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Supporting Information

Oxygen Vacancy on TiO_2 Promoted the Activity and Stability of Supported Pd Nanoparticles for Oxygen Reduction Reaction

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Experimental Section

1. Preparation of TiO_2-V_O (700) and TiO_2-V_O (900)

The as-prepared TiO_2(B) nanosheets were annealed at 700 °C or 900 °C (heating rate of 2 °C min^{-1}) for 3 h under flowing Ar atmosphere in a horizontal quartz tube furnace. The obtained samples at 700 °C and 900 °C were denoted as TiO_2-V_O (700) and TiO_2-V_O (900), respectively.

2. Preparation of 10 wt% Pd/ TiO_2-V_O (700) and 10 wt%TiO_2-V_O (900) catalysts

The 10 wt% Pd/ TiO_2-V_O (700) catalyst was prepared by pyrolyzing a mixture of 11.6 mg $Pd(acac)_2$ and 40 mg TiO_2-V_O (700), followed by fully grounding the mixture in an agate mortar. Pyrolysis was carried out at 300 °C (heating rate of 3 °C min^{-1}) for 3 h under flowing Ar gas. For comparison, 10 wt% Pd/TiO_2-V_O (900) was prepared as the same procedure above.

3. Preparation of 5 wt%Pd/TiO_2-V_O and 20 wt%TiO_2-V_O catalysts

The 5 wt% Pd/TiO_2-V_O was prepared by pyrolyzing a mixture of 5.8 mg $Pd(acac)_2$ and 40 mg TiO_2-V_O obtained via Ar treatment at 800 ° C, followed by fully grounding the mixture in an agate mortar. Pyrolysis was carried out at 300 °C (heating rate of 3 °C min^{-1}) for 3 h under flowing Ar gas. For comparison, 20 wt% Pd/TiO_2-V_O was prepared as the same procedure above.

Supplementary Results

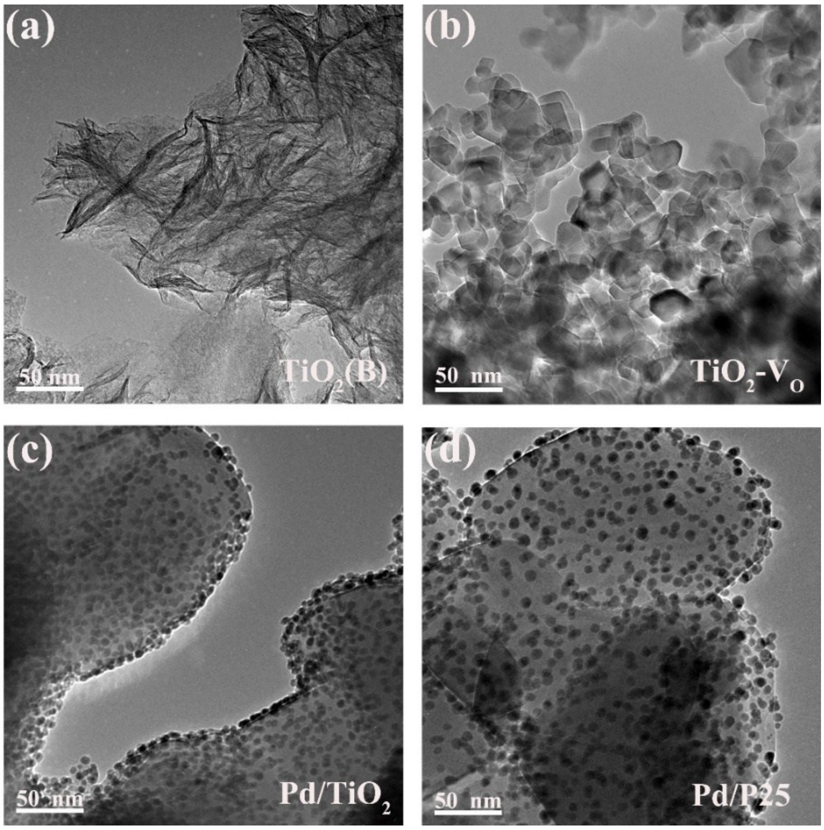

Fig. S1 TEM images of (a)TiO_2(B), (b) TiO_2-V_O, (c) Pd/TiO_2 and (d) Pd/P25 with scale bars of 50 nm.

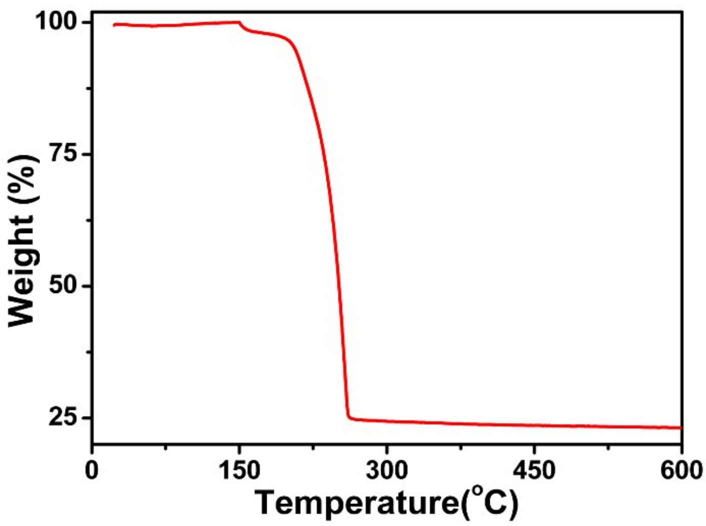

Fig. S2 TGA of Pd(acac)$_2$

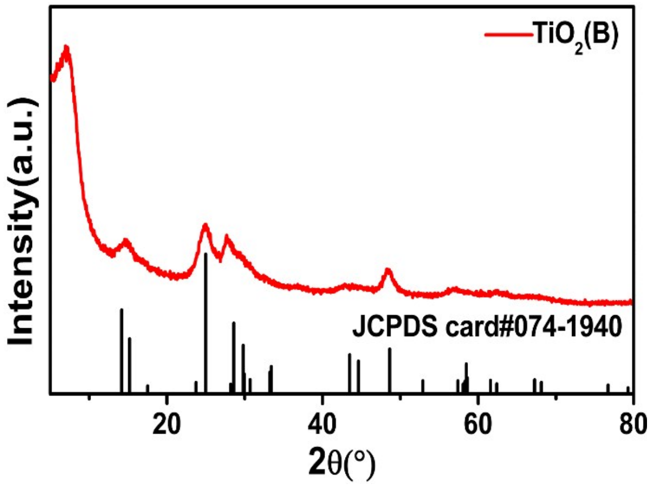

Fig. S3 XRD pattern of TiO_2 (B)

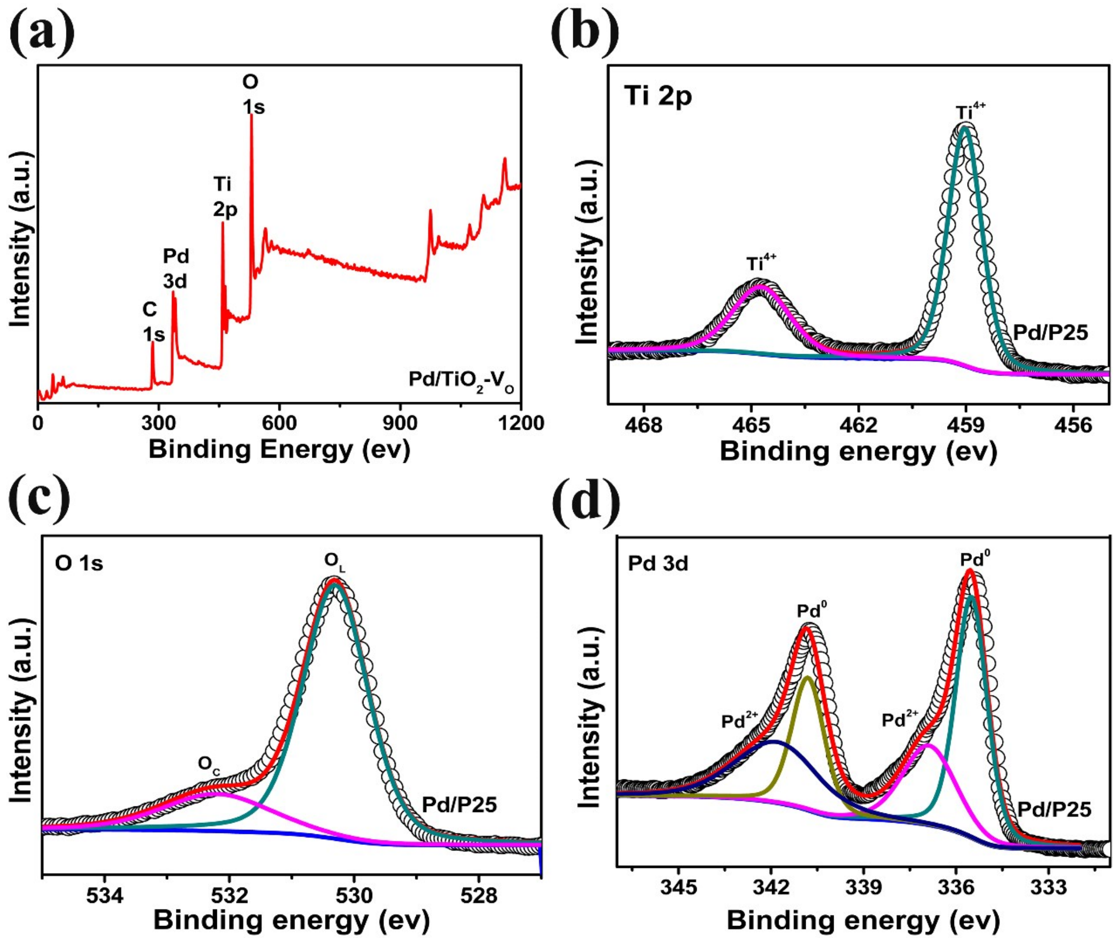

Fig. S4 XPS results of catalysts. (a) Survey spectrum of Pd/TiO_2-V_O; (b)Ti 2p, (c) O 1s and (d) Pd 3d XPS high-resolution spectra of Pd/P25.

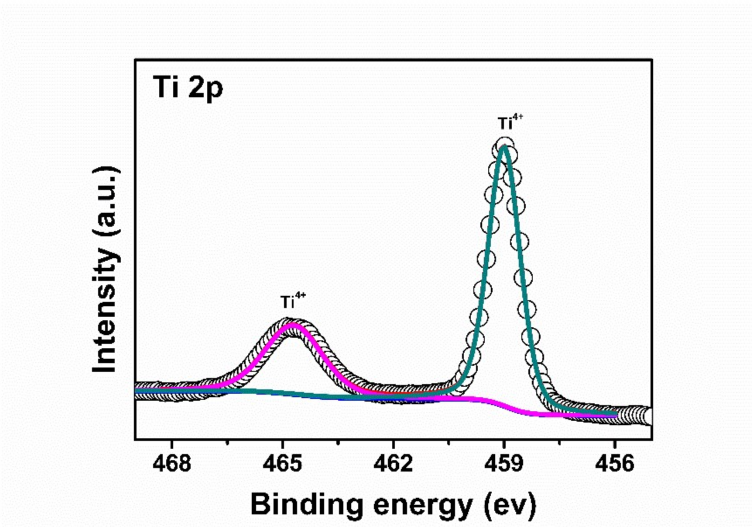

Fig. S5 XPS spectrum of Ti 2p for TiO_2-V_O.

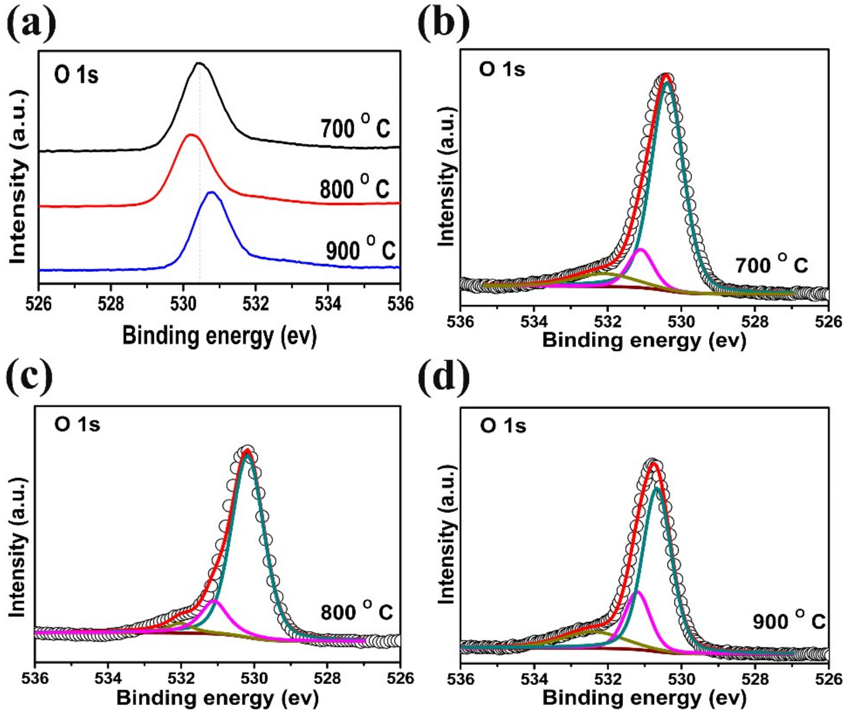

Fig. S6 O 1s high-resolution XPS spectra of TiO_2-V_O (700), TiO_2-V_O (800) and TiO_2-V_O (900).

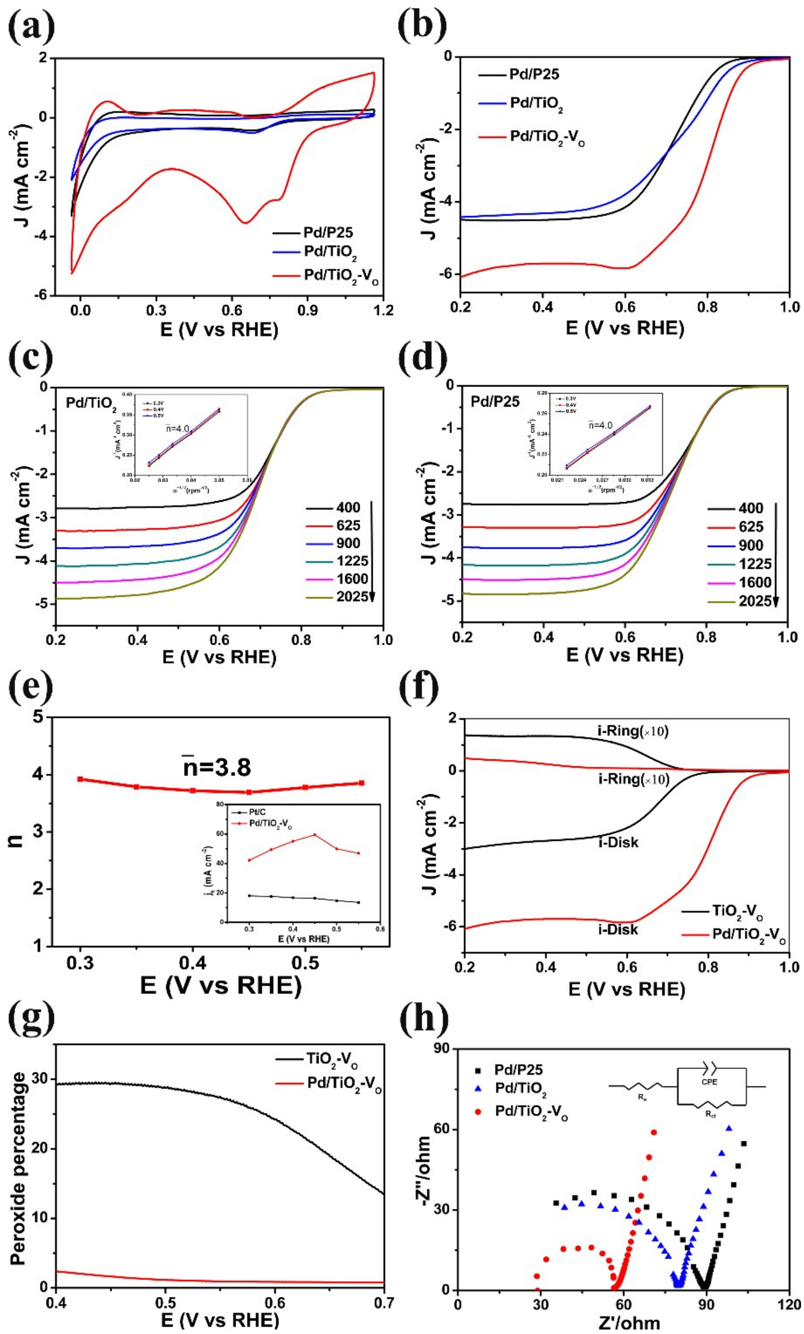

Fig. S7 Electrochemical properties of catalysts. (a) Cyclic voltammetry curves of Pd/TiO_2-V_O, Pd/TiO_2 and Pd/P25 catalysts in O_2-saturated 0.1 M KOH solution, scan rate 100 mV s^{-1}. (b) Polarization curves of Pd/TiO_2-V_O and Pd/TiO_2, Pd/P25, Pt/C catalysts, rotation speeds 1600 rpm, scan rate 20 mV s^{-1}. LSV curves obtained at different rotation speeds (400-2025 rpm) in 0.1 M KOH solution for (c) Pd/TiO_2 and (d) Pd/P25. The insets in Fig. S5c and Fig. S5d show the Koutechy-Levich plots and the numbers of electron transfer calculated from K-L analysis for Pd/TiO_2 and Pd/P25, respectively. (e) Numbers of electron transfer calculated from K-L analysis of Pd/TiO_2-V_O (inset: calculated kinetic current densities on the electrodes of Pt/C and Pd/TiO_2-V_O). (f) RRDE measurements (1600 rpm) of TiO_2-V_O and Pd/TiO_2-V_O.(g) Peroxide percentage of TiO_2-V_O and Pd/TiO_2-V_O. (h) Nyquist plot of EIS for ORR on Pd/P25, Pd/TiO_2 and Pd/TiO_2-V_O electrodes in 0.1 M KOH at open circuit voltage (inset: the corresponding equivalent circuit diagram of Nyquist plot of Pd/TiO_2-V_O. Rs: an electrolyte resistance, Rct: a charge transfer resistance, CPE: a constant phase element).

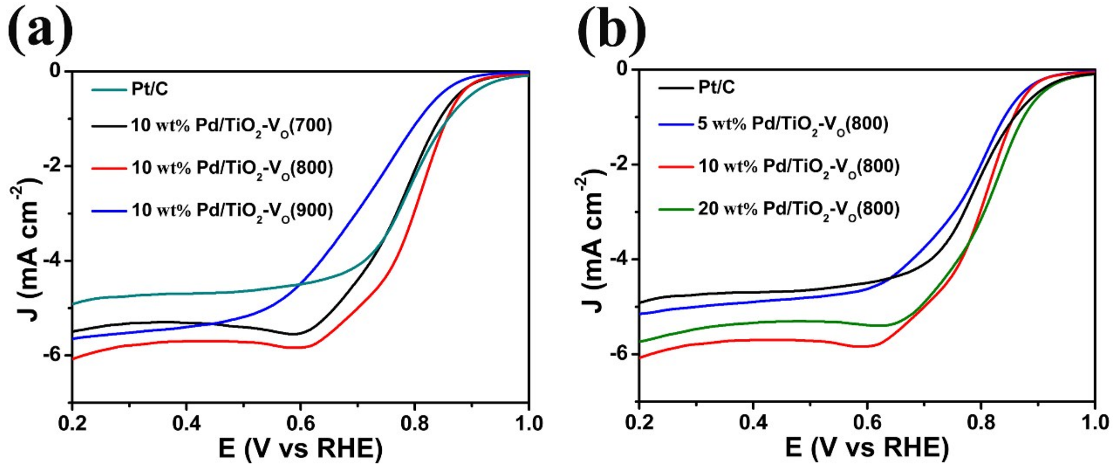

Fig. S8 Polarization curves of different catalysts with rotation speed of 1600 rpm and scan rate of 20 mV s^{-1} (a) Pt/C, 10 wt% Pd/TiO_2-V_O (700), 10 wt% Pd/TiO_2-V_O (800) and 10 wt% Pd/TiO_2-V_O (900). (b) Pt/C, 5 wt% Pd/TiO_2-V_O (800), 10 wt% Pd/TiO_2-V_O (800) and 20 wt% Pd/TiO_2-V_O (800).

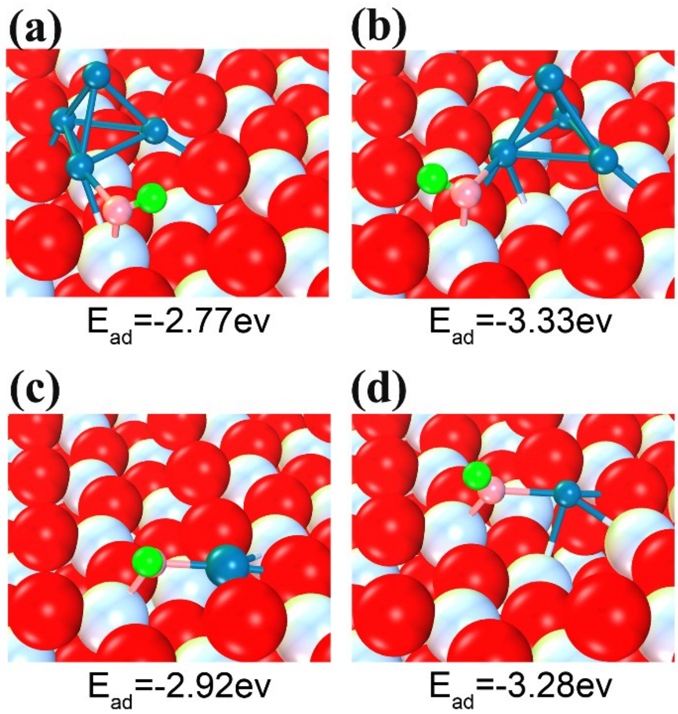

Fig. S9 Optimized structures and adsorption energies of OH adsorbed on (a) Pd_4/TiO_2, (b) Pd_4/TiO_2-V_O, (c) Pd/TiO_2 and (d) Pd/TiO_2-V_O.

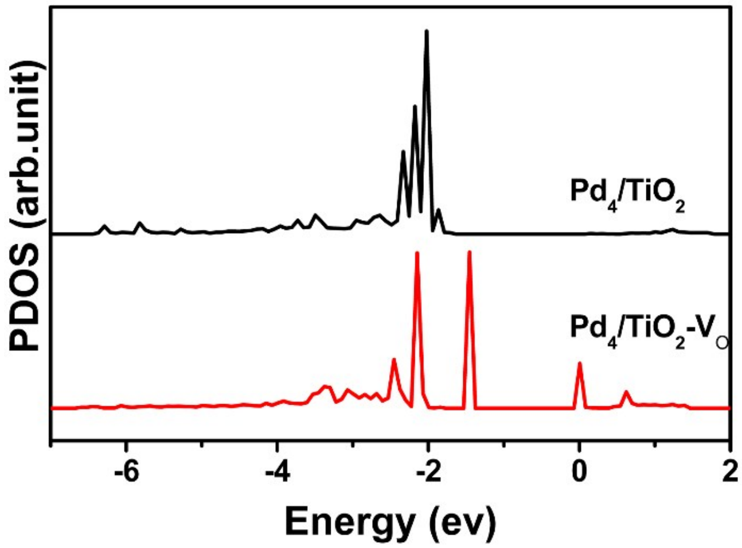

Fig. S10 The PDOS of Pd_4 over TiO_2 and TiO_2-V_O.

Table S1 V_O content of TiO_2-V_O (700), TiO_2-V_O (800) and TiO_2-V_O (900) obtained from XPS analysis.

sample	V_O content wt %
TiO_2-V_O (700)	12.4
TiO_2-V_O (800)	14.6
TiO_2-V_O (900)	19.8

Table S2 Pd content of Pd/P25, Pd/TiO_2 and Pd/TiO_2-V_O obtained from XPS analysis.

sample	Pd content wt %
Pd/P25	9.56
Pd/TiO_2	9.38
Pd/TiO_2-V_O	9.50

Table S3 Comparison of the ORR activity in 0.1 M KOH of the 10 wt% Pd/TiO_2-V_O with that of some recently reported Pd-based catalysts.

Catalyst	Pd loading (wt %)	Support	Rotation speed (rpm)	Onset potential (v VS RHE)	Half-wave potential (v VS RHE)	Reference
Pd/TiO_2-V_O	10	TiO_2-V_O	1600	0.98	0.83	This work
Pd/TiO_{2-X}	25	TiO_{2-X}	2000	0.94	0.80	*ACS Appl. Mater. Interfaces* 2016,8,27654
Pd/TiO_{2-X}: N	25	TiO_{2-X}: N	2000	0.94	0.81	*ACS Appl. Mater. Interfaces* 2016,8,27654
Pd_3Pb/TiO_2	5	TiO_2	**2500**	0.98	0.85	*J. Appl. Electrochem.* (2016) 46:745
Ni@Pd_3/C	**17**	C	1600	0.98	0.86	*J. Mater. Chem. A* 2017, 5,9233
$Au_{10}Pd_{40}Co_{50}$	46	/	1600	-	0.83	*Nat. Commun.* 2014, **5**, 5185