were detected. Scale bar: 5 nm.

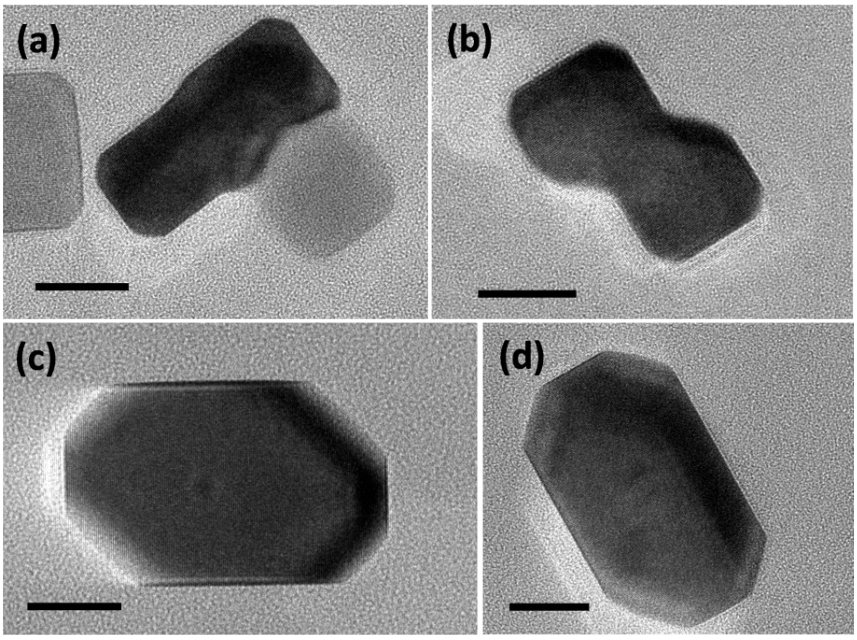

Fig. S4 TEM images of Pd NCs at 300℃in 1 bar H_2.(a, b) The cubic Pd NCs are sintering, (c, d) Truncated Pd NCs resulted from the coalescence of cubic particles. Scale bar: 10 nm.

Ⅲ. Computational details

Spin-polarized density functional theory (DFT) calculations are performed to calculate the adsorption energies by applying the Vienna Ab-initio Simulation Package (VASP). The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional is used to calculate the adsorption energies of H_2 on Pd surfaces. Revised gradient-corrected functional of Perdew, Burke and Erzernhof (RPBE) is used to get the adsorption energies of O_2on Pd surfaces. (4×4) slab and (1×1) slab models are built to get the adsorption energies E_{ads} and interaction energies w between adsorbates.

$$E_{ads\ c(4\times4)} = E_{gas/slab(4\times4)} - E_{slab(4\times4)} - E_{gas}$$
$$E_{ads\ c(1\times1)} = E_{gas/slab(1\times1)} - E_{slab(1\times1)} - E_{gas}$$
$$w = \frac{E_{ads\ c(4\times4)} - E_{ads\ c(1\times1)}}{z}$$

$z$is the coordination number of adsorbates.

The slab models contain 6 layers with 2 layers fixed at the bottom. Pd surfaces along Z axis is separated with a 15 Å vacuum space. The cut energy is 400 eV. The convergence of the electronic self-consistent is 10^{-5} eV. The force convergence criteria in a conjugate-gradient algorithm is 0.05 eV/Å respectively.

To obtain the stable adsorption configurations and adsorption energies of O_2/H_2 on Pd surfaces, different possible adsorption sites are tested. For O_2 adsorption, the adsorption sites are labeled by the position of each O atom in Fig. S5. For H_2 adsorption, the top, bridge and hollow/fcc sites are tested (Fig. S6). The adsorption energies are listed in table S1 and S2.

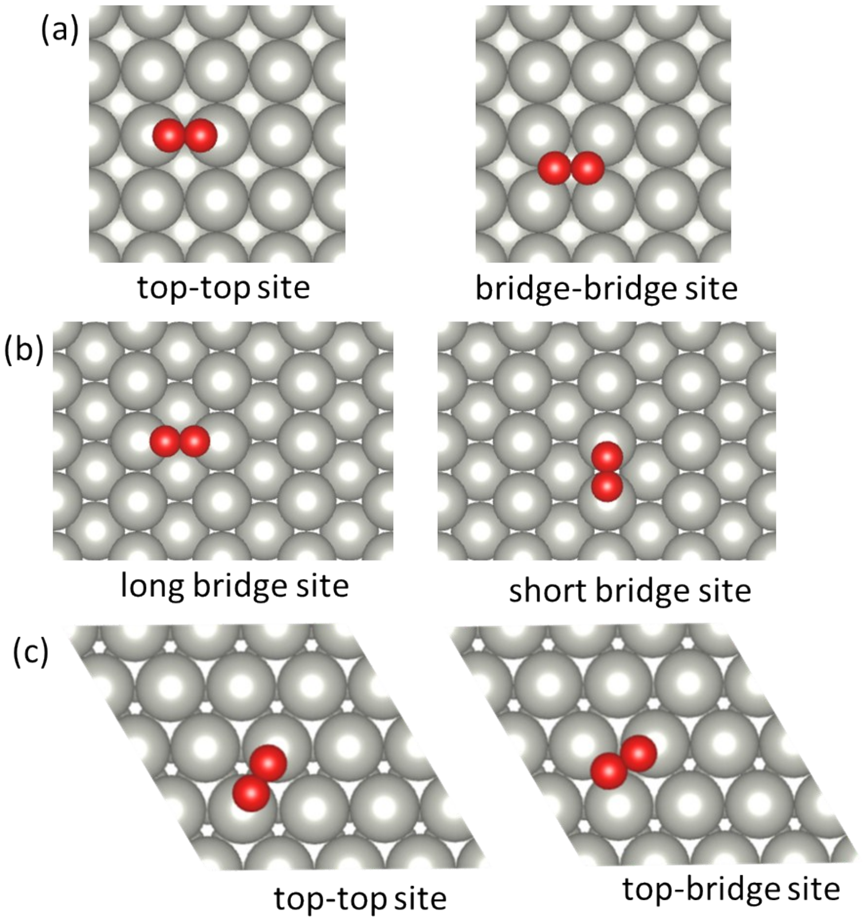

Fig. S5 Top view of the optimized structures of O_2 adsorbed on Pd (100) surface (a), (110) surface (b) and (111) surface (c).

Table S1 The adsorption energies of O_2 on Pd surface at different sites labeled in Fig. S5.

	top-top site	**bridge-bridge site**
(100)	-0.639	-0.956
	long bridge site	**short bridge site**
(110)	-0.804	-0.951
	top-top site	**top-bridge site**
(111)	-0.389	-0.364

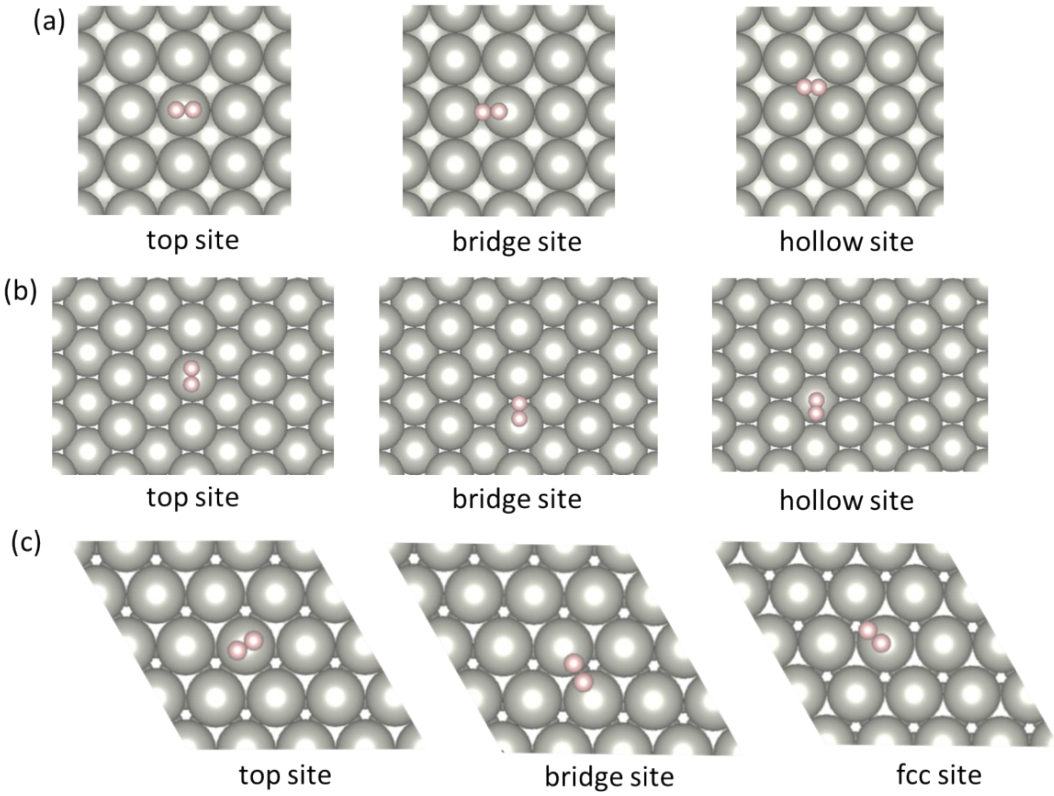

Fig. S6 Top view of the optimized structures of H_2 adsorbed on Pd (100) surface (a), (110) surface (b) and (111) surface (c).

Table S2 The adsorption energies of H_2 on Pd surface at different sites labeled in Fig. S6.

	top site	**bridge site**	**hollow/fcc site**
(100)	-0.348	-0.353	0.007
(110)	-0.433	-0.415	0.001
(111)	-0.251	-0.102	-0.235

Ⅳ.References

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Ⅴ. Captions for Movie

Movie S1. The in situ shape evolution of the cubic Pd NC at 200℃ in 1 bar O_2projected along the [001] direction (2 times faster).