Supplementary Material

Constructing Anatase/Rutile TiO₂ Homojunction-Supported Pd Electrocatalyst *via* Band Alignment and Oxygen Vacancy Engineering for Direct Methanol Fuel Cells

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S1. Materials characterizations

Under JSM-7800F field emission scanning electron microscope (SEM), we obtained the SEM images to investigate surface morphology. Transmission electron microscopy (TEM) and high-resolution TEM using an FEI Tecnai G2 F20 were employed to analyze homojunctions and Pd dispersion. The phase structure was collected through X-ray diffraction (XRD) analysis using a PANalytical X'Pert Powder diffractometer. Then, this study quantified the content of Pd in the prepared samples by inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent 5110). Chemical information and band structure were further examined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha instrument) and valence band XPS (VB-XPS, Thermo Scientific ESCALAB 250Xi), respectively. Oxygen vacancy was identified via electron paramagnetic resonance (EPR) spectroscopy using a Bruker EMXplus machine. UV–visible diffuse reflectance spectra (DRS) was conducted using a UH5700 spectrophotometer.

S2. Electrochemical measurement

ORR measurements were assessed on a CHI760E electrochemical workstation in a three-electrode cell. A saturated Ag/AgCl electrode served as the reference electrode, a platinum sheet $(1 \times 1 \text{ cm}^2)$ as counter electrode, a glassy carbon rotating disk electrode (RDE, 5 mm in diameter) as working electrode. Catalyst inks were formulated through the dispersion method using 2 mg of catalyst and 1 mg of carbon black (conductive agent) in 403 µL ethanol, 403 µL ultrapure water, and 10 µL Nafion solution. The inks were drop-cast onto the RDE (loading 0.25 µg cm⁻²) and air-dried in air. The reversible hydrogen electrode (RHE) was used as the control for all potentials.

At 50 mV s⁻¹, this study performed Cyclic voltammetry (CV) in an N₂-saturated 0.1 M KOH solution (0.05-1.2V). Linear sweep voltammetry (LSV) was obtained by a RDE in an O₂-saturated 0.1 M KOH solution from 0.05 to 1.2 V at 20 mV s⁻¹ and 1600 rpm. LSV curves were also measured at rotating speeds ranging from 900 to 2500 rpm.

The kinetic current density was calculated by:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L}$$
(1)

where J is the current density observed in the experiment, J_K , and J_L are respectively the kinetic and the limiting current densities.¹

The mass activity was normalized relative to the Pd or Pt metal loading.²

$$MA = \frac{J_k(A)}{m_{Pd/Pt}(mg)}$$
(2)

Rotating ring-disk electrode (RRDE) experiment was carried out to identify the electron transfer number (n) and H_2O_2 selectivity:

$$\%(H_2O_2) = 200 \times \frac{I_R/N}{I_D + I_R/N}$$
 (3)

$$n = 4 \times \frac{I_D}{I_D + I_R/N} \tag{4}$$

where I_D and I_R are respectively the disk and the ring currents, and N is the current collection efficiency of the Pt ring. N is a constant value of 0.26 in this study.³

With an O_2 -saturated 0.1 M KOH solution used, electrochemical impedance spectra (EIS) were characterized with an AC amplitude of 5 mV between 0.1 kHz to 100 kHz.

MOR tests were performed in the three-electrode cell by a DH7002A workstation at room temperature. The electrochemical performance of the catalysts was evaluated by CV, LSV and chronoamperometry (CA) tests in N₂-saturated 1.0 M KOH + 1.0 M CH₃OH. The ORR-LSV was measured in an O₂-saturated 1.0 M KOH + 1.0 M CH₃OH solution at 1600 rpm with a scan rate of 20 mV s⁻¹ to assess the selectivity and methanol tolerance of the catalysts. CO stripping experiments were performed by the reported method.⁴

The CO stripping experiment was made to confirm the electrochemically active surface areas (ECSA) for the catalysts:

$$ESCA = \frac{Q_{CO}}{0.42 * m_{Pd/Pt}} = \frac{S_{CO}}{0.42 * m_{Pd/Pt} * v}$$
(5)

where Q_{CO} is the quantity of electron transfer, S_{CO} is the peak area of CO_{ads} oxidation peak, v is the scan rate of CO stripping experiment, and $m_{Pd/Pt}$ denotes the mass of Pd or Pt supported on the electrode. The value 0.42 (mC·cm⁻²) represents the charge for CO adsorption by Pd or Pt in a monolayer.⁵

S3. Density functional theory (DFT) calculations

All computational models are constructed using Material Studio 2023 and position in a box that included an 18 Å vacuum layer to minimize the influence of Z-axis periodicity. Structural optimization and reaction free energy calculations are performed using the CP2K package with spin polarization

enabled.^{6, 7} The Perdew-Burke-Ernzerhof (PBE) functional ⁸, Goedecker, Teter, and Hutter (GTH) pseudopotentials ⁹ and Double-zeta quality MOLOPT basis sets ¹⁰ are employed, with a cutoff of 500 Ry. Dispersion corrections for the normal exchange-correlation (XC) function are applied using the DFT-D3 method.¹¹ Periodic boundary conditions are enabled during calculations, with all atoms in a fully relaxed state. The convergence criteria for maximum atomic displacement and force are respectively set to 3.0×10^{-3} Å and 4.5×10^{-4} Hartree/Å.

S4. Additional Figs in supporting information



Fig. S1. (a, b) SEM images of pristine TiO_2 . (c) Length size distribution of pristine TiO_2 .



Fig. S2. TEM images of (a) A/R-TiO₂ and (b-c) Pd/A/R-TiO₂.



Fig. S3. SAED pattern of Pd/A/R-TiO₂.



Fig. S4. (a, b) TEM images and of Pd/A-TiO₂. (c) The Pd particle size distribution of Pd/A-TiO₂. (d) HRTEM image of Pd/A-TiO₂. (e) The distances between adjacent lattice fringes of Pd (111) and anatase (101) facets. (f) SAED pattern of Pd/A-TiO₂.



Fig. S5. (a, b) TEM images and of Pd/R-TiO₂. (c) The Pd particle size distribution of Pd/R-TiO₂. (d) HRTEM image of Pd/R-TiO₂. (e) The distances between adjacent lattice fringes of Pd (111) and rutile (110) facets. (f) SAED pattern of Pd/R-TiO₂.



Fig. S6. (a-c) TEM images and HRTEM image of Pd/C. (d) The Pd particle size distribution of Pd/C.



Pt/C.



Fig. S8. XPS survey spectra of (a) Pd/A-TiO₂, (b) Pd/A/R-TiO₂, (c) Pd/R-TiO₂ and (d) Pd/C.



Fig. S9. CV curves (scan rate: 50 mV s⁻¹) of Pd/A-TiO₂, Pd/A/R-TiO₂, Pd/R-TiO₂, Pd/C and Pt/C in O₂- and N₂-saturated 0.1 M KOH solution.



Fig. S10. LSV curves (scan rate: 20 mV/s) of Pd/A-TiO₂, Pd/A/R-TiO₂, Pd/R-TiO₂, Pd/C and Pt/C at different rotating speeds in O₂-saturated 0.1 M KOH.



Fig. S11. Multiple LSV curves Pd/A/R-TiO₂.



Fig. S12. K-L plots and electron transfer numbers (n) of Pd/A/R-TiO₂.



Fig. S13. XPS survey spectra Pd/A/R-TiO₂ after stability test.



Fig. S14. CV curves (scan rate: 50 mV s⁻¹) of Pd/A-TiO₂, Pd/A/R-TiO₂, Pd/R-TiO₂, Pd/C and Pt/C in 1.0 M KOH solution.



Fig. S15. ORR-LSV curves with and without methanol for Pd/A/R-TiO₂ in 0.1 M KOH.



Fig. S16 Structural models of (a) Pd/A-TiO₂, (b) Pd/A/R-TiO₂, (c) Pd/R-TiO₂. Gray: Pd, blue: Ti, red: O.



Fig. S17. The averaged-plane charge density difference at $Pd/A/R\text{-}TiO_2$ homojunction interface.



Fig. S18. Structural models of OH adsorbed on (a) Pd/A-TiO₂, (b) Pd/A/R-TiO₂, (c) Pd/R-TiO₂. Gray: Pd, blue: Ti, red: O, white: H.

S5. Additional tables in supporting information

Catalysts	ICP-OES			
	Pd Loading (wt%)			
Pd/A-TiO ₂	18.76			
Pd/A/R-TiO ₂	19.28			
Pd/R-TiO ₂	17.70			

 $Table \ S1. \ Pd \ Loading \ (wt \ \%) \ in \ Pd/A-TiO_2, \ Pd/A/R-TiO_2 \ and \ Pd/R-TiO_2 \ obtained \ by \ ICP-OES.$

sample	E _g (eV)	E _{VB} (eV)	E _{CB} (eV)
A-TiO ₂	3.29	2.35	5.64
R-TiO ₂	2.96	2.21	5.17

Table S2. The Band Structure Comparison of A-TiO $_2$ and R- TiO $_2$.

	Ti ³⁺		Ti ⁴⁺	Ti ³⁺ /Ti ⁴⁺		
Catalysts	binding energy (eV)	ratio (%)	binding energy (eV)	ratio (%)	ratio (%)	
D1/A T'O	458.04	5.55	458.97	62.81	0.04	
$Pd/A-11O_2$	463.33	3.08	464.71	28.56	8.84	
Pd/A/R-TiO ₂	458.64	9.70	459.57	56.97	17.00	
	463.93	4.85	465.34	28.48	17.02	
Pd/R-TiO ₂	458.09	7.09	459.13	60.54	11 51	
	463.38	3.54	464.90	28.83	11./1	

Table S3. Results of the Fit of the Ti 3d Spectra.

	O _{lat} O _{def}		ef	Oa	$O_{def} / (O_{lat} + O_{def} + O_{ads})$		
Catalysts	binding energy (eV)	ratio (%)	binding energy (eV)	ratio (%)	binding energy (eV)	ratio (%)	ratio (%)
Pd/A-TiO ₂	530.19	63.45	531.97	20.37	532.86	16.18	20.37
Pd/A/R-TiO ₂	530.76	33.25	532.35	32.16	533.54	34.59	32.16
Pd/R-TiO ₂	530.46	53.52	532.12	21.10	533.27	25.38	21.10

Table S4. Results of the Fit of the O 1s Spectra.

	Pd ⁰		Pd ²⁺	-	$Pd^{0}/(Pd^{0} + Pd^{2+})$
Catalysts	binding energy (eV)	ratio (%)	binding energy (eV)	ratio (%)	ratio (%)
	335.13	34.05	336.29	23.99	50.74
$Pd/A-T_1O_2$	340.43	24.32	341.59	17.64	58.74
Pd/A/R-TiO ₂	335.70	36.04	336.73	21.81	(2.1.(
	341.00	26.12	342.03	16.03	62.16
	335.35	35.03	336.23	23.31	(0.0 5
Pd/R-TiO ₂	340.65	25.02	341.53	16.64	60.05
Pd/C	335.91	29.24	337.13	29.09	50 10
	341.21	20.88	342.43	20.79	50.12

Table S5. Results of the Fit of the Pd 3d Spectra.

Catalysts	E _{1/2} J _L	MA (A mg ⁻¹ Pd/Pt)		SA (mA cm ⁻²)		Tafel	
Catalysts	(V)	(mA cm ⁻²)	0.85 V	0.90 V	0.85 V	0.90 V	(mV/dec)
Pd/A-TiO ₂	0.905	5.18	0.96	0.25	2.56	0.66	63.3
Pd/A/R-TiO ₂	0.929	5.31	4.27	0.66	8.72	1.35	54.9
Pd/R-TiO ₂	0.917	5.06	1.35	0.34	3.29	0.82	59.6
Pd/C	0.844	4.70	0.16	0.05	0.81	0.24	106.5
Pt/C	0.871	5.25	0.33	0.08	2.44	0.60	89.8

Table S6. Comparison of the electrocatalytic performance of Pd/A-TiO₂, Pd/A/R-TiO₂, Pd/R-TiO₂, Pd/C and Pt/C towards ORR.

Catalysts	Electrolyte	Onset potential (V)	E _{1/2} (V vs. RHE)	Ref.
Pd/A/R-TiO ₂	0.1 M KOH	1.02	0.929	This work
Pd/a-MnO ₂	0.1 M KOH		0.87	12
600-Pd/HGDY	0.1 M KOH		0.90	13
Pd _{NC} /Pd-NC800	0.1 M KOH		0.85	14
Pd/TiO _{2-x} NS	0.1 M KOH	0.935	0.82	15
Pd/N–HsGY	0.1 M KOH	0.96	0.849	16
Sub-5 nm Pd Ths	0.1 M KOH	1.025	0.864	17
Pd/Co ₃ O ₄ -N-C-300	0.1 M KOH		0.93	18
Pd metallene/C	0.1 M KOH	1.02	0.90	19
Pd-Gd ₂ O ₃ /C	0.1 M KOH	0.986	0.877	20

Table S7. Comparison of ORR activity parameters of $Pd/A/R-TiO_2$ with those of previously reported Pd-based intermetallic catalysts.

Catalysts	Onset potential	CO oxidation onset potential	ESCA (m ² g ⁻¹)	MA (A mg ⁻¹ _{Pd/Pt})	SA (mA cm ⁻²)
Pd/A-TiO ₂	0.454	0.645	37.59	2.86	7.61
Pd/A/R-TiO ₂	0.360	0.620	46.34	4.10	8.85
Pd/R-TiO ₂	0.400	0.652	41.90	3.65	8.72
Pd/C		0.781	19.58	0.32	1.63
Pt/C	0.398	0.664	22.17	1.56	7.03

Table S8. Comparison of the electrocatalytic performance of Pd/A-TiO₂, Pd/A/R-TiO₂, Pd/R-TiO₂, Pd/C and Pt/C towards MOR.

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