Supporting Information

Surface Facet of Palladium Nanocrystals: a Key Parameter to the Activation of Molecular Oxygen for Organic Catalysis and Cancer Treatment

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Experimental Details

Nanocrystal Synthesis. The Pd nanocubes were synthesized according to our previously reported protocol:[1] they were prepared as follows: 0.105 g of poly(vinyl pyrrolidone) (PVP, M.W.=55,000, Sigma-Aldrich, 856568-100g), 0.060 g of L-ascorbic acid (Sigma-Aldrich, A0278-25g) and 0.300 g of KBr were dissolved in 8 mL of deionized water at room temperature. The solution was placed in a 3-neck flask (equipped with a reflux condenser and a magnetic Teflon-coated stirring bar) and heated in air at 80 ºC for 5 min. Meanwhile, 0.065 g of potassium palladium(II) chloride (K_2PdCl_4, Aladdin, 1098844-1g) was dissolved in 3 mL of deionized water at room temperature. The Pd stock solution was then injected into the flask through a syringe pump. Heating of the reaction at 80 ºC was continued in air for 3 h. The samples were washed with acetone and then with ethanol three times to remove most of the PVP and other molecules by centrifugation. For the Pd octahedrons, they were prepared as follows: 0.105 g of poly(vinyl pyrrolidone) (PVP, M.W.=55,000, Sigma-Aldrich, 856568-100g), 0.060 g of citric acid (Sigma-Aldrich, 251275-100g) and 0.060 g of L-ascorbic acid (Sigma-Aldrich, A0278-25g) were dissolved in 8 mL of deionized water at room temperature. The solution was placed in a 3-neck flask (equipped with a reflux condenser and a magnetic Teflon-coated stirring bar) and heated in air at 120 ºC for 5 min. Meanwhile, 0.065 g of potassium palladium(II) chloride (K_2PdCl_4, Aladdin, 1098844-1g) was dissolved in 3 mL of deionized water at room temperature. The Pd stock solution was then injected into the flask through a syringe pump at 5 mL/h. Heating of the reaction at 120 ºC was continued in air for 3 h. The samples were washed with acetone and then with ethanol three times to remove most of the PVP and other molecules by centrifugation.

Characterizations. The morphologies of nanocrystals were examined by transmission electron microscopy (TEM), using a JEOL JEM-2010 LaB6 high-resolution transmission electron microscope operated at 200 kV. High-resolution TEM (HRTEM) images were taken on a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV. The concentrations of Pd nanocrystals were measured as follows: the nanocrystals were dissolved with a mixture of HCl and HNO_3 (3:1, volume ratio) which was then diluted with 1%

HNO_3. The concentration of palladium was then measured with a Thermo Scientific PlasmaQuad 3 inductively-coupled plasma mass spectrometry (ICP-MS).

Supplementary Table S1. Calculation for the numbers of Pd atoms exposed on the surface of nanocrystals.*

	m [a]	N_t [b]	N_s [c]	Percentage of surface atoms	$N_{e\&c}$ [d]	Percentage of edge and corner atoms
~ 14 nm Nanocubes	36	178956	14702	8.22%	416	2.32‰
~ 6 nm Octahedrons	23	8119	1938	23.87%	258	31.78‰
~ 7 nm Nanocubes	19	25327	3890	15.36%	212	8.37‰
~ 20 nm Nanocubes	50	485150	28814	5.94%	584	1.20‰
~ 21 nm Octahedrons	78	316394	23718	7.35%	918	2.90‰

* Calculations were performed by assuming that all the nanocrystals had perfect cubic or octahedral morphologies.[2] [a] m, defined as the number of atoms lying on an equivalent edge (corner atoms included). [b] N_t, the total number of atoms (Nanocubes: $N_t = 4m^3-6m^2+3m$; Octahedrons: $N_t = ⅓m(2m^2+1)$). [c] N_s, the number of surface atoms (Nanocubes: $N_s = 12m^2-24m+14$; Octahedrons: $N_s = 4m^2-8m+6$). [d] $N_{e\&c}$, the number of edge and corner atoms (Nanocubes: $N_{e\&c} = 12(m-2)+8$; Octahedrons: $N_{e\&c} = 12(m-2)+6$).

Supplementary Table S2. Simulation results for total energy and adsorption energy of O_2 on Pd(100) facet in different adsorption configurations corresponding to Figure S7.

O_2 on Pd(100)	**b1**	**b2**	**t1**	**t2**	**t3**	**t4**
total energy / eV	-849.17	-849.46	-849.52	-849.64	-848.64	-848.67
E_{adsorb} **/ eV**	-1.01	-1.30	-1.36	-1.48	-0.48	-0.51
magnetic moment of O_2 / μB	0.486	0.028	0.025	0.017	0.978	0.993

$$E_{adsorb} = E_{O_2\ on\ Pd} - E_{O_2} - E_{Pd}$$

Supplementary Table S3. Simulation results for total energy and adsorption energy of O_2 on Pd(111) facet in different adsorption configurations corresponding to Figure S8.

O_2 on Pd (111)	b1	b2	h1	h2	h3	h4	t1	t2
total energy / eV	-423.21	-423.89	-423.69	-423.87	-423.83	-423.80	-423.33	-423.42
E_{adsorb} **/ eV**	0.05	-0.63	-0.43	-0.61	-0.57	-0.54	-0.07	-0.16
magnetic moment of O_2 / μB	1.515	0.549	0.335	0.536	0.532	0.295	0.976	0.933

$$E_{adsorb} = E_{O_2\ on\ Pd} - E_{O_2} - E_{Pd}$$

Supplementary Table S4. Oxidation of glucose by Pd nanocrystals with molecular oxygen at 50ºC.

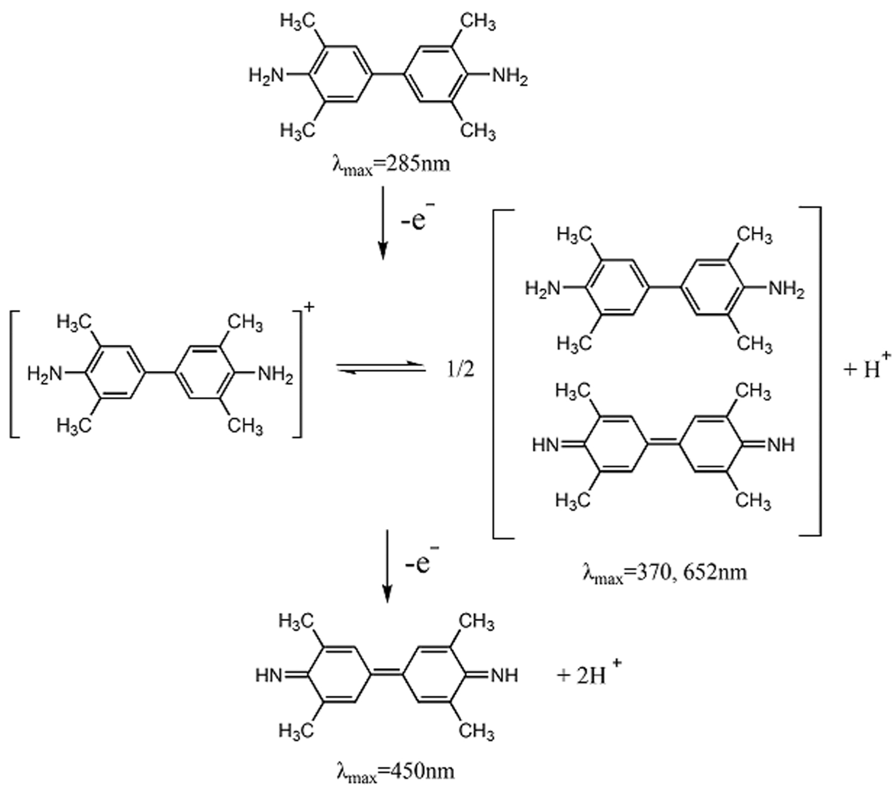
catalyst	mol_{surf}‰	mol_{total}%	time (min)	yield%	TON_{surf}	TON_{total}
14 nm nanocubes[#]	0.04	0.05	120	8	1908	157
14 nm nanocubes[‡]	0.08	0.1	60	9	1132	93
14 nm nanocubes[‡]	0.08	0.1	120	10	1199	99
14 nm nanocubes	0.8	1.0	60	44	541	44
14 nm nanocubes	0.8	1.0	120	48	585	48
14 nm nanocubes	0.8	1.0	960	53	650	53
14 nm nanocubes	1.6	2.0	30	68	412	34
14 nm nanocubes	1.6	2.0	60	82	498	41
14 nm nanocubes	1.6	2.0	120	85	516	42
14 nm nanocubes[£]	1.6	2.0	120	1	8	1
6 nm octahedrons	0.8	0.3	30	6	68	16
6 nm octahedrons	0.8	0.3	60	8	93	22
6 nm octahedrons	0.8	0.3	120	8	103	24
6 nm octahedrons	1.6	0.7	30	15	92	22
6 nm octahedrons	1.6	0.7	60	24	151	36
6 nm octahedrons	1.6	0.7	120	35	214	51
6 nm octahedrons	2.3	1.0	30	34	141	34
6 nm octahedrons	2.3	1.0	60	52	216	52
6 nm octahedrons	2.3	1.0	120	70	291	70
7 nm nanocubes	1.6	1.0	30	66	424	65
7 nm nanocubes	1.6	1.0	60	76	491	75
7 nm nanocubes	1.6	1.0	120	86	553	85
7 nm nanocubes	3.1	2.0	30	90	291	45
7 nm nanocubes	3.1	2.0	60	99	323	50

7 nm nanocubes	3.1	2.0	120	99	337	52
20 nm nanocubes	1.6	2.7	30	69	430	26
20 nm nanocubes	1.6	2.7	60	83	518	31
20 nm nanocubes	1.6	2.7	120	88	545	32
20 nm nanocubes	1.2	2.0	30	32	271	16
20 nm nanocubes	1.2	2.0	60	40	341	20
20 nm nanocubes	1.2	2.0	120	48	413	25
21 nm octahedrons	1.6	2.2	30	12	73	5
21 nm octahedrons	1.6	2.2	60	24	153	11
21 nm octahedrons	1.6	2.2	120	33	209	15
21 nm octahedrons	0.7	0.5	30	8	155	11
21 nm octahedrons	0.7	0.5	60	11	226	17
21 nm octahedrons	0.7	0.5	120	13	262	19
none			960	0	-	-

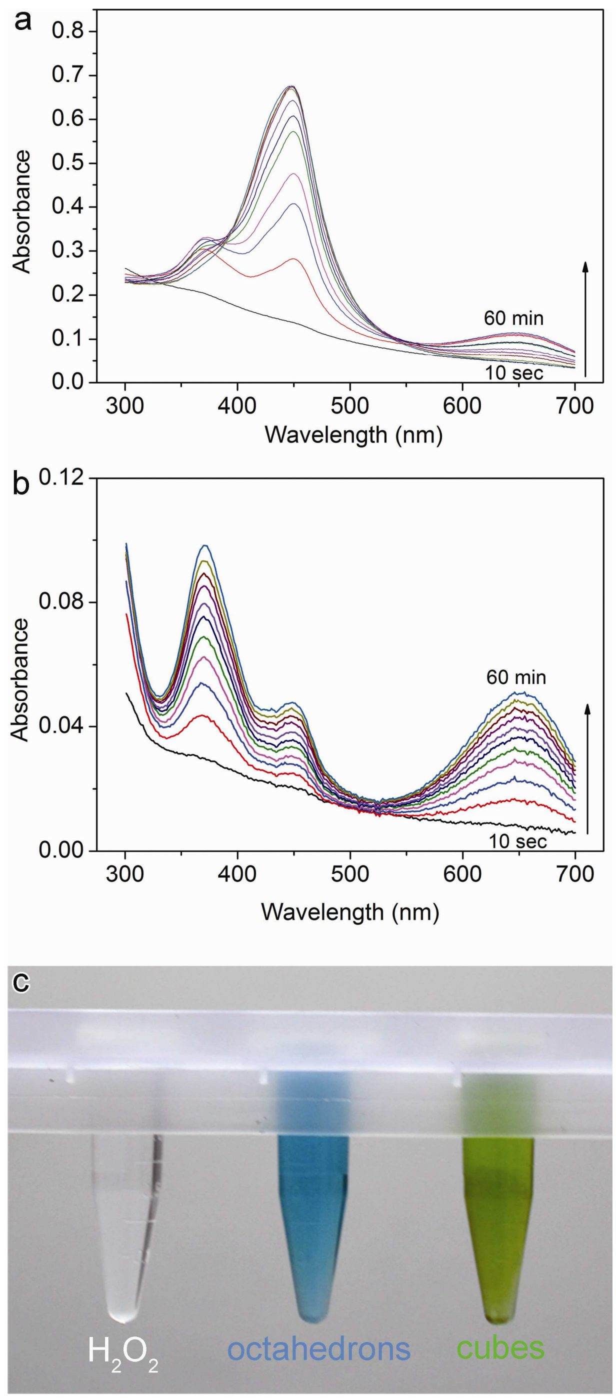
[#] Glucose in H_2O as solvent (300 mM); [‡] glucose in H_2O as solvent (150 mM); [£] Addition of 4 mg carotene as $^1O_2$ scavenger.

Supplementary Table S5. Oxidation of glucose by 14-nm Pd nanocubes (1.6 mol_{suf}‰) with molecular oxygen under illumination of different light sources at 50ºC for 120 min.

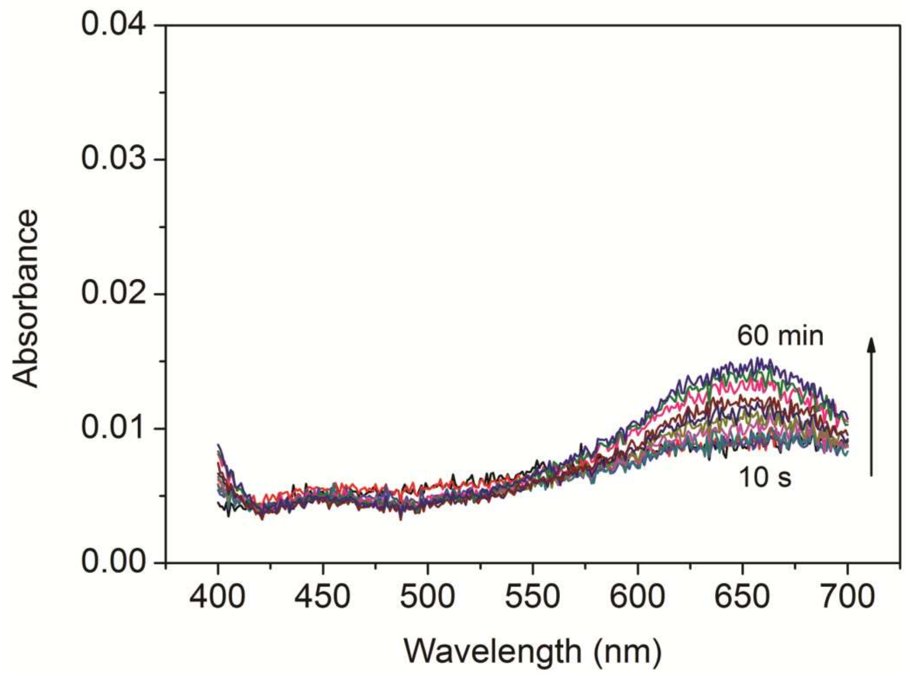
	Dark	**UV**	**Visible-light**
Yield%	83.73	83.66	86.55



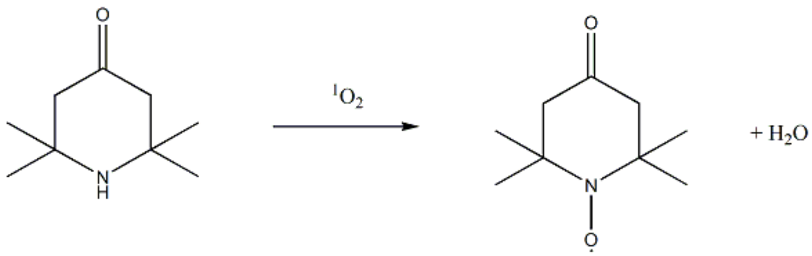
Supplementary Figure S1. Reaction pathway for the oxidation of the benzidine derivative, 3,5,3‘,5’-tetramethylbenzidin (TMB).[3]



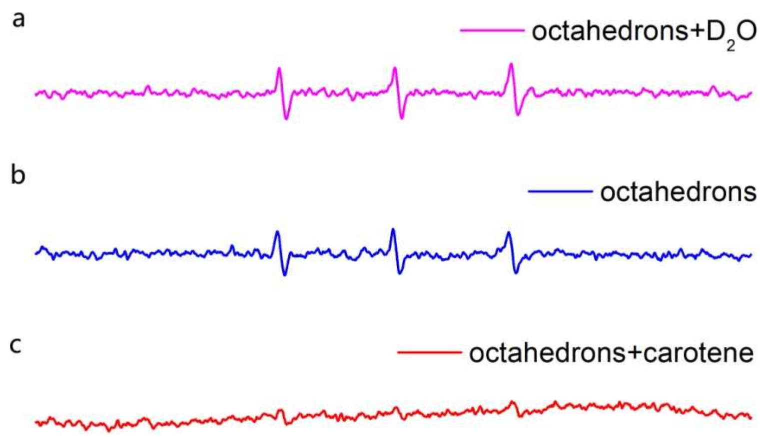
Supplementary Figure S2. UV-vis spectra of the samples after mixing TMB solution with different Pd nanocrystals: (a) nanocubes and (b) octahedrons. (c) Photographs of TMB solution mixed with H_2O_2, Pd octahedrons and nanocubes at 10 ˚C for 24 h, respectively.



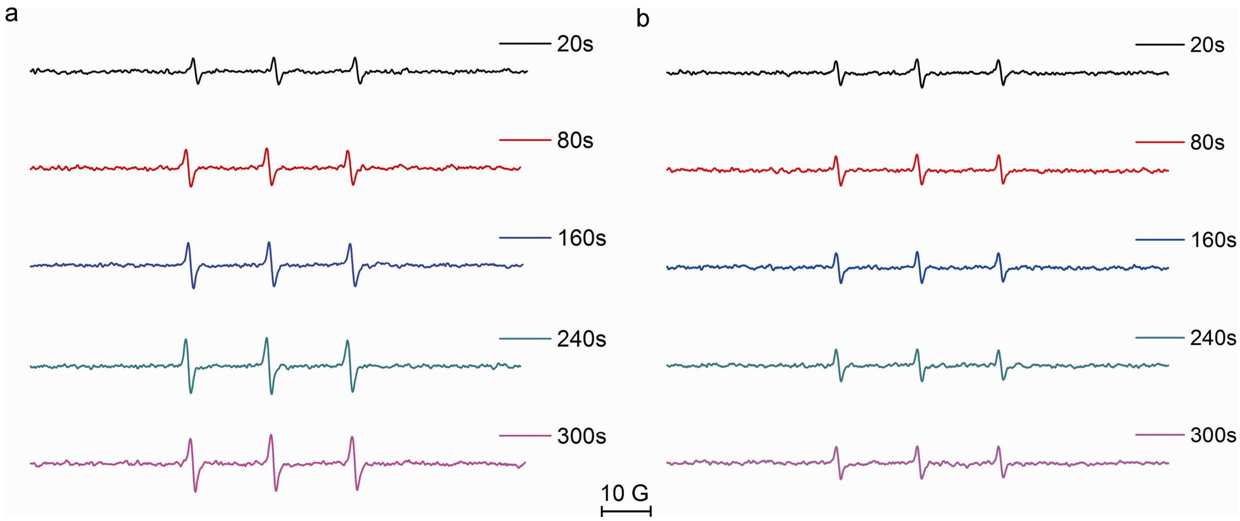
Supplementary Figure S3. UV-vis spectra of the samples after mixing TMB solution with hydrogen peroxide.



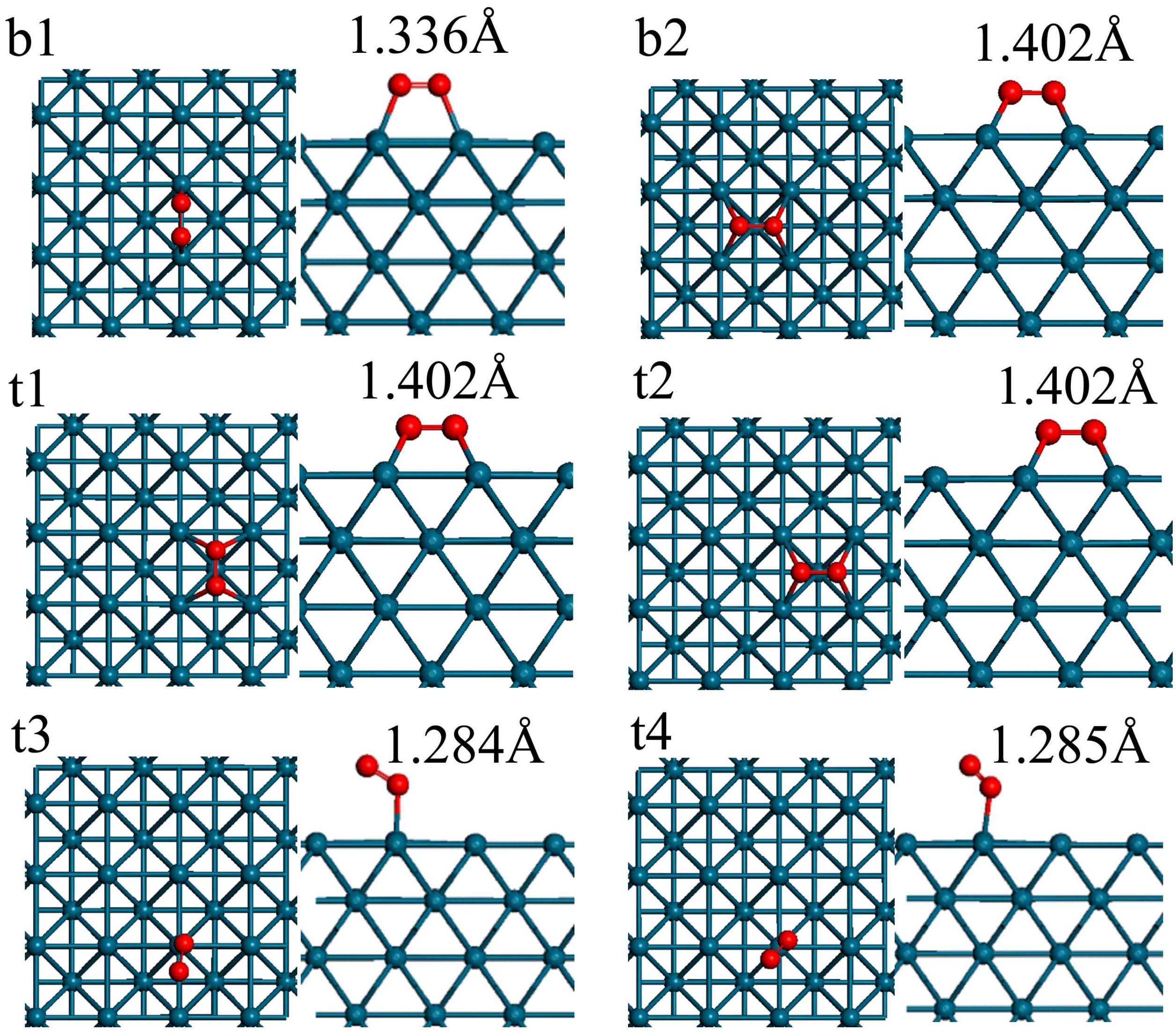
Supplementary Figure S4. Reaction pathway for the oxidation of the 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TMP).[4]



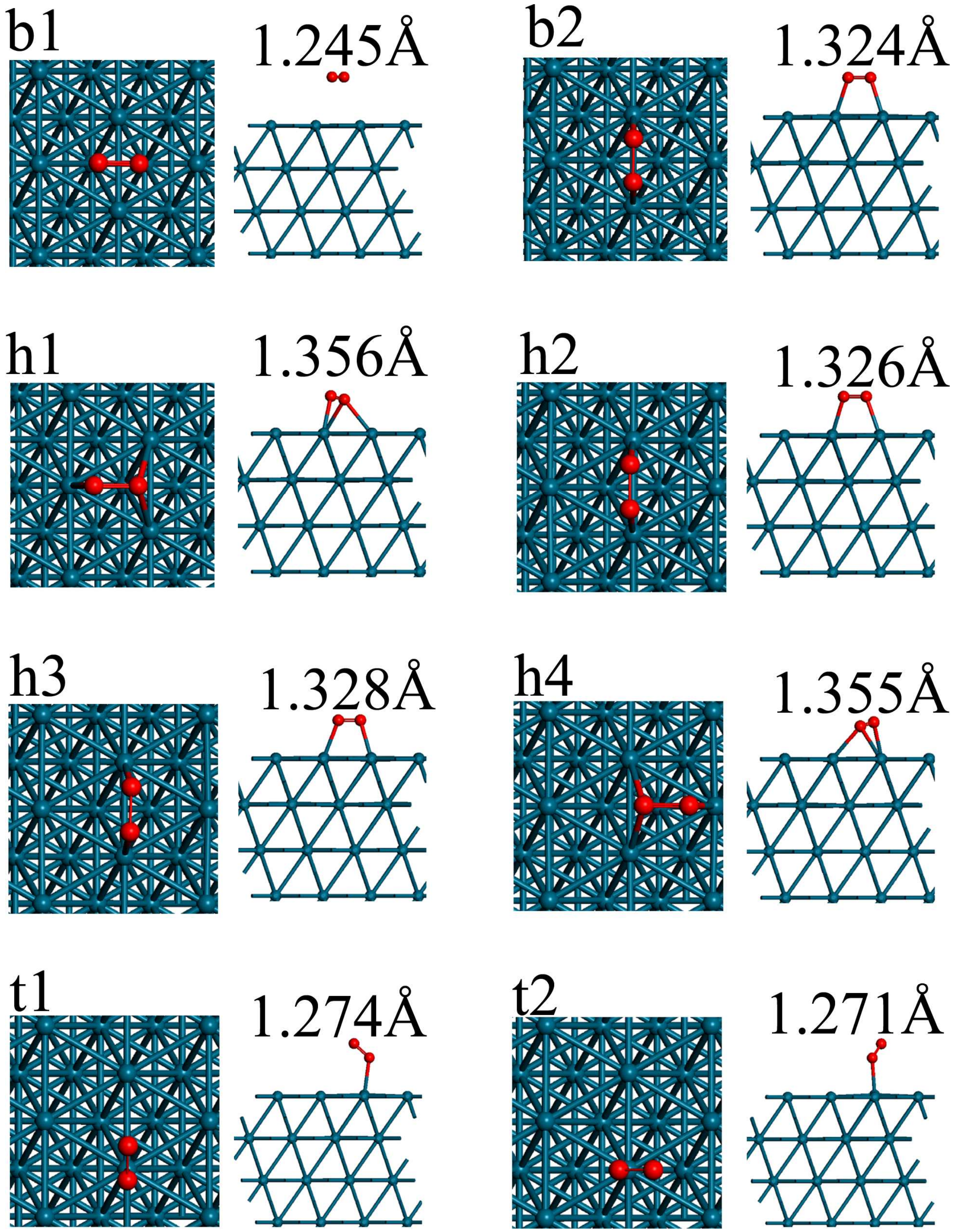
Supplementary Figure S5. ESR spectra of the samples after mixing 4-oxo-TMP solution with Pd octahedrons in different conditions: (a) in D_2O; (b) in H_2O; (c) in the presence of carotene.



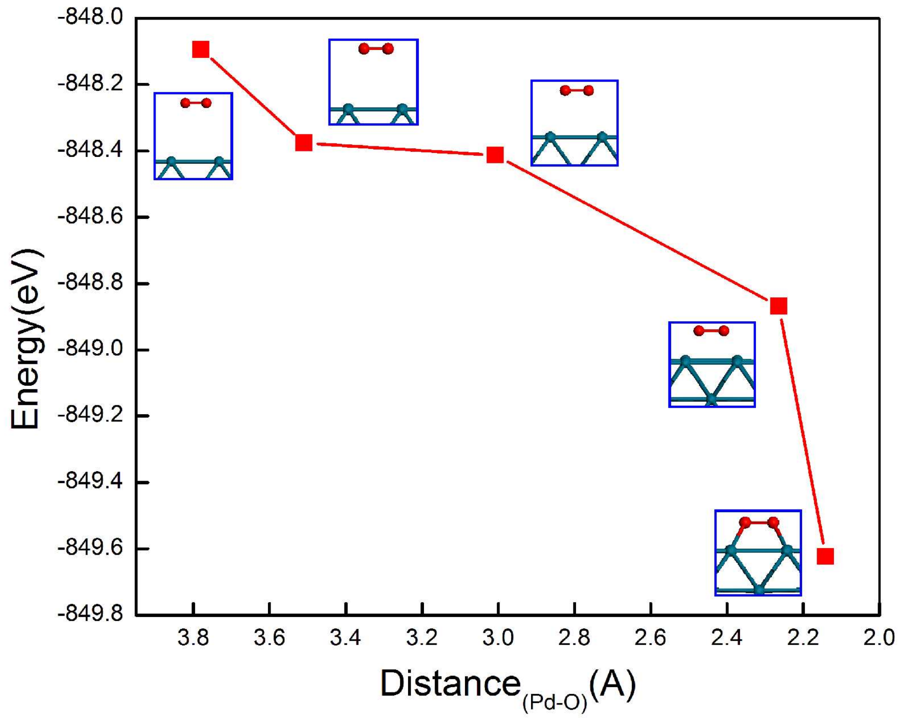
Supplementary Figure S6. ESR spectra of the samples after mixing 4-oxo-TMP solution with Pd nanocubes under irradiation of visible light source (ν > 400 nm) for different time (20-300 sec) in different conditions: (a) without thermostatic adjustment; (b) with thermostatic maintenance at 20ºC.



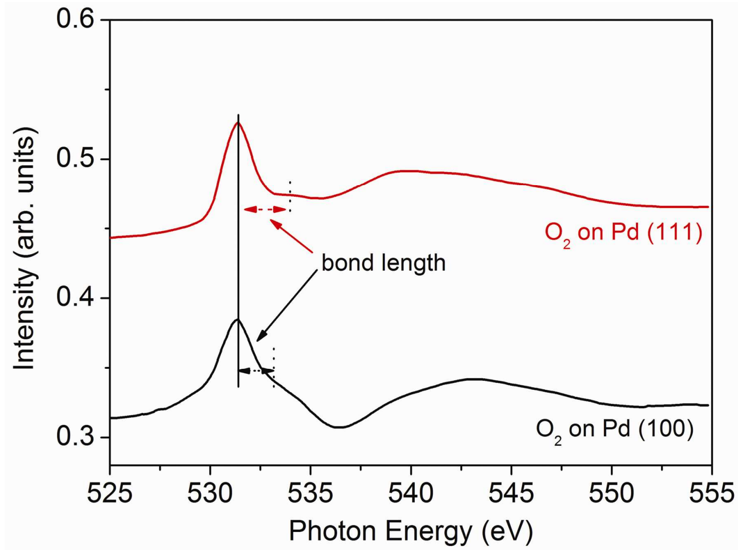
Supplementary Figure S7. Six adsorption configurations of O_2 on Pd(100) facet in the simulation. The spheres in dark cyan color and red color denote the Pd and O atoms, respectively.



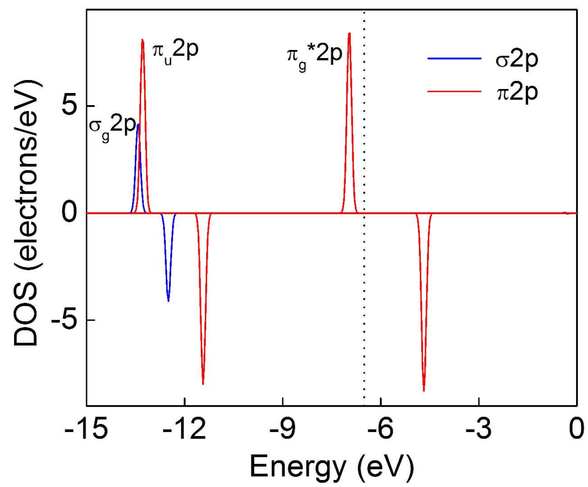
Supplementary Figure S8. Eight adsorption configurations of O_2 on Pd(111) facet in the simulation. The spheres in dark cyan color and red color denote the Pd and O atoms, respectively.



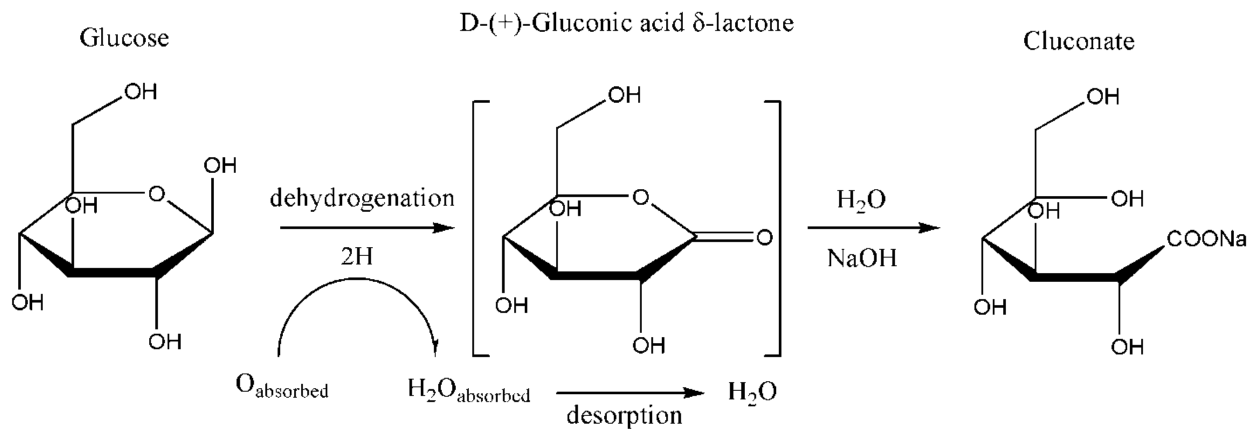
Supplementary Figure S9. Curve showing the evolution of the total energy during the adsorption of oxygen to palladium {100} surface.



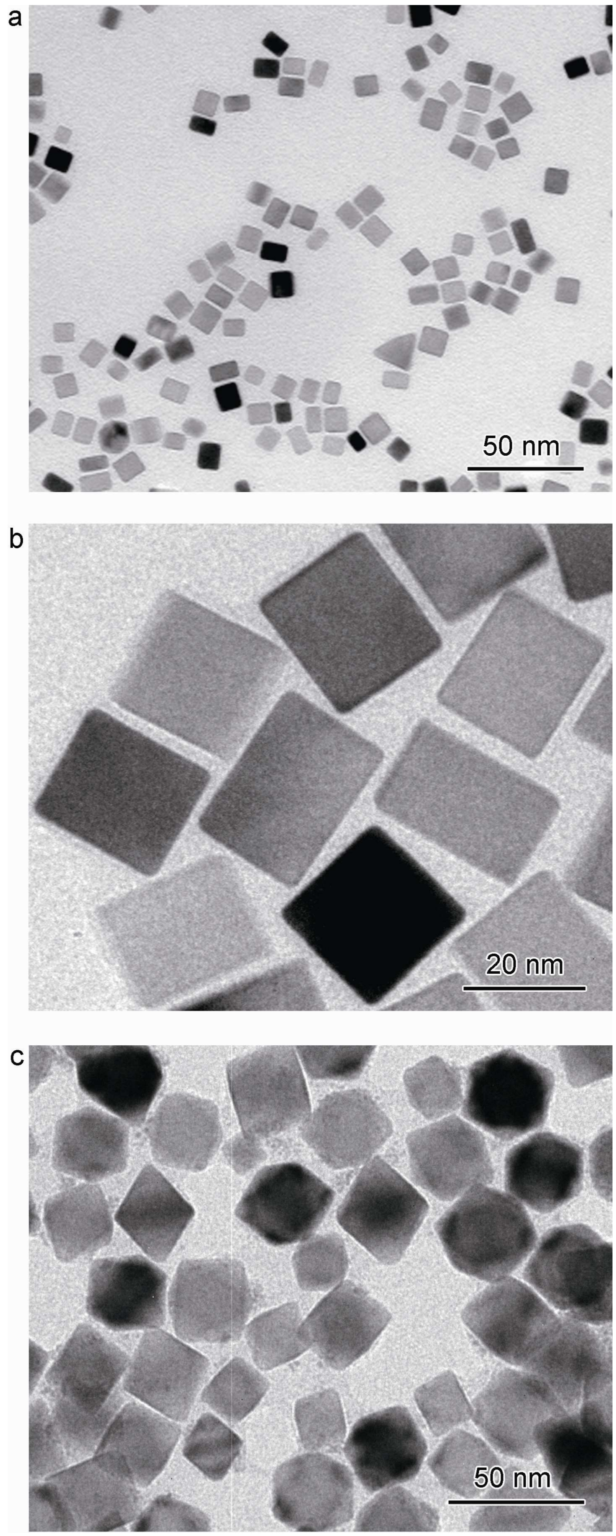
Supplementary Figure S10. O *K*-edge NEXAFS spectra of O_2 on Pd nanocubes and Pd octahedrons.



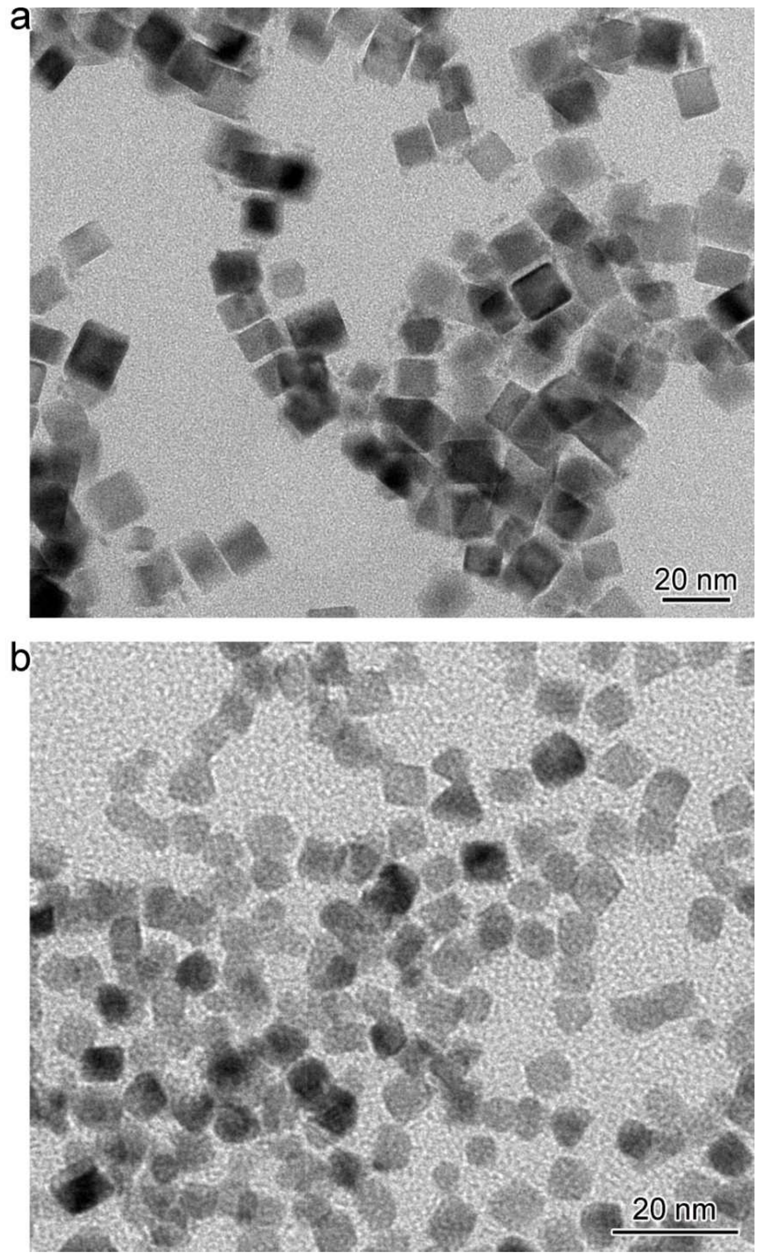
Supplementary Figure S11. The projected density of states (PDOS) diagrams of free molecular O_2.



Supplementary Figure S12. Reaction pathway for the oxidation of glucose.[5]



Supplementary Figure S13. TEM images of the Pd nanocubes and octahedrons at different sizes used in the investigations: (a) 7-nm nanocubes; (b) 20-nm nanocubes; (c) 21-nm octahedrons.



Supplementary Figure S14. TEM images of the Pd nanocrystals in Figure 2 after the oxidation of glucose: (a) nanocubes and (b) octahedrons.

Supplemental References

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