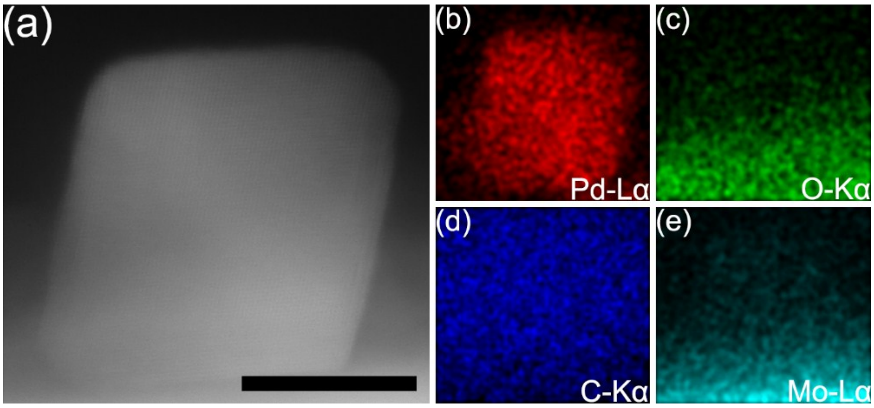
Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information (ESI)

In-situ TEM study of the surface oxidation of palladium nanocrystals assisted by electron irradiation

Dejiong Zhang,[a] Chuanhong Jin,*[a] He Tian,[a] Yalin Xiong,[a] Hui Zhang,[a] Peisheng Qiao,[b] Jie Fan,[b] Ze Zhang,[a] Z. Y. Li*[c,a] and Jixue Li*[a]

[a.] *State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang, 310027, P. R. China. E-mail: chhjin@zju.edu.cn, jx_li@zju.edu.cn*
[b.] *Key Lab of Applied Chemistry of Zhejiang Province, Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang, 310027, P. R. China*
[c.] *Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham, B152TT, United Kingdom. E-mail: z.li@bham.ac.uk*



Element	series	Net	[norm. wt.%]	[norm. at.%]	Error in wt.% (3 Sigma)
Oxygen	K-series	6792	0.81	0.64	0.15
Carbon	K-series	80913	94.01	98.70	8.59
Palladium	L-series	15438	1.86	0.22	0.63
Molybdenum	L-series	29506	3.32	0.44	1.07
		total	100	100	

Fig. S1 More detailed EDS mapping results corresponding the one in Fig. 1. (a)-(e): the HAADF, the mapping of Pd-Lα, O-Kα, C-kα, and Mo-Lα, respectively. The scale bar is 10 nm. The table gave the quantitation analysis of listed elements.

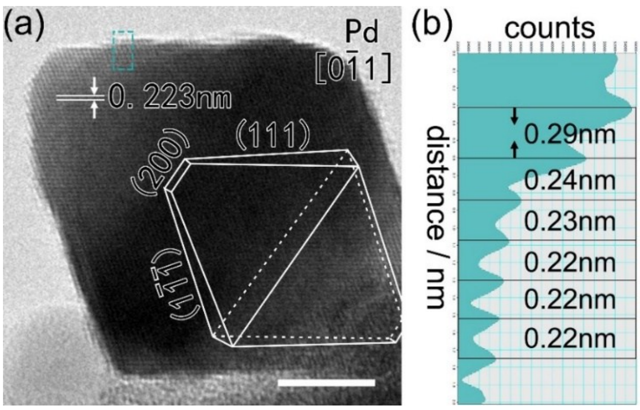


Fig. S2 (a) HRTEM characterization the octahedral palladium nanocrystal, which was enclosed by {100} and {111} facets in a viewing direction of [01]. The schematic diagram in inset showed the three-dimensional visualization of octahedron structure with two vertices truncated. The scale bar is 5 nm. (b) Line profile analysis of the step edge region on Pd(111) planes, corresponding the square with dash lines in Fig. S2a. The error bar is ±0.01 nm.

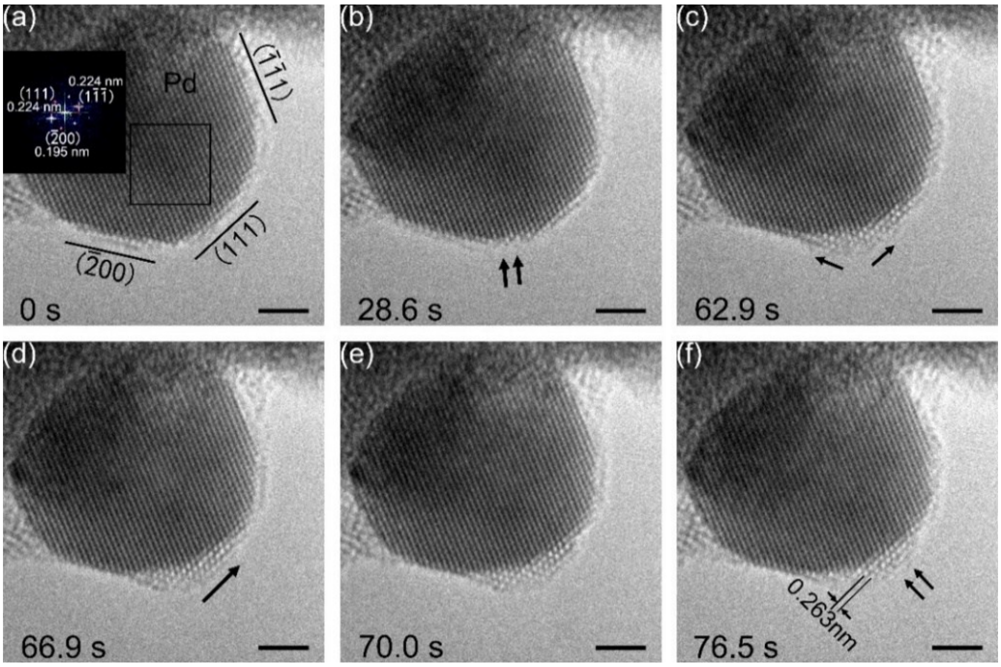


Fig. S3 Another example of a spherical Pd nanoparticle proceeded similar surface oxidation evolutions induced by the electron beam irradiation. The electron beam intensity was 1.9 A/cm^2 and the oxygen partial pressure was 3.0×10^{-2} Pa. The oxidation started at the vertex sites of Pd(111) and Pd(00) planes. Finally, the PdO oxide of about four layers was formed on Pd(111) surface at 76.5 s. The scale bars are 2 nm.

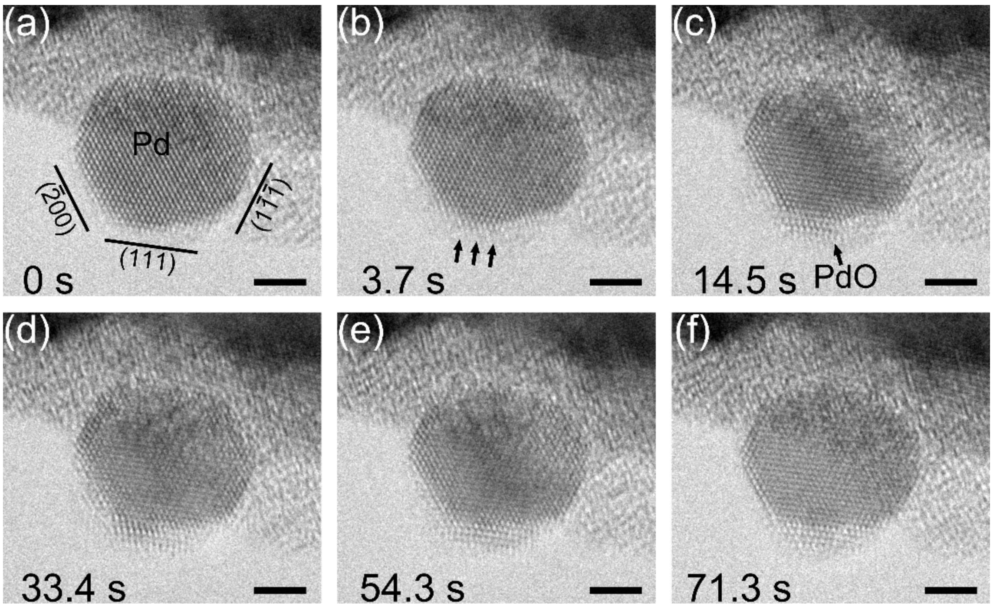


Fig. S4 Time sequential HRTEM images showing the *in-situ* beam induced oxidation of a spherical Pd nanoparticle under oxygen partial pressure of 5.0×10^{-2} Pa. The electron beam intensity was 1.8 A/cm^2. The scale bars are 2 nm.

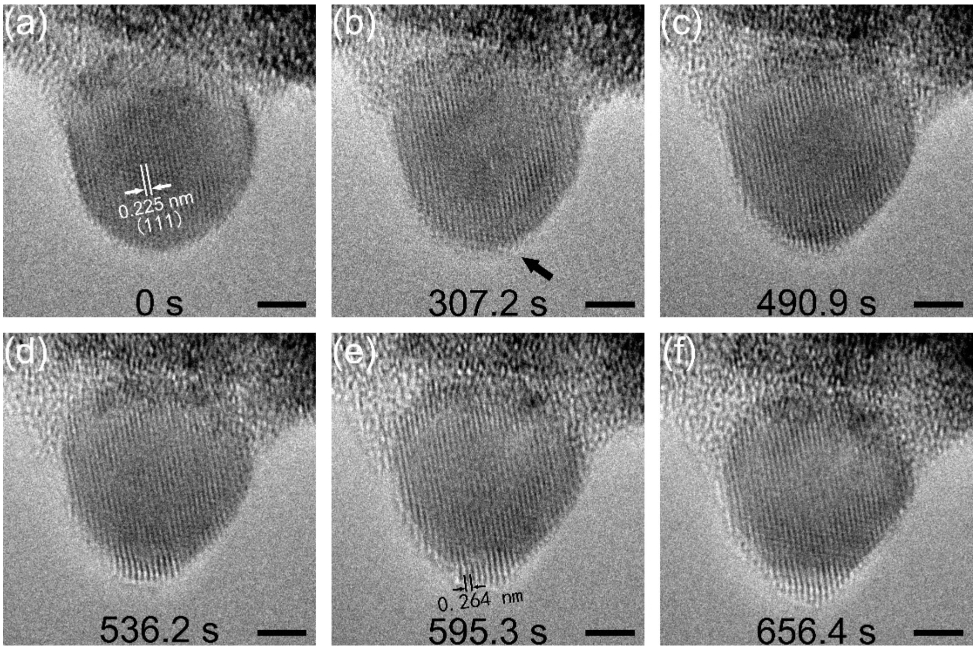


Fig. S5 Time sequential HRTEM images of the oxidation results at a low electron dose irradiation. The electron beam intensity was 0.6 A/cm^2 and the oxygen partial pressure was 1.9×10^{-4} Pa. The scale bars are 2 nm.

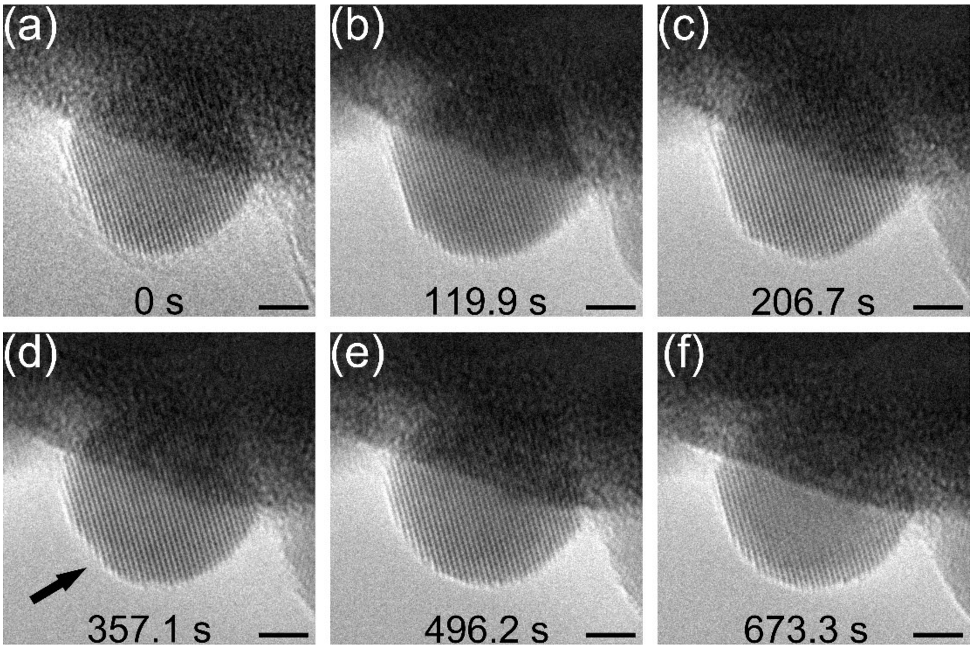
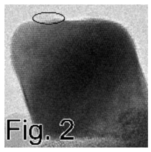
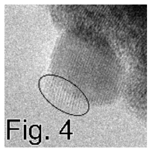
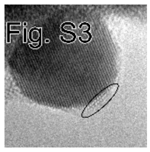
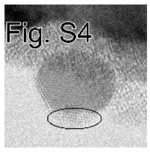
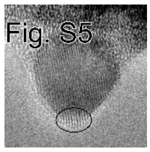
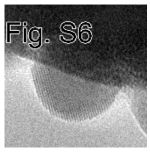


Fig. S6 Time sequential HRTEM images showing the electron beam irradiation results on a spherical Pd nanoparticle in nitrogen gas partial pressure of 9.8×10^{-2} Pa. The electron beam intensity was at 3.9 A/cm^2. The electron irradiation was found to have knock-on damages on surface atoms, especially the atoms at vertex sites pointed by the black arrow. In N_2 ambient, no observed oxidation occurred. The scale bars are 2 nm.

Table S1 Listed table for the *in-situ* irradiation experiments given in the maintext and ESI

No.	Morphology and Size	Gas and Pressure	E-beam Intensity	t_1 (s)	t_2 (s)	area ratio	HRTEM Results
①	Octahedron ~20 nm	O_2 6.8×10^{-5} Pa	9.5 A/cm^2	41.6	258.1	1.3%	
②	Sphere ~7 nm	O_2 1.9×10^{-4} Pa	3.3 A/cm^2	185.5	386.3	20.6%	
③	Sphere ~9 nm	O_2 3.0×10^{-2} Pa	1.9 A/cm^2	28.6	76.5	4.9%	
④	Sphere ~7 nm	O_2 5.0×10^{-2} Pa	1.8 A/cm^2	3.7	71.3	13.4%	
⑤	Sphere ~8 nm	O_2 1.9×10^{-4} Pa	0.6 A/cm^2	307.2	656.4	9.4%	
⑥	Sphere ~ 7 nm	N_2 9.8×10^{-2} Pa	3.9 A/cm^2	—	673.3	—	

- t_1: initial reaction time
- t_2: total observed reaction time
- area ratio = (oxide area marked by oval)/(the remaining Pd area), the estimation was all based on projected area, since the shape and thickness of formed oxide were unknown.

Table S2 Conclusions for the factors that affected the irradiation oxidation experiments

Factors		Conclusions
size	①/②	Smaller sized nanocrystal had higher reaction rate and larger extent of oxide formation.
O_2 partial pressure	②/③④	Higher O_2 partial pressure speeded up the on-set of oxidation and accelerated the oxidation reaction rate even at a lower electron dose.
E-beam intensity	②/⑤	Lower e-beam intensity proceeded lower oxidation reaction rate.
O_2 & N_2	②/⑥	In N_2 ambient, no observed oxidation occurred.

Table S3 A list of lattice spacings of Pd(111)

$d_{(111)}$ / nm	particles size	Synthesis method	Characterization method	references
0.2245	powder	—	diffractometer	[1]
0.23	5 nm	magnetron sputtering	STEM	[2]
0.225	3-5 nm	gas-aggregated sputtering	TEM	[3]
0.223	4.5 nm	oleylamine-mediated synthesis	TEM	[4]
0.224	15 nm	galvanic surface replacement reaction	TEM	[5]
0.224	4.8±0.5 nm	solution method	TEM	[6]
0.223±0.005 **0.224±0.008**	~20 nm ~7 nm	solution method	TEM	this work

- STEM: scanning transmission electron microscopy
- TEM: transmission electron microscopy

Table S4 Crystallographic parameters for palladium oxides

Composition	Crystal system	Space Group	lattice parameters (nm)			references
			a	b	c	
PdO	Tetragonal	P42/mmc (131)	0.3043	—	0.5330	[7]
	Tetragonal	I4/mmm (139)	0.2967	—	0.5315	[8]
	Face-centered cubic	Fm-3m (225)	0.5650	—	—	[9]
PdO_2	Tetragonal	P42/mnm (136)	0.4483	—	0.3101	[10]
$Pd_{0.5}Pd_3O_4$	cubic	Pm-3n (223)	0.5756	—	—	[11]
Pd_2O	cubic	Pn-3m(224)	0.4280	—	—	[12]

Estimation of the temperature rise by electron beam heating

$$\Delta T = \frac{I}{\pi \kappa e}\left(\frac{\Delta E}{d}\right)\ln\frac{b}{r_0}$$

$$\frac{dE}{dx} = \frac{4\pi}{m_e c^2}\cdot\frac{n}{\beta^2}\cdot\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\cdot\left[\ln\left(\frac{2m_e c^2\beta^2}{I_e\cdot(1-\beta^2)}\right)-\beta^2\right]$$

$$n = \frac{N_A\cdot Z\cdot\rho}{M_\mu}$$

The temperature rise on palladium nanocrystal resulting from electron beam irradiation has been estimated according to the equations listed above.[13,14] ΔT is the expected temperature rise, I is the beam current, κ is the thermal conductivity of the sample, e is the electron charge, m_e is the rest mass, b is the radius of the heat sink, r_0 is the beam radius, c is the speed of light, $\beta = v/c$ (v is the velocity of electrons), ε_0 is the vacuum permittivity, I_e is the mean excitation energy of the sample, Z is atomic number, N_A is the Avogadro number, ρ is the density and M_μ is the Molar mass. The values of parameters are summarized in the Table below. The temperature rise on palladium nanocrystals was calculated less than 1 K. The present was a simplified estimation, even by incorporating more different models, no big difference on temperature raise was found.

Table S3 values of parameters for palladium used in the above equations

Z	ρ **(Kg/m³)**	I_e **(eV)**	M_μ **(g/mol)**	κ **(W/m/K)**	m_e **(Kg)**	ε_0 **(F/m)**
46	12.02×10^3	460	106.4	71.8	9.11×10^{-31}	8.85×10^{-12}
v **(m/s)**	c **(m/s)**	β	b **(mm)**	r_0 **(nm)**	I **(nA)**	ΔT **(K)**
2.33×10^8	3.0×10^8	0.78	1.5	100	<10	<1

References

1 Pd (T = 300 K) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2012" in SpringerMaterials (http://materials.springer.com/isp/crystallographic/docs/**sd_0451914**)

2 D. Pearmain, S. J. Park, A. Abdela, R. E. Palmer and Z. Y. Li, *Nanoscale*, 2015, **7**, 19647-19652.

3 P. Grammatikopoulos, C. Cassidy, V. Singh and M. Sowwan, *Sci. Rep.,* 2014, **4**, 5779.

4 V. Mazumder and S. Sun, *J. Am. Chem. Soc.*, 2009, **131**, 4588-4589.

5 Y. Guo, Y. T. Xu, G. H. Gao, T. Wang, B. Zhao, X. Z. Fu, R. Sun and C. P. Wong, *Catal. Commun.,* 2015, **58**, 40-45.

6 Y. Piao, Y. Jang, M. Shokouhimehr, I. S. Lee and T. Hyeon, *Small*, 2007, **3**, 255-260.

7 PdO (T = 300 K) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2012" in SpringerMaterials (http://materials.springer.com/isp/crystallographic/docs/**sd_0557856**)

8 PdO hp Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2012" in SpringerMaterials (http://materials.springer.com/isp/crystallographic/docs/**sd_1301469**)

9 PdO Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2012" in SpringerMaterials (http://materials.springer.com/isp/crystallographic/docs/**sd_0260839**)

10 PdO_2 Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2012" in SpringerMaterials (http://materials.springer.com/isp/crystallographic/docs/**sd_0376377**)

11 $Pd_{0.5}Pd_3O_4$ ($Pd_{3.5}O_4$) Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2012" in SpringerMaterials (http://materials.springer.com/isp/crystallographic/docs/**sd_0541973**)

12 Pd_2O Crystal Structure: Datasheet from "PAULING FILE Multinaries Edition – 2012" in SpringerMaterials (http://materials.springer.com/isp/crystallographic/docs/**sd_0260836**)

13 Y. Jiang, Y. Wang, Y. Y. Zhang, Z. Zhang, W. Yuan, C. Sun, X. Wei, C. N. Brodsky, C.-K. Tsung, J. Li, X. Zhang, S. X. Mao, S. Zhang and Z. Zhang, *Nano Res.*, 2014, **7**, 308-314.

14 R. F. Egerton, P. Li and M. Malac, *Micron*, 2004, **35**, 399-409.