Supporting Information for

Vanadium oxide as an electron buffer to stabilize palladium for electrocatalytic hydrodechlorination

Meiqin Shi,[a] Yifei Ren,[a] Shuyuan Xu,[a] Xiaofeng Xu,[a] Fanfei Sun*[bc] and Yuanbin She*[a]

[a] College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, Zhejiang, People's Republic of China.
[b] Shanghai Synchrotron Radiation Facility, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201204, People's Republic of China.
[c] Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, People's Republic of China

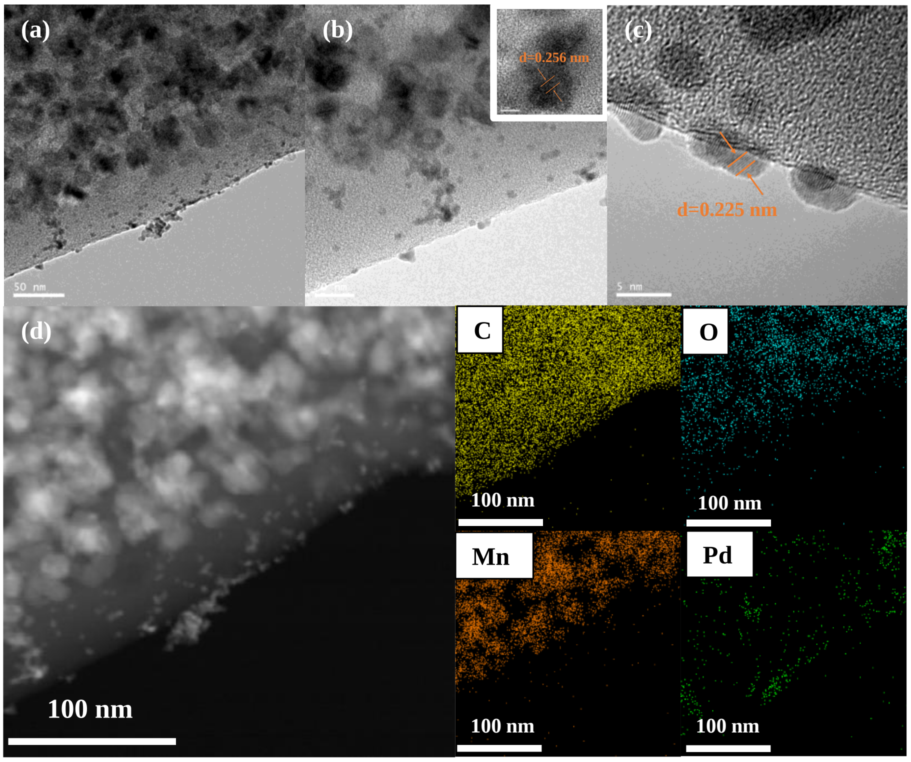

Fig. S1 Characterization images of sample Pd/MnO/C-800 (a, b) TEM, (c) HRTEM, (d) TEM-EDX mapping

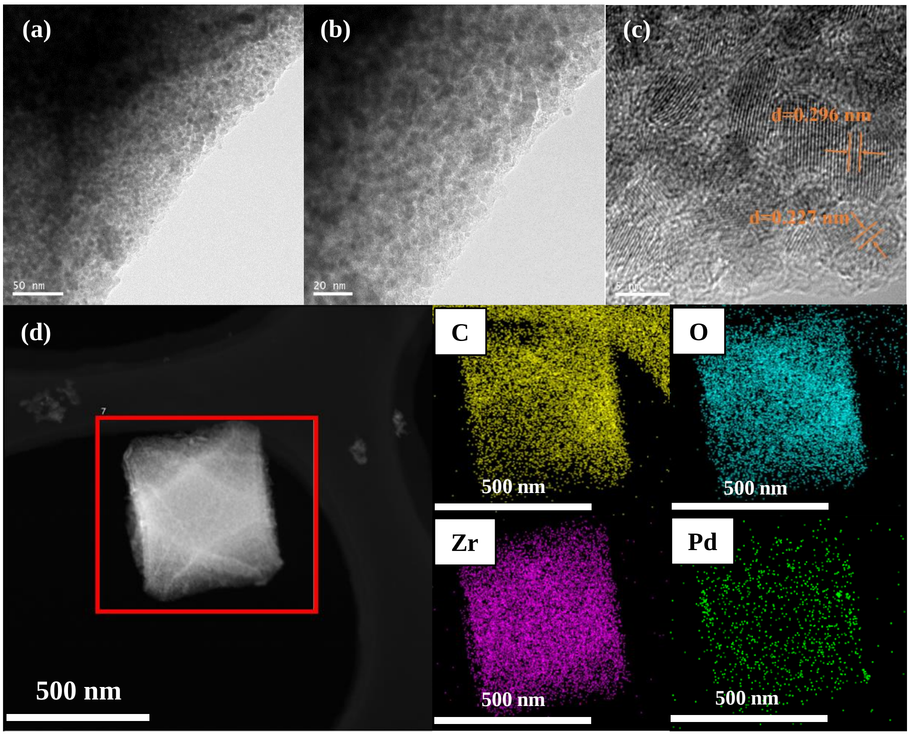

Fig. S2 Characterization images of sample Pd/ZrO_2/C-800 (a, b) TEM, (c) HRTEM, (d) TEM-EDX mapping

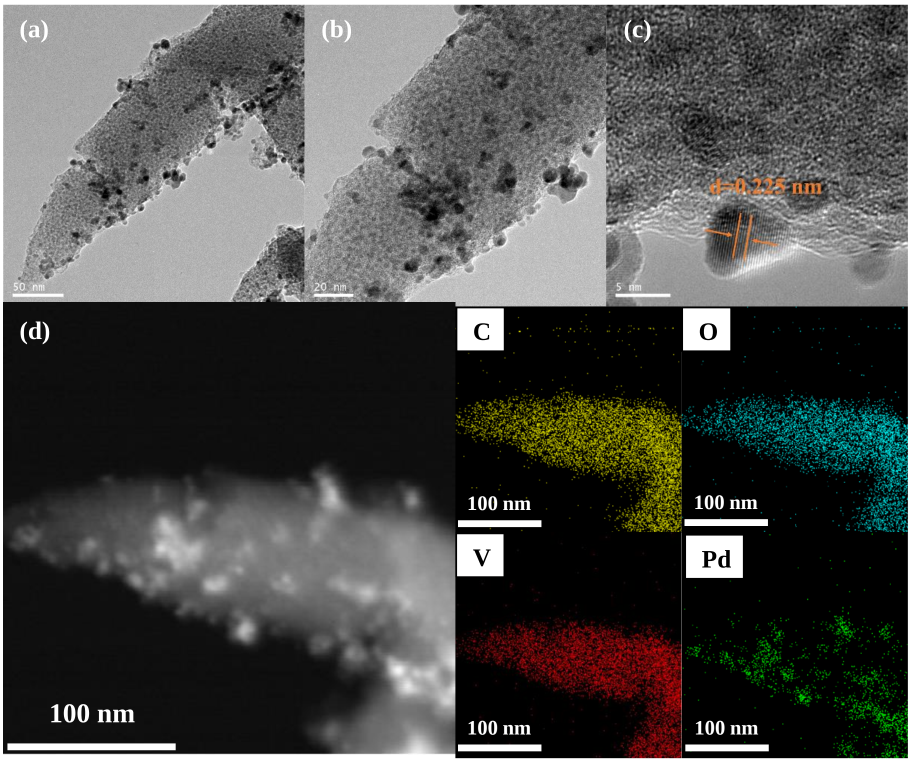

Fig. S3 Characterization images of sample Pd/VOx/C-600 (a, b) TEM, (c) HRTEM, (d) TEM-EDX mapping

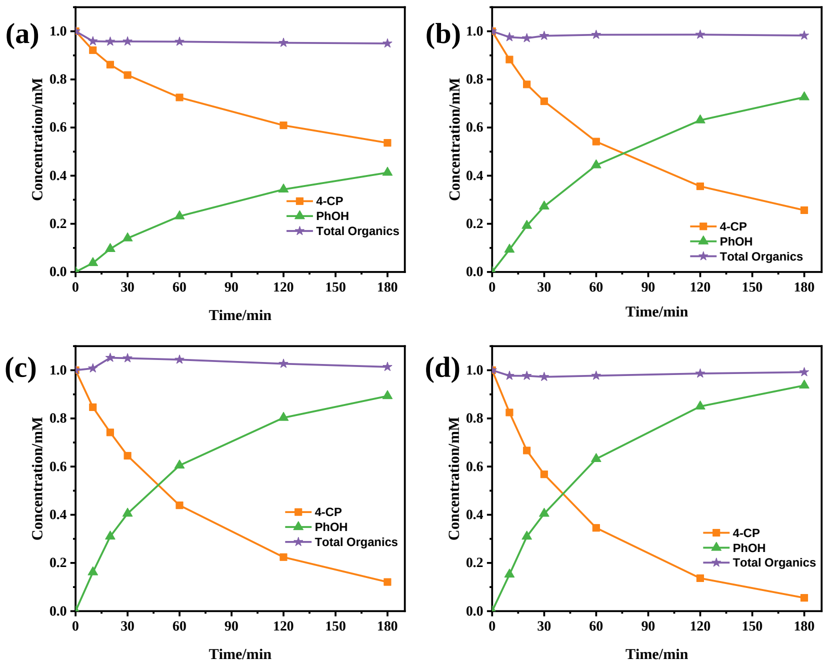

Fig. S4 Electrocatalytic hydrodechlorination product selectivity of (a) Pd/MnO/C-800, (b) Pd/ZrO_2/C-800, (c) Pd/VOx/C-600 and (d) commercial Pd/C. Reaction conditions: T = 30 ℃, electrolyte: 30 mL PBS solution, concentration of 4-CP = 1 mM, N_2 atmosphere

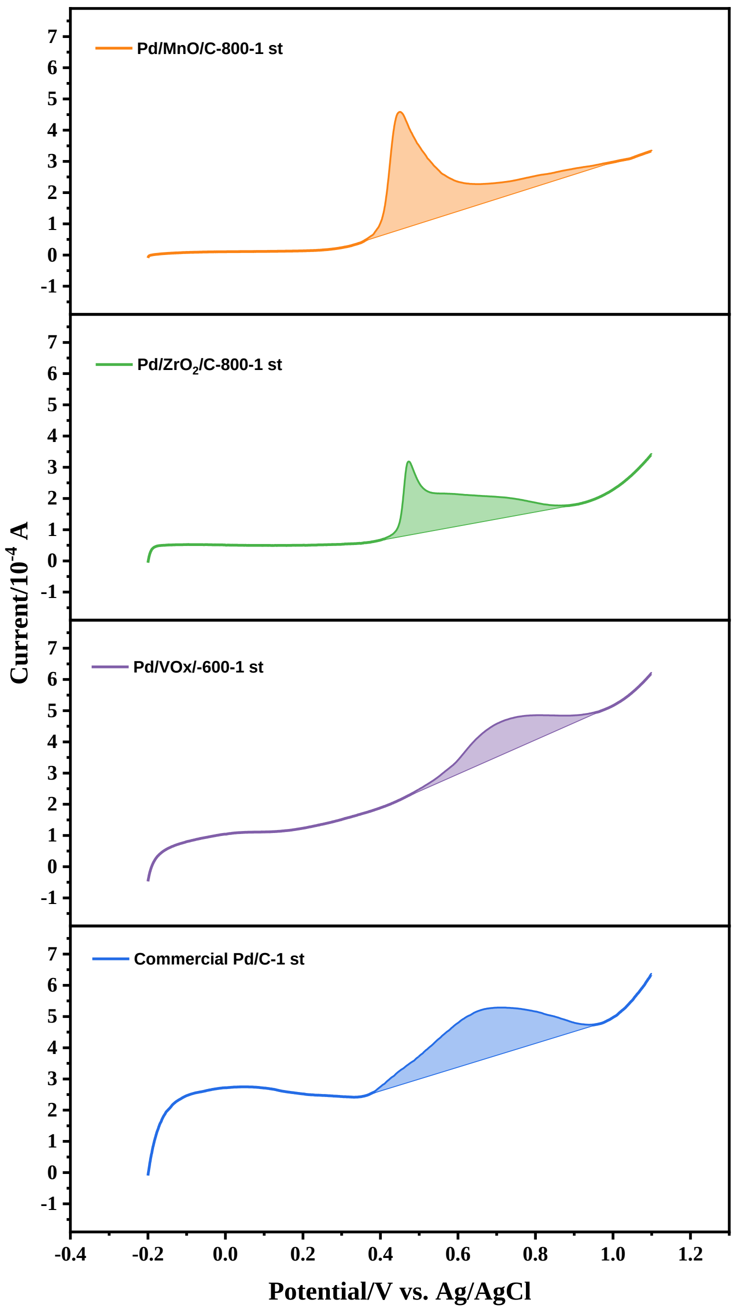

Fig. S5 CO stripping curves on Pd/MnO/C-800, Pd/ZrO_2/C-800, Pd/VOx/C-600 and commercial Pd/C electrodes tested in 30 mL PBS solution (pH = 7)

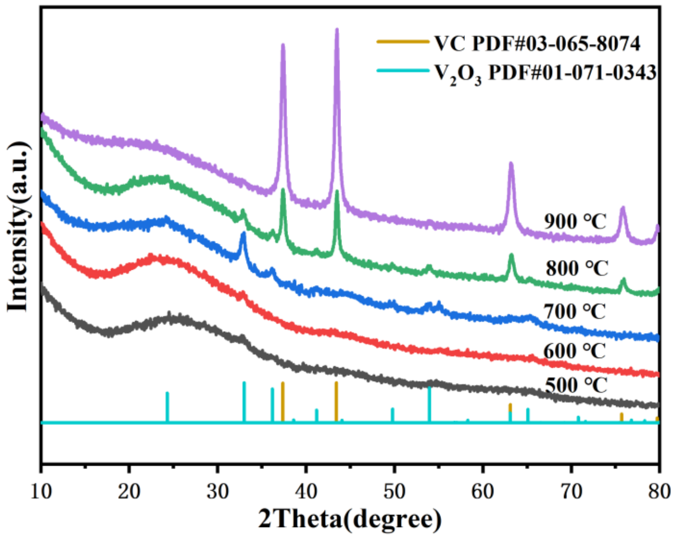

Fig. S6 XRD analysis for the V-MOF (COMOC-3) after pyrolysis at 500 - 900 °C

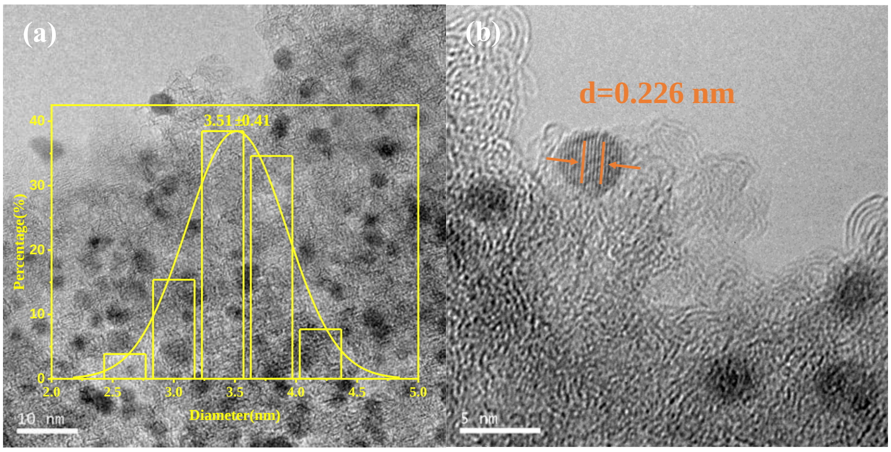

Fig. S7 TEM images of (a, b) commercial Pd/C. Inset shows the particle size distribution

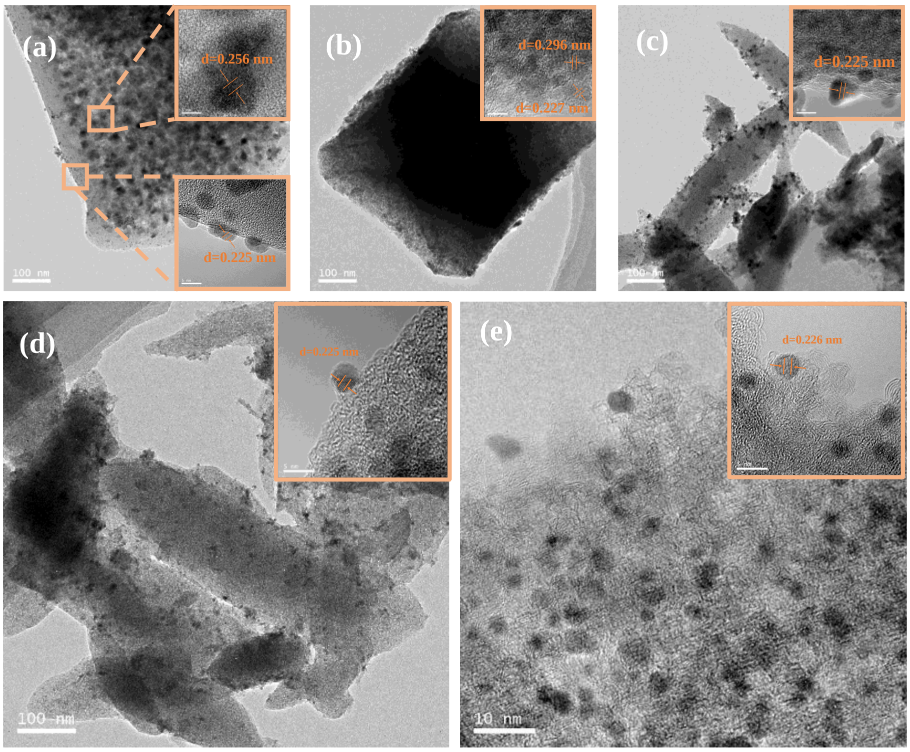

Fig. S8 TEM images of (a) Pd/MnO/C-800, (b) Pd/ZrO_2/C-800, (c) Pd/VOx/C-600, (c) Pd/VOx/C-700, (d) Commercial Pd/C

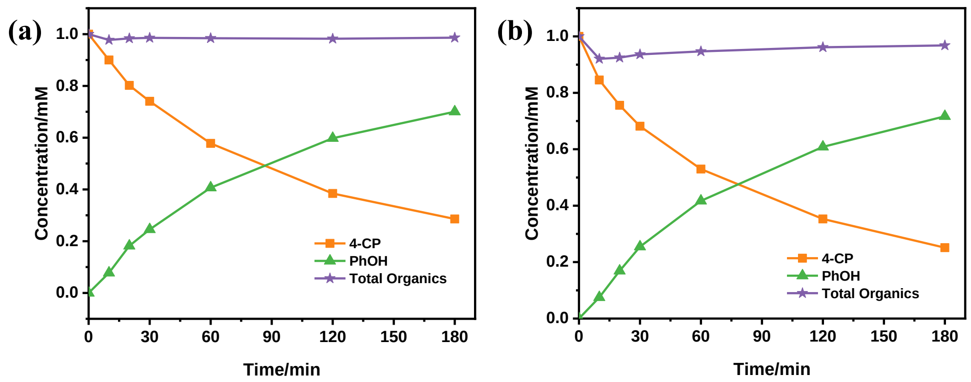

Fig. S9 Electrocatalytic hydrodechlorination product selectivity of (a) Pd/VOx/C-500 and (b) Pd/VC/C-900. Reaction conditions: T = 30 ℃, electrolyte: 30 mL PBS solution, concentration of 4-CP = 1 mM, N_2 atmosphere

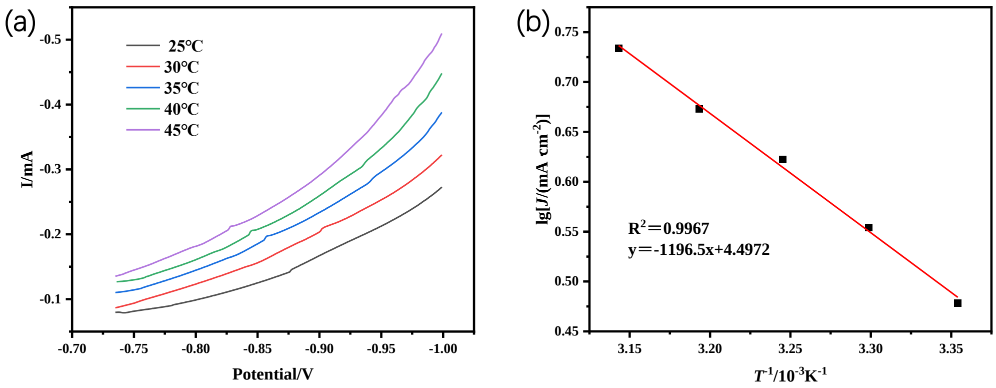

Fig. S10 Cathodic polarization curves of Pd/VOx/C-700 electrode in 30 mL pH=7 100 mM PBS with 5.0 mM 4-CP under different temperatures (a) and relationship between lgJ and 1/T (b)

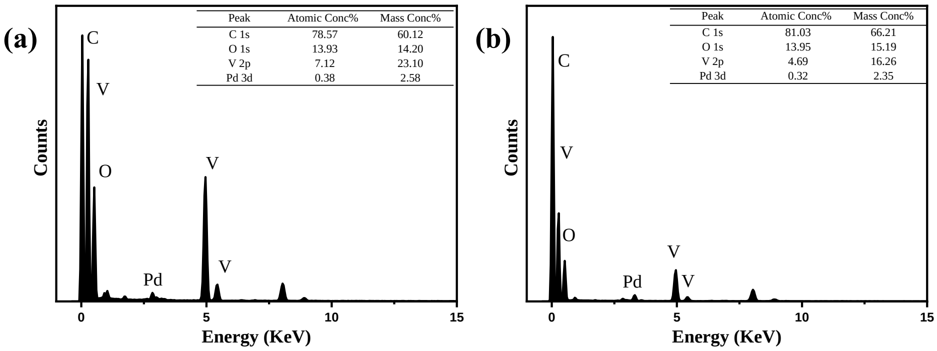

Fig. S11 TEM-EDS analysis of (a) Pd/VOx/C-700-before (powder sample) and (b) Pd/VOx/C-700-after

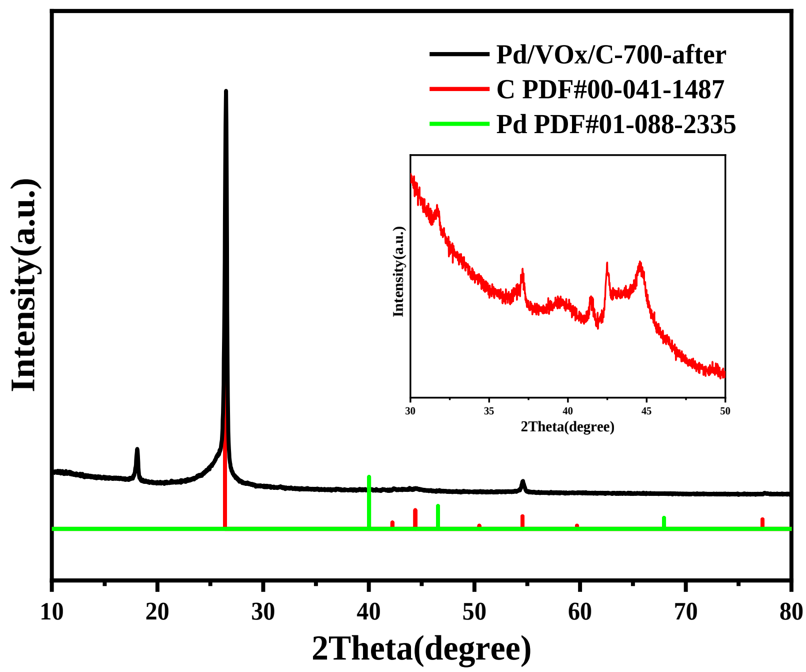

Fig. S12 XRD of Pd/VOx/C-700 after cycle test

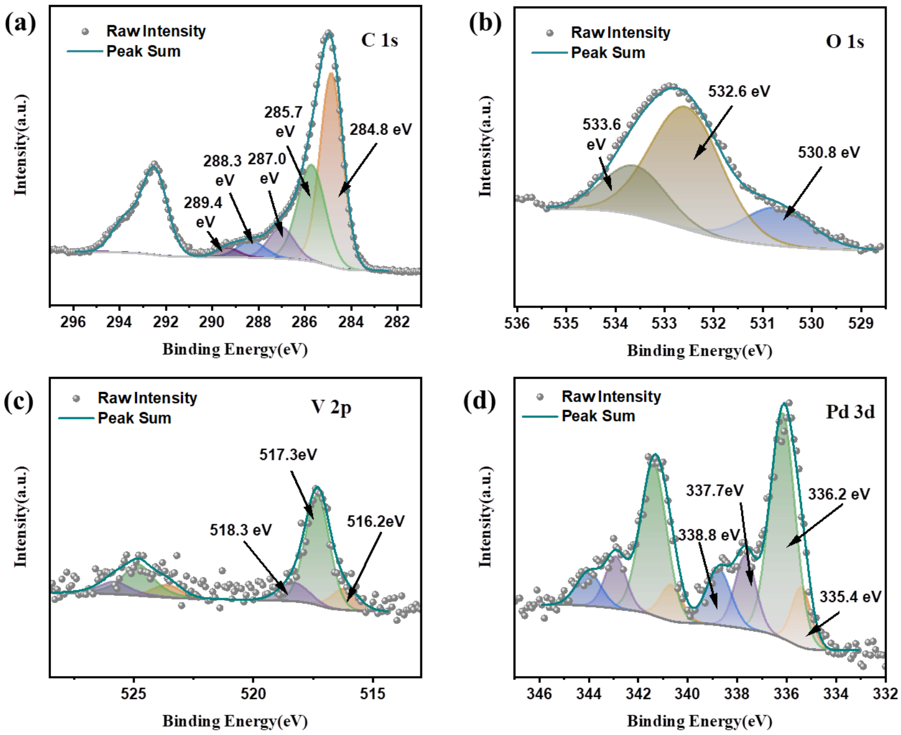

Fig. S13 XPS of (a) C 1s, (b) O 1s, (c) V 2p and (d) Pd 3d for Pd/VOx/C-700 after cycle test

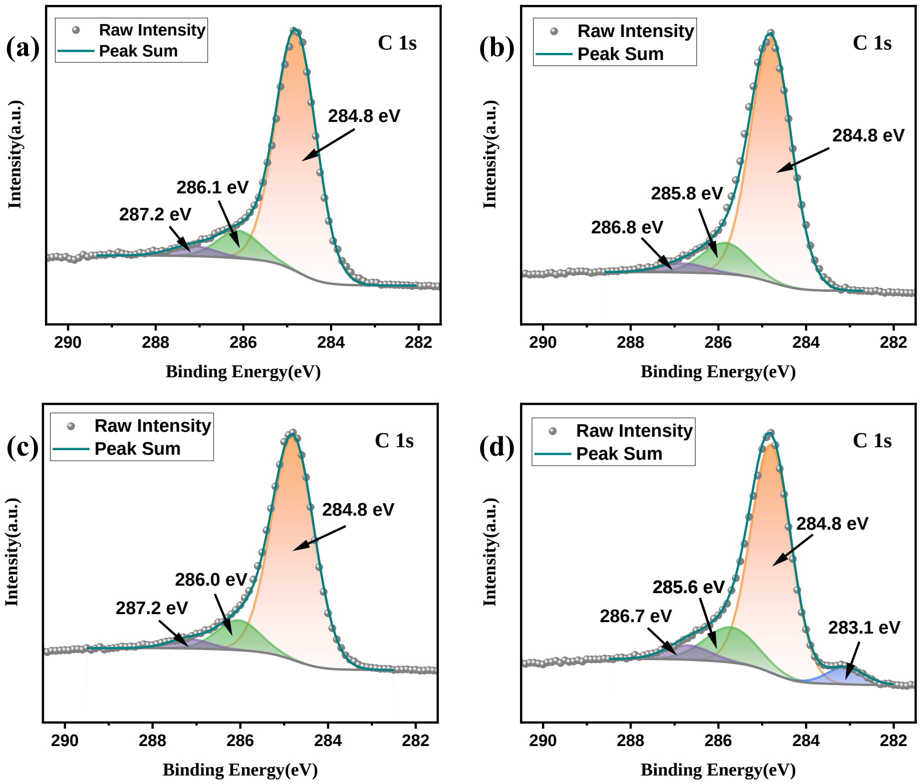

Fig. S14 C 1s XPS spectra of (a) commercial Pd/C, (b) Pd/VOx/C-500, (c) Pd/VOx/C-700, (d) Pd/VC/C-900

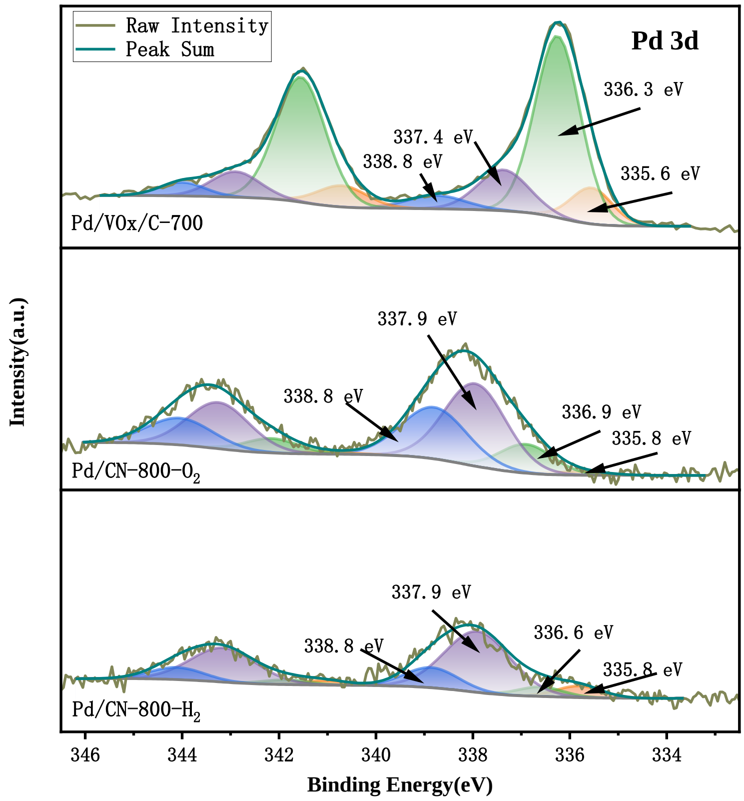

Fig. S15 Pd 3d region in Pd/VOx/C-700, Pd/CN-800-O_2 and Pd/CN-800-H_2

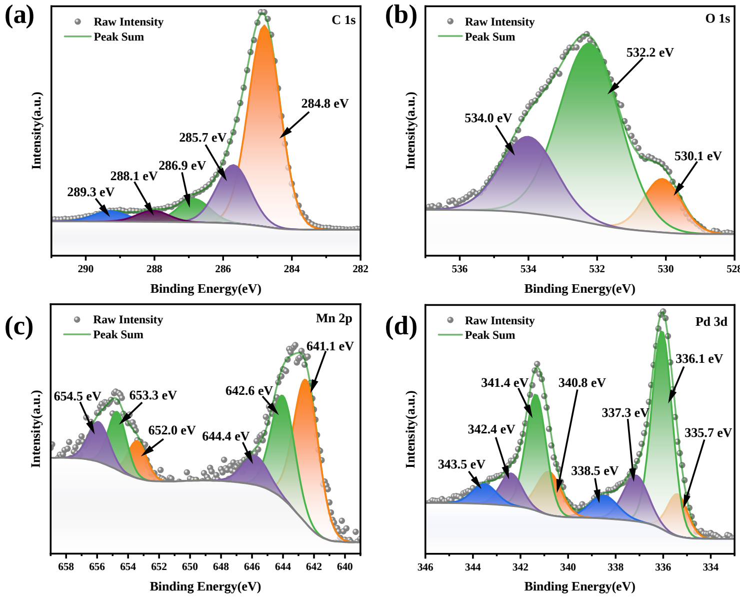

Fig. S16 (a) C 1s, (b) O 1s, (c) Mn 2p and (d) Pd 3d XPS spectra of Pd/MnO/C-800

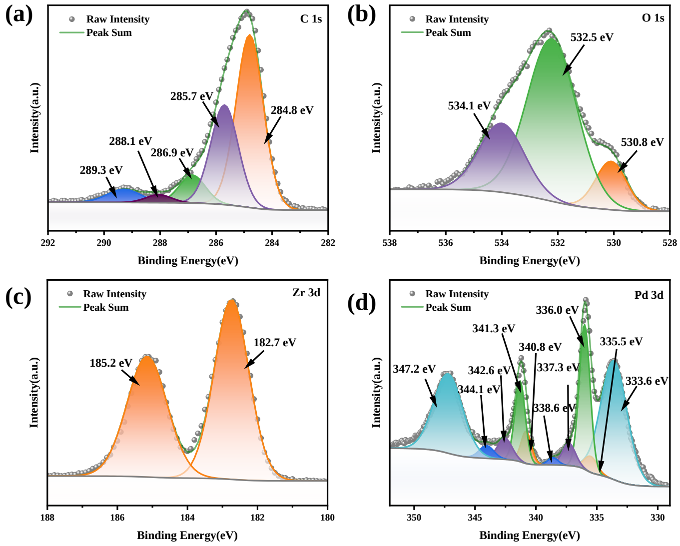

Fig. S17 (a) C 1s, (b) O 1s, (c) Zr 3d and (d) Pd 3d XPS spectra of Pd/ZrO_2/C-800

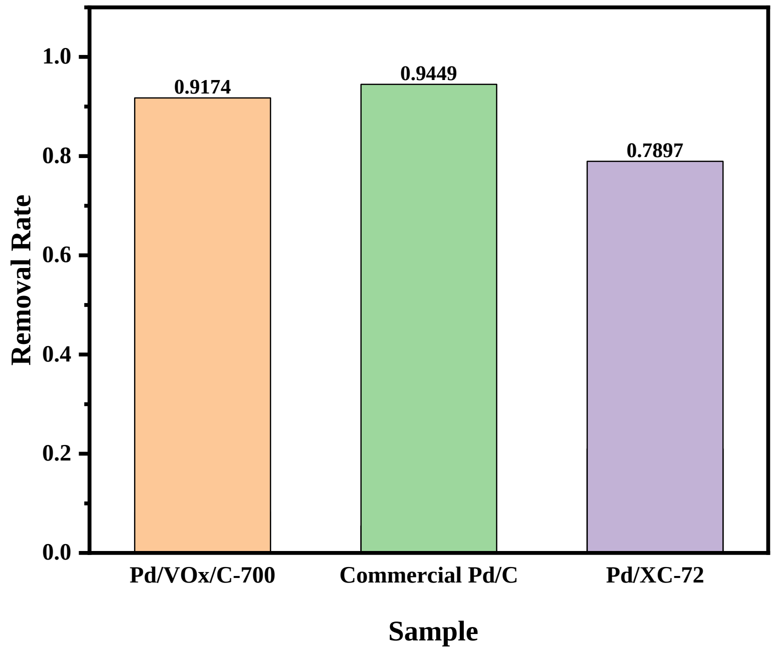

Fig. S18 EHDC performance of Pd/VOx/C-700,commercial Pd/C and Pd/XC-72

Table S1. k_{ap} and the normalized k_{ap} for EHDC of 4-CP on Pd-based catalysts supported by different oxides

Pd-based catalysts	k (min^{-1})	R^2	ECSA (cm^{-2})	normalized k_{ap} ($min^{-1}\cdot cm_{Pd}^{-2}$)
Pd/MnO/C-800	0.00332	0.9530	2.6707	0.00123
Pd/ZrO_2/C-800	0.00750	0.9812	1.6359	0.00458
Pd/VOx/C-600	0.01170	0.9960	1.2108	0.00966
Commercial Pd/C	0.01595	0.9984	2.3963	0.00666

Table S2. Activity comparison of Pd/VOx/C-700 with representative nano-Pd and Pd film electrocatalysts for the dichlorination of chlorophenol

Cathode	electrolytes	Concentration of Reactant(4-CP)	Pd loading (mg/cm^{-2})	DA [a] ($mmol·g^{-1}·h^{-1}$)	Main product[b]	Refs
Pd-P -60	25 mM K_2SO_4	0.38 mM	0.08	10.8	phenol	[1]
Pd/PPy-rGO/ Ni foam	100 mM Na_2SO_4	0.78 mM	0.43	24.7	phenol	[2]
Pd/Ni_2P-NF	50 mM Na_2SO_4	0.38 mM	0.41	9.0	phenol	[3]
Pd/rGO/ Ni foam	50 mM Na_2SO_4	1 mM	2.6	36.1	phenol	[4]
A-Pd-NC/CP	100 mM PBS	1 mM	0.022	72.0	phenol	[5]
TiO_2 @PDA/Pd	100 mM PBS	1 mM	0.093	23.9	phenol	[6]
Pd/CN-800/CP	100 mM PBS	1 mM	0.051	43.3	phenol	[7]
Pd-Cu/PPy/NF	50 mM Na_2SO_4	1.56 mM	0.265	44.2	phenol	[8]
Pd/VOx/C-700/CP	100 mM PBS	1 mM	0.031	72.6	phenol	This work

[a] Dechlorination activity (DA) was calculated at optimal conditions. [b] The main product at the point of dechlorination reaction where the DA was calculated. PPy-rGO= polypyrrole-reduced graphene oxide.

Table S3. Fitted Pd peak areas ratio of Pd/MnO/C-800 and Pd/ZrO_2/C-800 catalysts in XPS

Catalysts	S1= (Pd^0) [a]	S2= ($Pd^{\delta+}$) [b]	S3= (Pd^{2+}) [c]	S4= (Pd-Cl) [d]	Sum [e]	(S2+S3) /S1	S1/ Sum	S2/ Sum	S3/ Sum	S4/ Sum
Pd/MnO/C -800	5500	13000	3600	2000	24100	3.02	22.82	53.94	14.94	8.30
Pd/ZrO_2/C -800	2500	18800	3500	900	25700	8.92	9.73	73.15	13.62	3.50

[a] The Fitted peak areas of Pd^0. [b] The Fitted peak areas of $Pd^{\delta+}$ ($0 < \delta < 2$). [c] The Fitted peak areas of Pd^{2+}. [d] The Fitted peak areas of Pd-Cl. [e] The total Fitted Pd peak area

1. Y. Chen, Z. Liu, S. Liu, Y. Cheng, C. Zhang, J. Jiao, Y. Lu, W. Wang, K. Sun, X. Bi, A. Han, B. Liu, Y. Pan, Y. Liu and C. Liu, *Appl. Catal., B*, 2021, **284**.
2. H. Yu, S. Yang, B. Zhao, Y. Lu, S. Zhu, X. Wang, W. Qin and M. Huo, *J. Electroanal. Chem.*, 2020, **869**, 114099.
3. J. Li, Y. Chen, R. Bai, C. Chen, W. Wang, Y. Pan and Y. Liu, *Chem. Eng. J.*, 2022, **435**, 134932.
4. Y. Liu, L. Liu, J. Shan and J. Zhang, *J. Hazard. Mater.*, 2015, **290**, 1-8.
5. Z. Mao, L. Liu, H. B. Yang, Y. Zhang, Z. Yao, H. Wu, Y. Huang, Y. Xu and B. Liu, *Electrochim. Acta*, 2021, **391**, 138886.
6. Z. Zhao, L. Yu, L. Zheng, T. Guo, Z. Lv, S. Song and H. Zheng, *J. Hazard. Mater.*, 2022, **435**, 128998.
7. S. Xu, B. Mei, F. Li, J. Mao, C. Huang, Y. Yan, N. Chen, Y. Xu and M. Shi, *Nanotechnology*, 2023, **34**, 445601.
8. Y. Lei, T. Li, L. Yang, Y. Peng, W. Xiong and D. Liu, *Appl. Surf. Sci.*, 2024, **654**, 159479.