Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Novel PdC monolayer with fully dispersed Pd atoms and rigid carbon backbone: an intrinsic versatile electrocatalyst for overall water-splitting and the corresponding reverse reaction

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Supporting Information (SI)

Supporting Figures

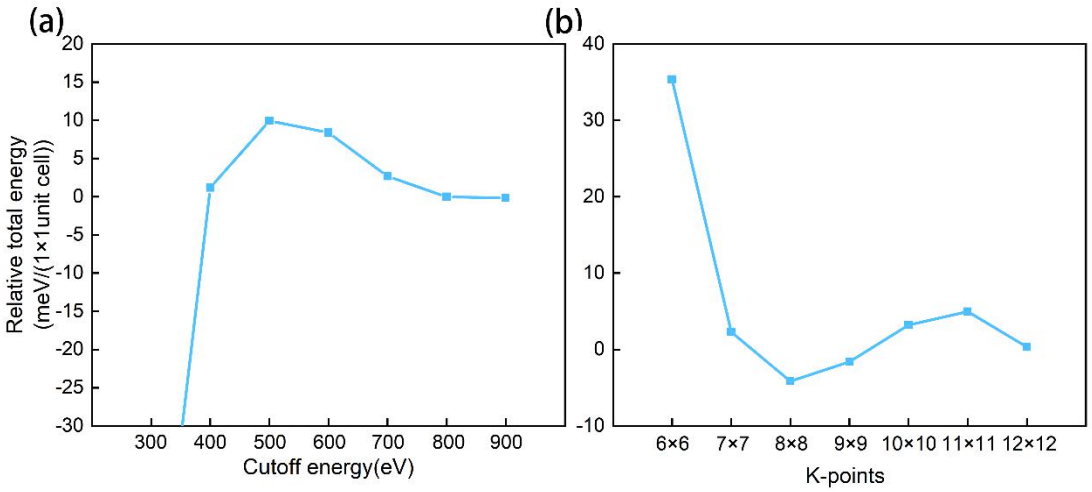

Fig. S1 The relative total energy as a function of (a) cutoff energy and (b) k-points mesh grids of the proposed 2D PdC structure.

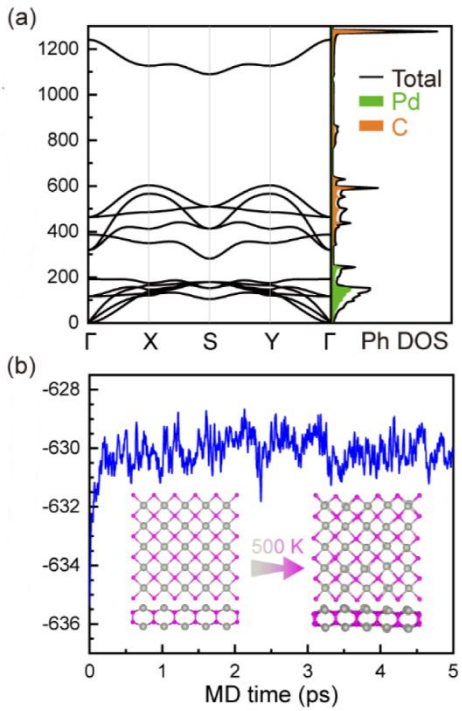

Fig. S2 (a) Phonon spectrum and phonon density of states of the β-PdC. (b) The fluctuation of the total energy of the β-PdC structure as a function of the molecular-dynamic simulation time at 500 K.

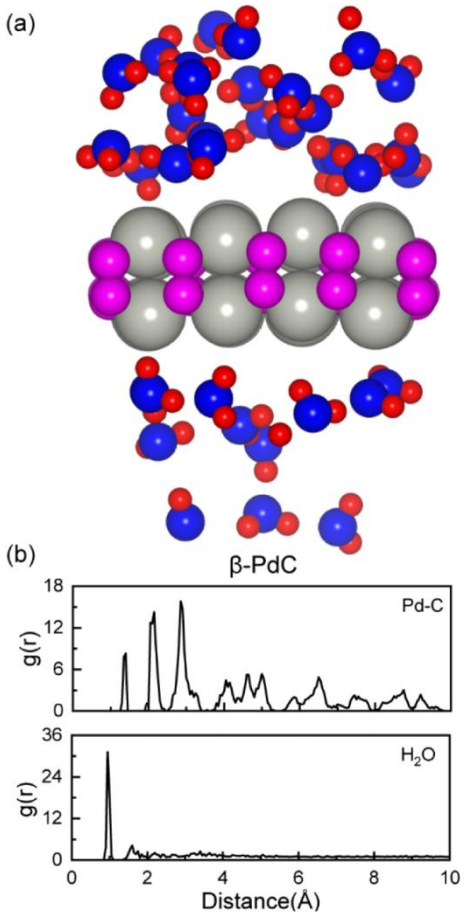

Fig. S3 (a) The structural evolution of β-PdC monolayer in liquid water after the AIMD simulation process at 300 K for 5 ps. (b)The normalized pair correlation functions of g(r) after the AIMD simulation process.

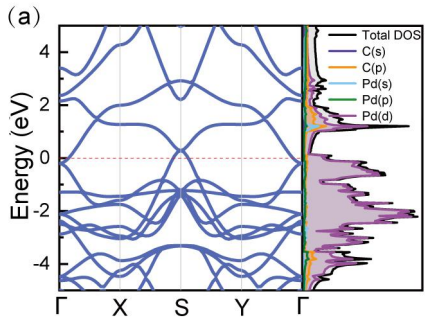

Fig. S4 Band structures and projected DOS of β-PdC monolayers, calculated by PBE functional. Red dashed lines represent the Fermi level at 0 eV.

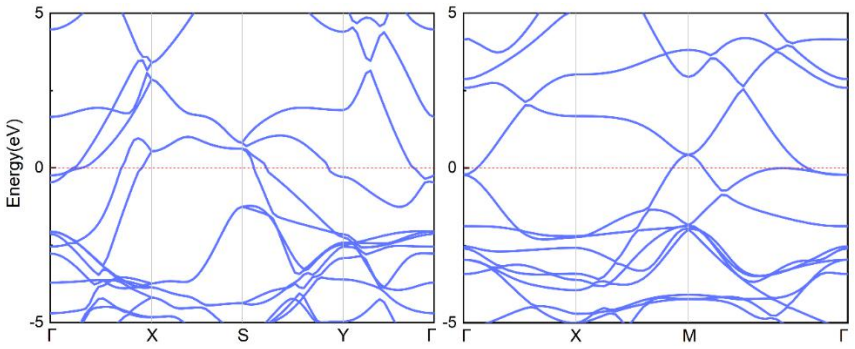

Fig. S5 Band structures of α-PdC and β-PdC with the scheme of HSE06 functional.

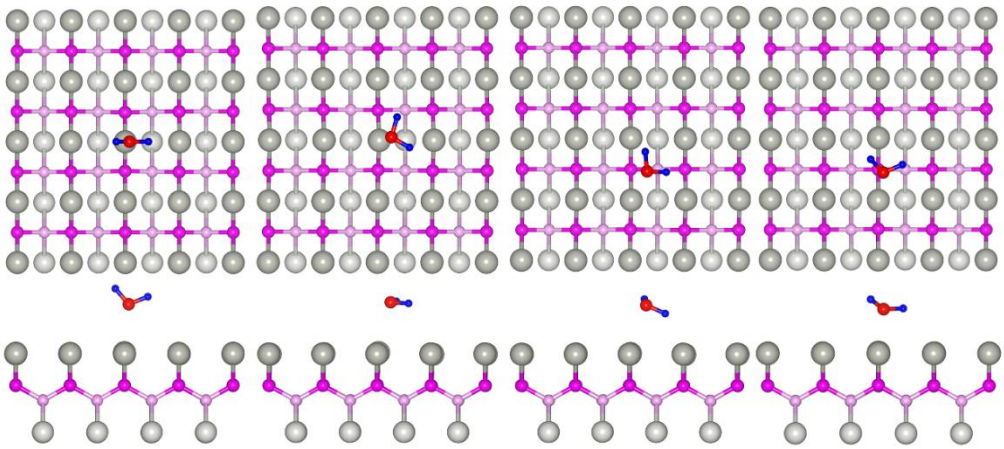

Fig. S6 The structures of the H_2O molecule adsorbed on the α-PdC in Site A, B, C, and D. The blue, gray, and pink balls represent H, Pd, and C atoms, respectively. The following figures adopt the same color code.

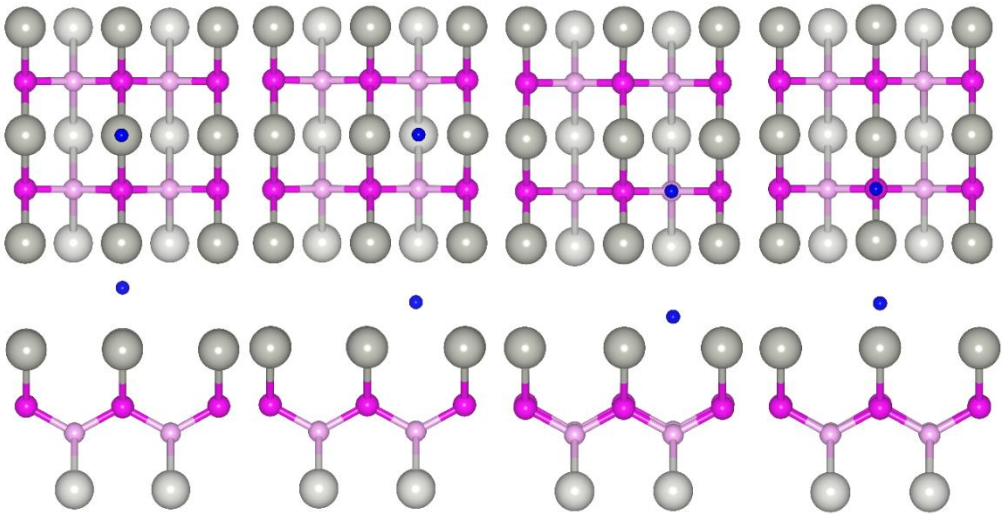

Fig. S7 The structures of the H atom adsorbed on the α-PdC in Site A, B, C, and D.

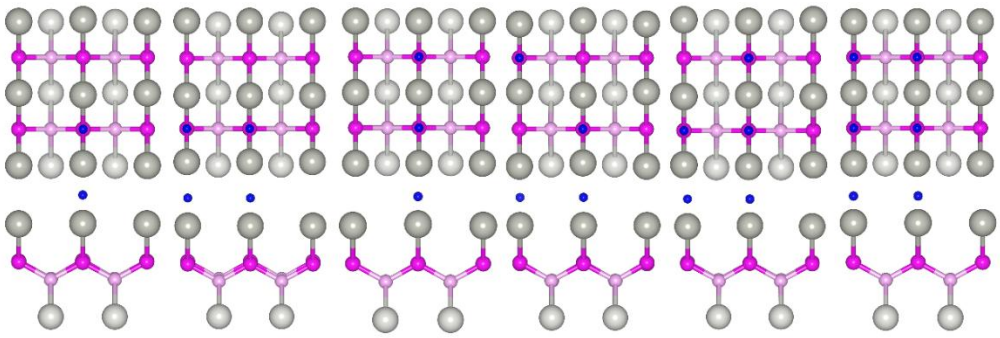

Fig. S8 The optimized structures of α-PdC with different H coverage from 1/4 to 1.

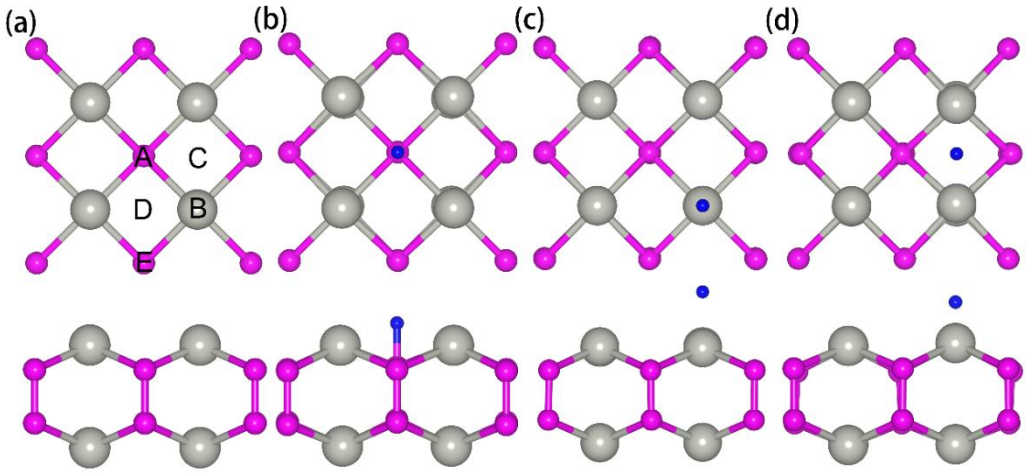

Fig. S9 (a) The β-PdC shown in a 2×2 supercell from the top and side views. (b), (c), and (d) show the structures of the first H atom adsorbs on the β-PdC in different sites as labeled in (a).

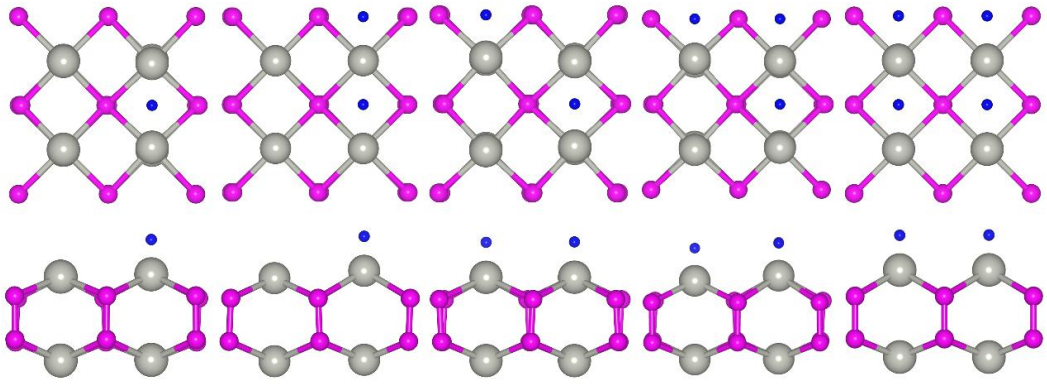

Fig. S10 The optimized structures of H on β-PdC with coverage from 1/4 to 1.

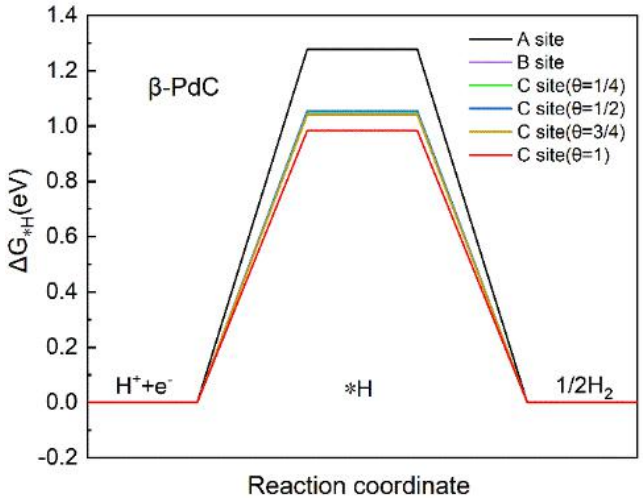

Fig. S11 Free energy diagram for H evolution of β-PdC in different stable sites or with different H coverage at potential U = 0 relative to the standard hydrogen electrode at pH = 0.

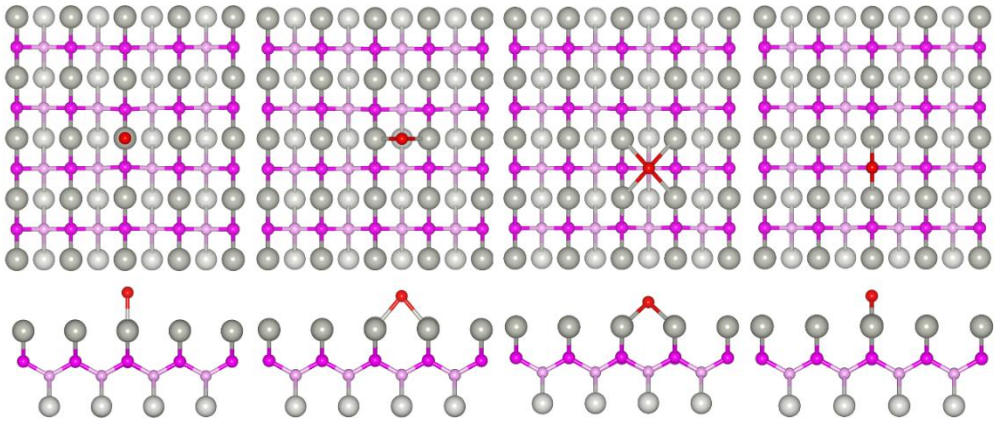

Fig. S12 The intermediate state *O adsorbs on Site A, B, C, and D of α-PdC.

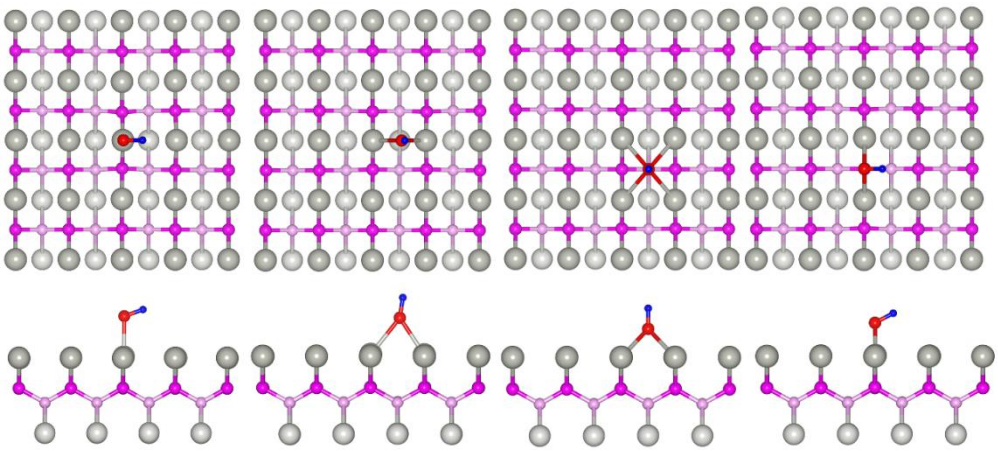

Fig. S13 The intermediate state *OH adsorbs on Site A, B, C, and D of α-PdC.

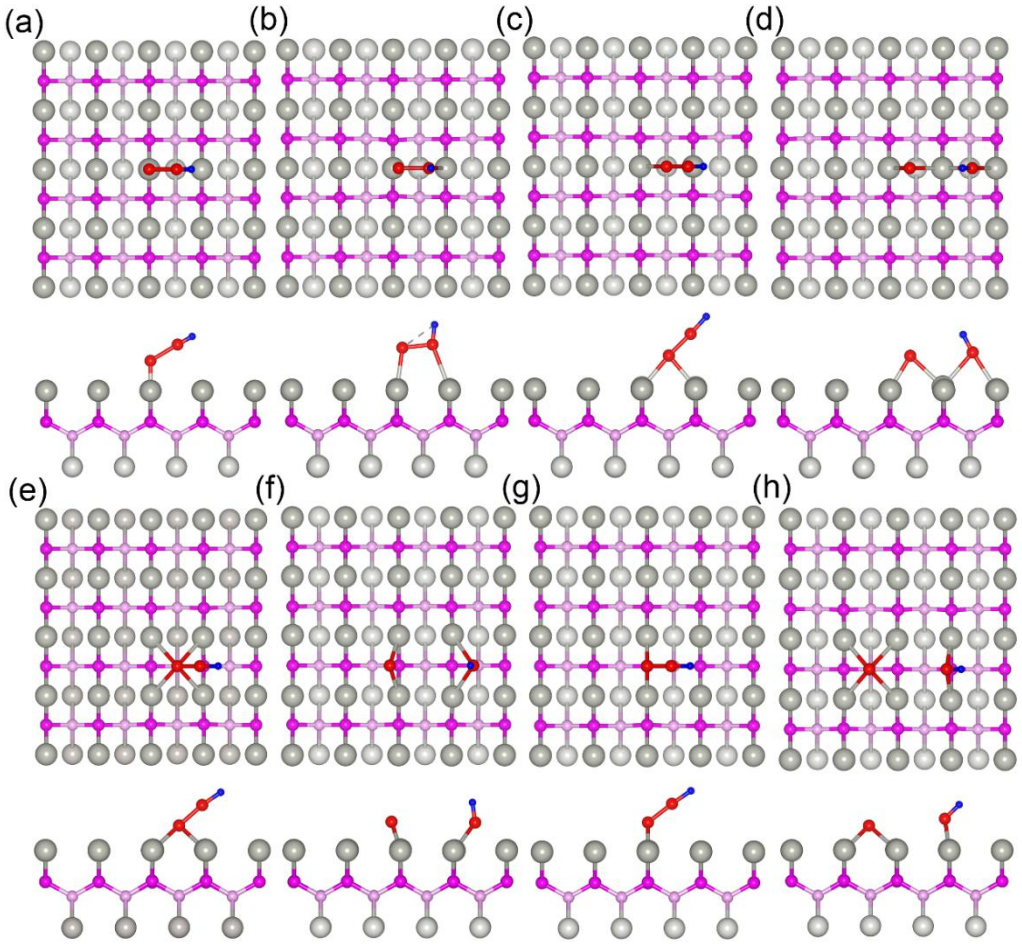

Fig. S14 The structure of intermediate state *OOH before((a), (c), (e), (g)) and after((b), (d), (f), (h)) structure relaxations on Site A, B, C, and D of α-PdC.

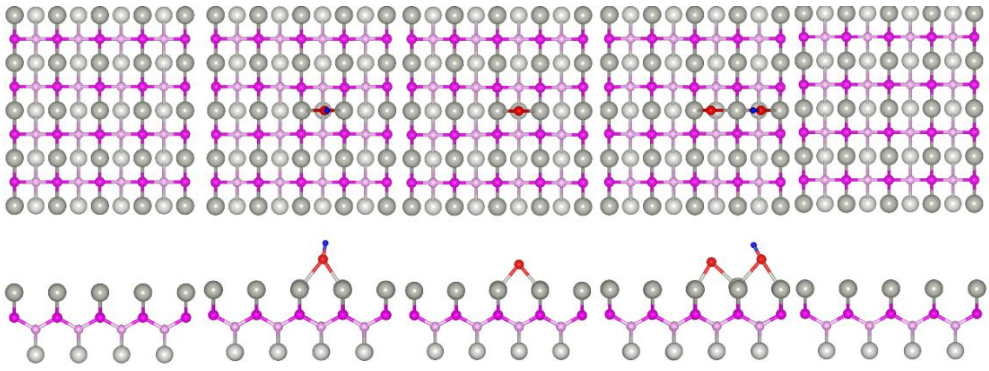

Fig. S15 The reaction processes involve all three intermediate states *OH, *O, *OOH on site B of α-PdC.

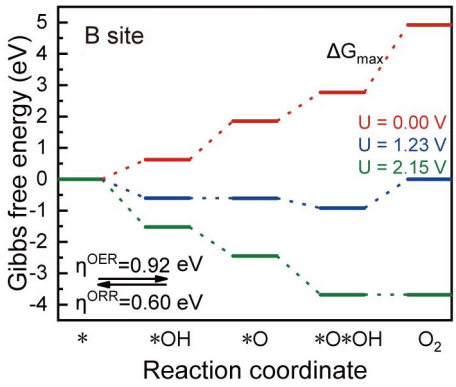

Fig. S16 Free energy diagram of α-PdC at the B site at different electrode potentials. ΔG_{max} denotes the rate-determining step.

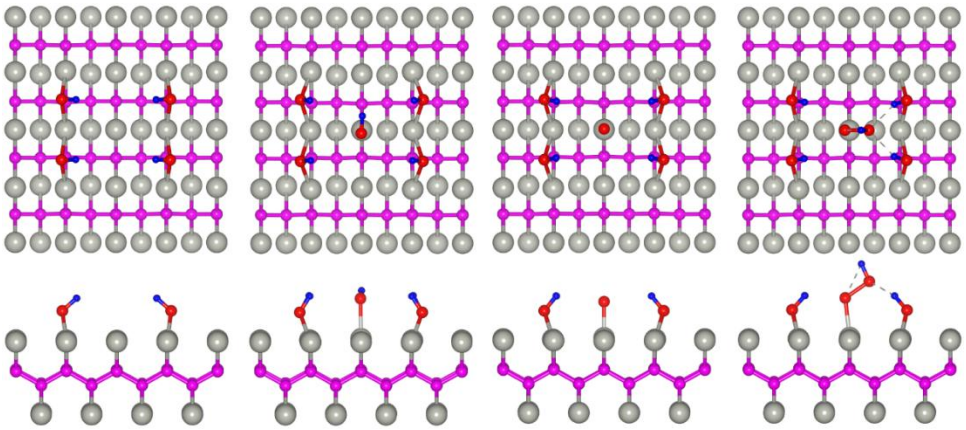

Fig. S17 The reaction process involves all 3 intermediate states (*OH, *O, and *OOH) on the D site of the OH-covered α-PdC.

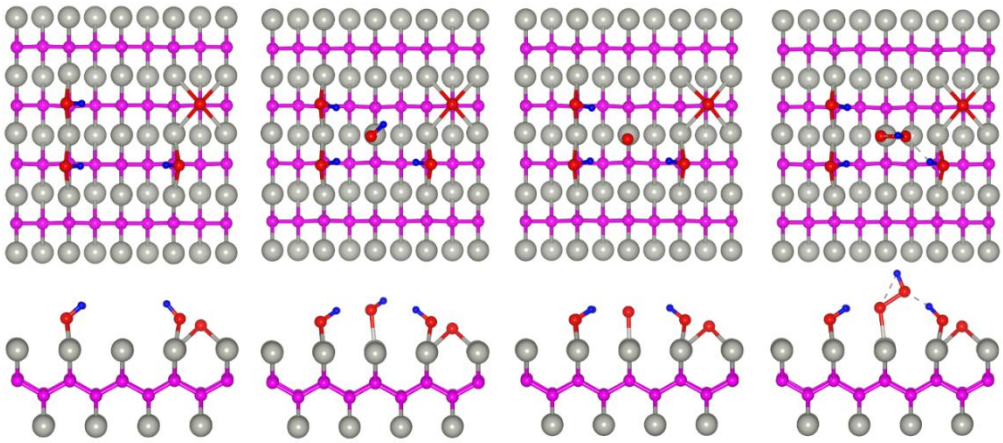

Fig. S18 The reaction process involves all 3 intermediate states (*OH, *O, and *OOH) at the A site of the OH, O-covered α-PdC.

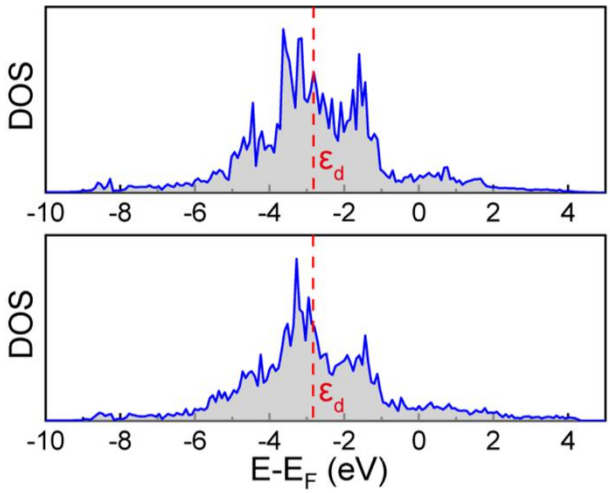

Fig. S19 The PDOS of d-band of the pristine α-PdC and O-covered α-PdC. The red dash line denotes the d-band center. The Fermi level is shifted to 0.

Supporting Tables

Table S1 The elastic constants of α- and β-PdC.

System	C_{11} (N/m)	C_{22} (N/m)	C_{12} (N/m)	C_{21} (N/m)	C_{66} (N/m)
α-PdC	385.94	123.88	1.10	1.10	2.80
β-PdC	171.72	171.72	77.92	77.92	11.35

Table S2 The Gibbs free energy of H_2O, H_2 and O_2.

System	E(DFT-D2) (eV)	ZPE (eV)	TS (eV)	$H_{thermal\ correction}$ +ZPE (eV)	G (eV)
H2O	-14.2425	0.5682	0.6699	0.6711	-14.2414
H2	-6.7732	0.2652	0.4019	0.3555	-6.8196
O2					-9.9235

Table S3. The bond length, bond angle, and adsorption energy of H_2O on different sites.

System (α-PdC)	O-H bond length(Å)	O-H bond angle(°)	ΔE(eV)
H_2O (gas)	0.97	104.99	
H_2O on Site A	0.97	109.08	-0.3684
H_2O on Site B	0.98	103.93	-0.4547
H_2O on Site C	0.99	103.68	-0.4187
H_2O on Site D	0.99	107.68	-0.5417

Table S4. The H adsorption energies of α-PdC on Site A-D.

System (α-PdC)	E(DFT-D2) (eV)	ΔE_{*H}(eV)	ZPE (eV)	TS (eV)	$H_{thermal\ correction}$ +ZPE (eV)	G (eV)	ΔG_{*H}(eV)
α-PdC	-108.2058		0	0	0	-108.2058	
A site	-111.4452	0.1473	0.1247	0.0253	0.1391	-111.3314	0.2843
B site	-111.5577	0.0347	0.1350	0.0018	0.1364	-111.4230	0.1926
C site	-111.6971	-0.1046	0.0761	0.0134	0.0857	-111.6248	-0.0092
D site	-112.0048	-0.4123	0.1695	0.0125	0.1784	-111.8389	-0.2233

Table S5. The H adsorption energies of α-PdC under coverage from 1/4 to 1.

System (coverage)	E(DFT-D2) (eV)	ZPE (eV)	TS (eV)	$H_{thermal\ correction}$ +ZPE (eV)	G (eV)	ΔG(eV)	ΔG_{*H}(eV)
1/4	-112.0048	0.1695	0.0125	0.1784	111.8389	-0.2233	-0.2233
1/2-1	-115.7105	0.3697	0.0152	0.3812	115.3445	-0.3191	-0.1595
1/2-2	-115.7497	0.3212	0.0262	0.3398	115.4362	-0.4107	-0.2054
1/2-3	-115.8457	0.3472	0.0253	0.3650	115.5061	-0.4806	-0.2403
3/4	-119.4203	0.5174	0.0289	0.5386	118.9106	-0.4753	-0.1584
1	-122.8451	0.6706	0.0367	0.6980	122.1838	-0.3387	-0.0847

Table S6. The H adsorption energies on site A, B, and C of β-PdC.

System	E(DFT-D2) (eV)	ΔE_{*H}(eV)	ZPE (eV)	TS (eV)	$H_{thermal\ correction}$ +ZPE (eV)	G (eV)	ΔG_{*H}(eV)
β-PdC	-107.3149		0	0	0	-107.3149	
A site	-109.5095	1.1920	0.2566c	0.3980	0.4609	-109.4467	1.2780
B site	-109.6913	1.0102	0.2536	0.4809	0.4932	-109.6789	1.0458
C site	-109.8300	0.8715	0.1634	0.0101	0.1709	-109.6691	1.0556