Supporting Information for:

Morphological Tuning Engineering of Pt@TiO_2/Graphene Catalysts with Optimal Active Surface of Support for Boosting Catalytic Performance to Methanol Oxidation

Kefu Zhang, Jun Qiu, Juan Wu, Yongqi Deng, Yihan Wu, Lifeng Yan*

Hefei National Laboratory for Physical Sciences at the Microscale, and Department of Chemical Physics, University of Science and Technology of China, Jinzairoad 96, Hefei, 230026, Anhui, China

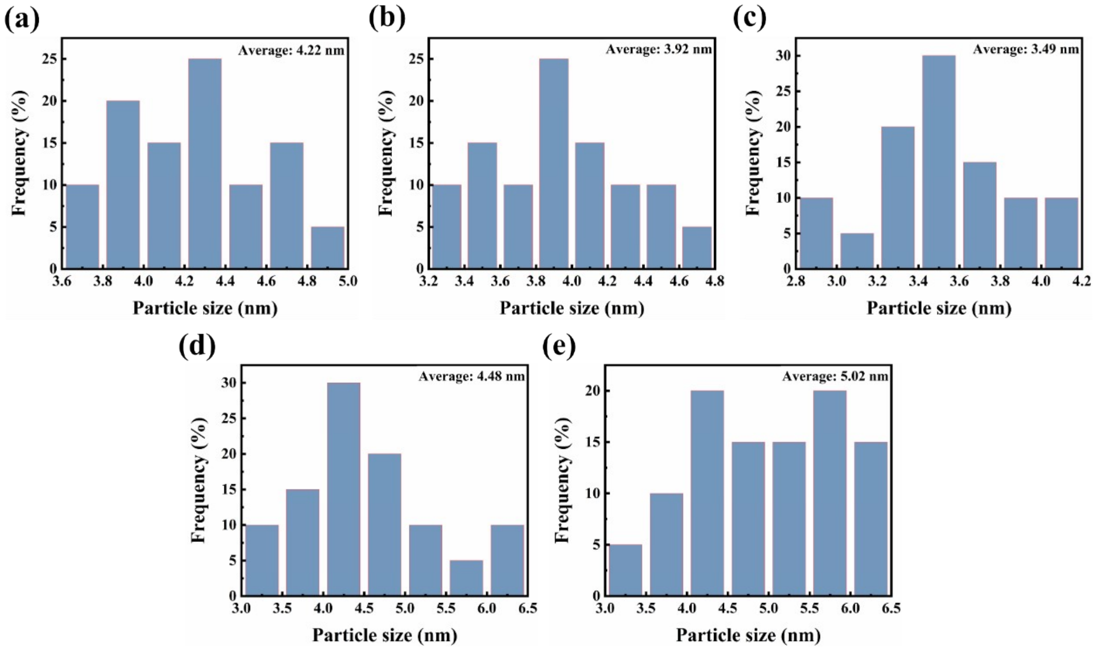

Fig. S1 The particle diameters distribution of Pt NPs. (**a**) UV-Pt@TONC/GN, (**b**) UV-Pt@TONC&R/GN, (**c**) UV-Pt@TONR/GN, (**d**) UV-Pt/GN and (**e**) UV-Pt@TiO_2.

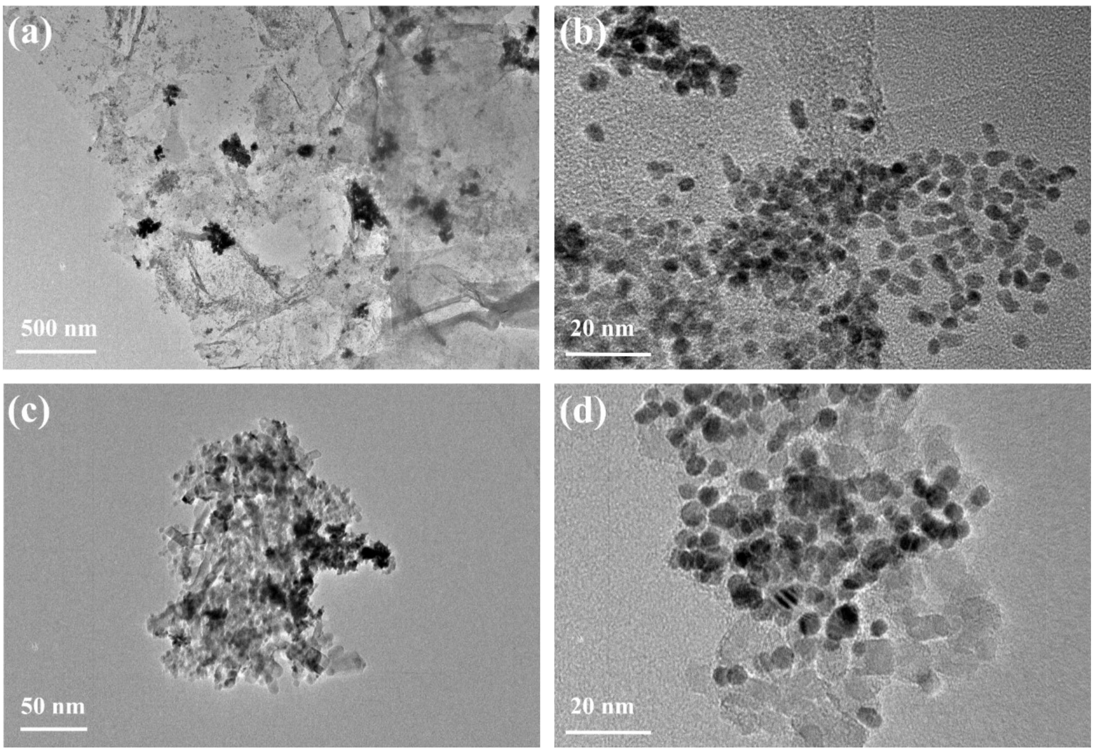

Fig. S2 TEM images of (**a,b**) UV-Pt/GN and (**c,d**) UV-Pt@TiO_2 catalysts synthesized with the same procedure.

Table S1 Surface compositions and oxidation states of Pt species derived from XPS analyses.

	Pt species (%)	
	Pt^0	Pt^{2+}
UV-Pt@TONR/GN	68.08	31.92
UV-Pt@TONC&R/GN	61.07	38.93
UV-Pt@TONC/GN	48.51	51.49
UV-Pt /GN	33.21	66.79
UV-Pt@TiO_2	42.30	57.70

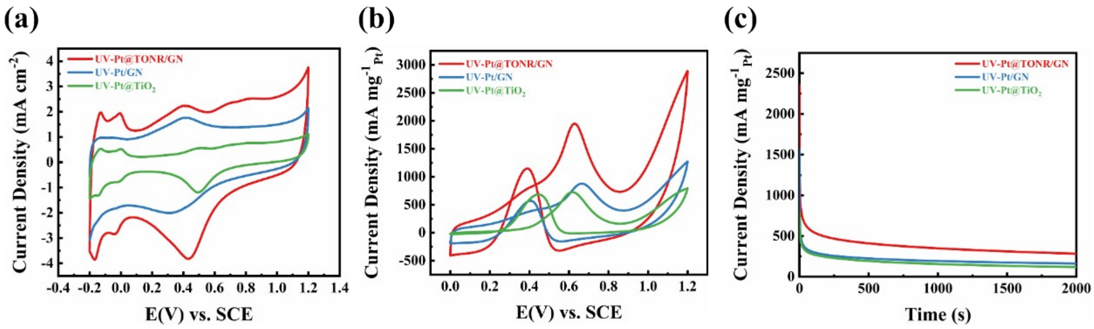

Fig. S3 (**a**) CV curves, (**b**) MOR measurements and (**c**) 2000s current−time (i−t) measurements of UV-Pt@TONR/GN, UV-Pt/GN and UV-Pt@TiO_2 catalysts in acid media.

Table S2 The electrochemical parameters of the designed catalysts in alkaline and acid media, respectively.

	Alkaline solution			Acid solution		
	ECSA (m^2 g^{-1})	MA (mA mg^{-1}_{Pt})	SA (mA cm^{-2})	ECSA (m^2 g^{-1})	MA (mA mg^{-1}_{Pt})	SA (mA cm^{-2})
UV-Pt@TONR/GN	51.55	3165.00	6.14	60.69	1945.63	3.21
UV-Pt@TONC&R/GN	46.43	2587.57	5.57	47.25	1367.39	2.89
UV-Pt@TONC/GN	43.71	1917.14	4.39	41.58	1037.67	2.50
Pt/GN	40.86	1447.20	3.54	36.07	876.58	2.43
Pt@TiO_2	36.12	924.8	2.56	39.32	724.41	1.84
Commercial Pt/C	42.40	686.95	1.62	40.98	445.37	1.09

Table S3 The performance of various MOR electrocatalysts in alkaline / acid electrolytes in recent years.

Catalyst	**Electrolyte**	**ECSA (m^2 g^{-1})**	**Mass activity (mA mg^{-1}_{Pt})**	**Ref.**
UV-Pt@TONR/GN	1 M KOH + 1 M CH_3OH	51.55	3165	This work
Pt–Ce(CO_3)OH/rGO	1 M KOH + 1 M CH_3OH	60.36	1447.5	1
$Pd_{59}Cu_{33}Ru_8$ NSs	1 M KOH + 1 M CH_3OH	35.3	1660.8	2
Pt/g-C_3N_4/MoS_2	1 M KOH + 1 M CH_3OH	--	1618	3
PtCu NFs	0.5 M KOH + 1 M CH_3OH	12.4	2110	4
Pt-NiO	1 M KOH + 1 M CH_3OH	26.0	880	5
Pt/Ni$(OH)_2$/rGO	1 M KOH + 1 M CH_3OH	64.1	1200	6
UV-Pt@TONR/GN	0.5 M H_2SO_4 + 1 M CH_3OH	60.69	1945.63	This work
Pt/NiCoP_x@NCNT-NG	0.5 M H_2SO_4 + 1 M CH_3OH	54.2	867	7
Pt-Ag DSNCs	0.5 M H_2SO_4 + 1 M CH_3OH	17.8	566.8	8
p-Pt/TNR@GC	0.5 M $HClO_4$ + 0.5 M CH_3OH	62.6	1120	9
PtRu NWs	0.5 M H_2SO_4 + 0.5 M CH_3OH	12.4	820	10
PtNi/ceria	0.1 M $HClO_4$ + 0.5 M CH_3OH	36.9	1500	11

$Pt/TiO_2/rGO$	0.5 M H_2SO_4 + 0.5 M CH_3OH	81.7	698.9	12

Equation S1:

$$J_p = 0.4463 \times (F^3/RT)^{1/2} \times n^{3/2} \times A \times D_0^{1/2} \times C_0^* \times v^{1/2}$$

Where F is the Faraday constant, R is the gas constant, T is the temperature of the electrooxidation reaction, n is the number of electrons transferred in the reaction, A is the surface area of the electrode, D_0 is diffusion coefficient;, C_0* is the initial concentration of electrolyte and v is the potential scan rate. The parameter values of F, R, T, A, D_0, C_0* are constant in the same experimental media, and the slope is determined by $n^{3/2}$.

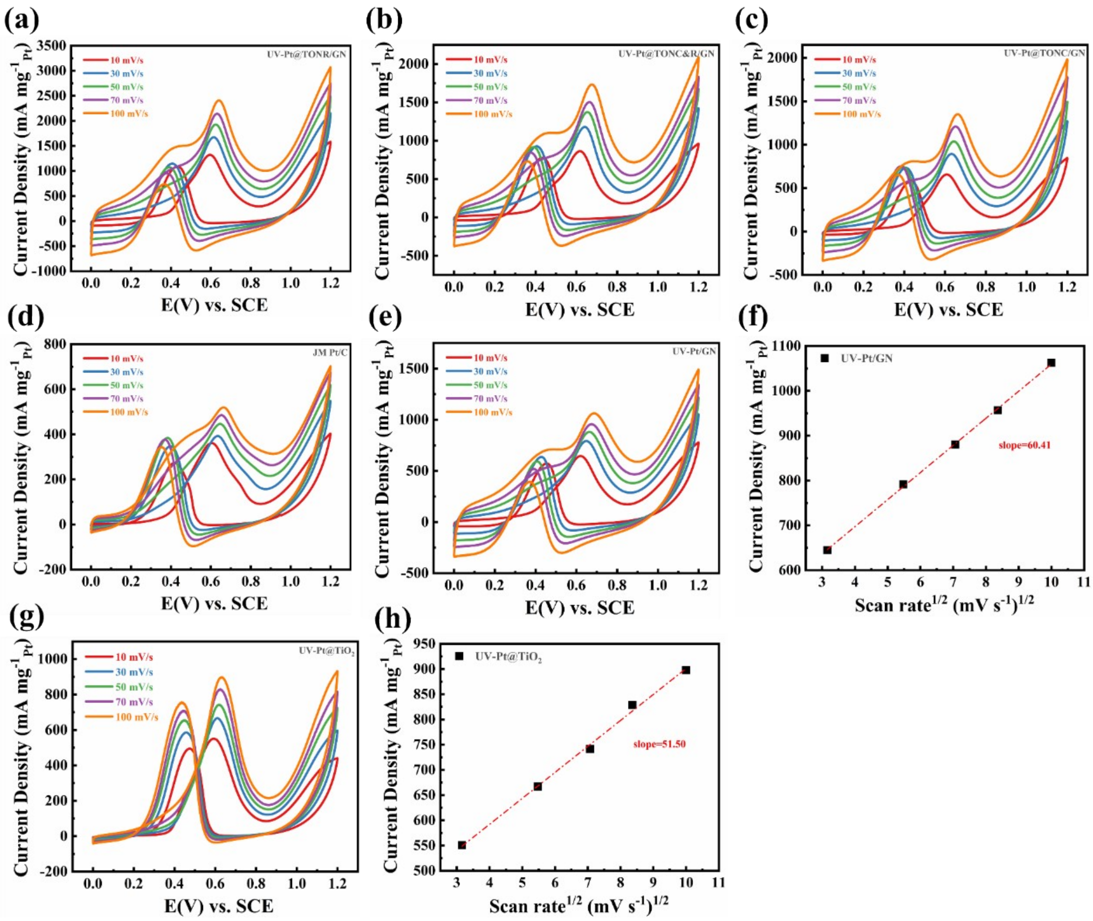

Fig. S4 CV curves of (**a**) UV-Pt@TONR/GN, (**b**) UV-Pt@TONC&R/GN, (**c**) UV-Pt@TONC/GN, (**d**) JM Pt/C, (**e**) UV-Pt/GN and (**g**) UV-Pt@TiO_2 at various scan rates. The corresponding linear relationship between peak current density and the square root of sweep rate of (**f**) UV-Pt/GN and (**h**) UV-Pt@TiO_2 in 0.5 M H_2SO_4 + 1 M CH_3OH solution.

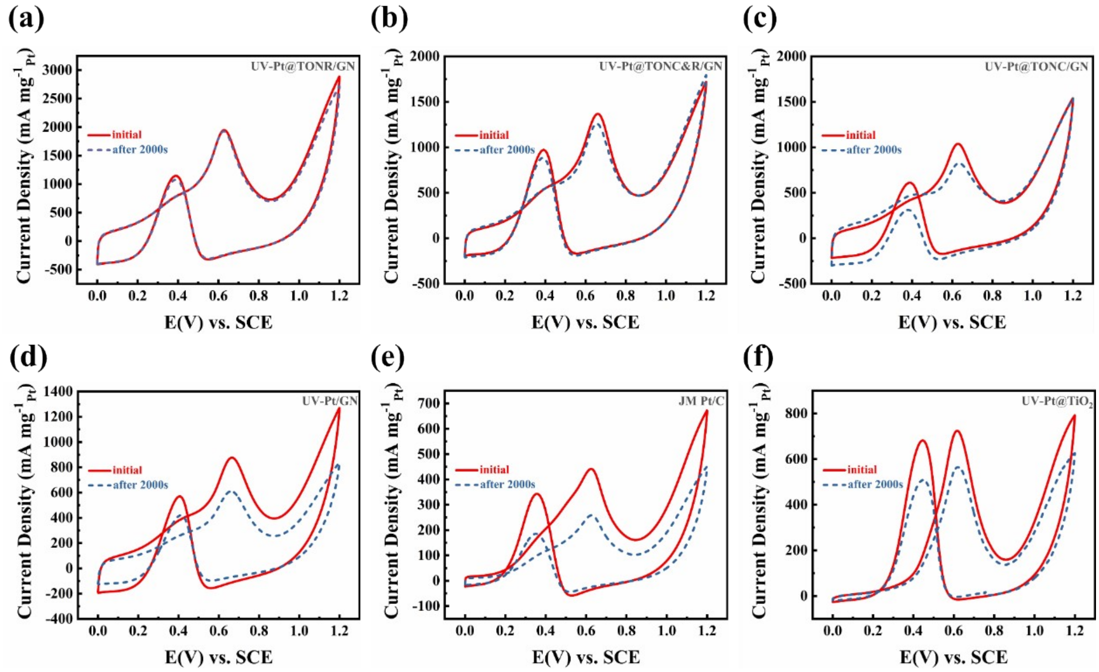

Fig. S5 CV curves of variously prepared catalysts before and after 2000 s i-t test in 0.5 M H_2SO_4 + 1 M CH_3OH solution.

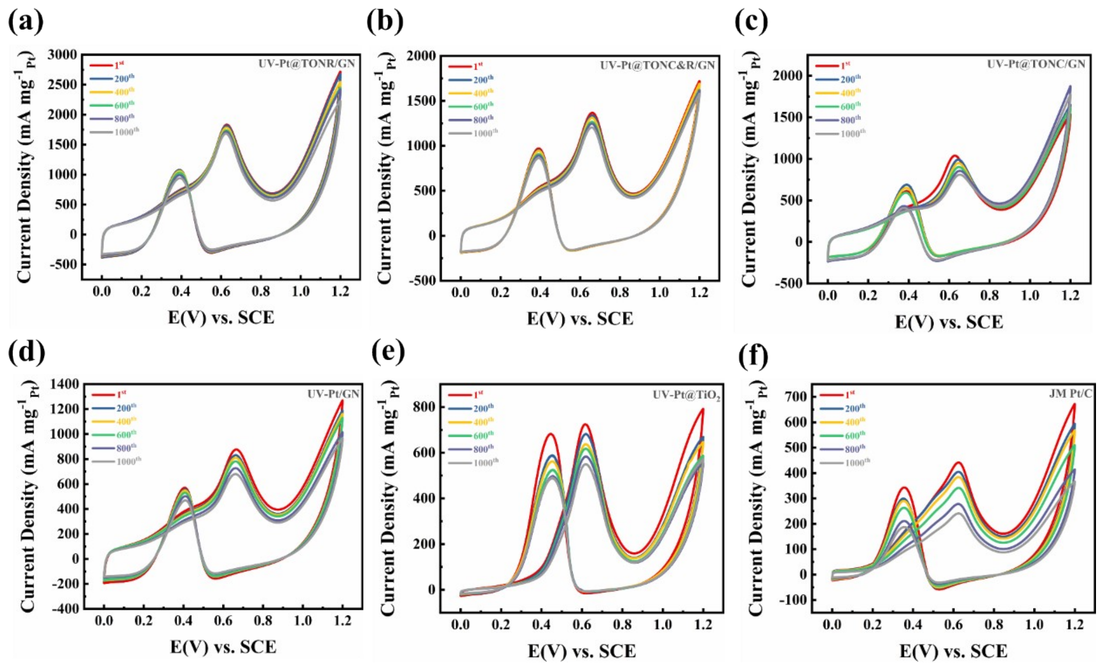

Fig. S6 MOR CV curves of (**a**) UV-Pt@TONR/GN, (**b**) UV-Pt@TONC&R/GN, (**c**)

UV-Pt@TONC/GN, (**d**) UV-Pt/GN, (**e**) UV-Pt@TiO_2 and (**f**) JM Pt/C sweep for 1000 cycles in 0.5 M H_2SO_4 + 1 M CH_3OH solution.

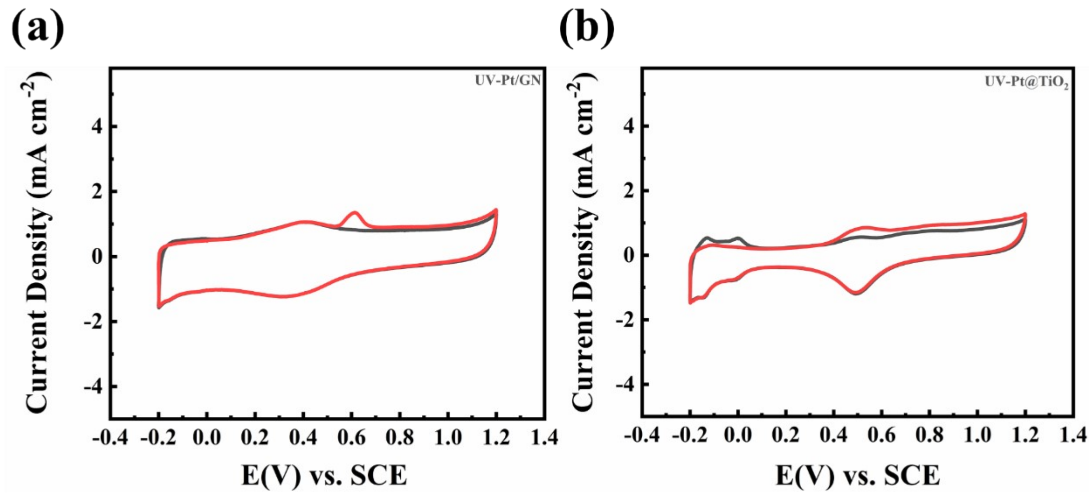

Fig. S7 CO-stripping voltammetry measurements of (**a**) UV-Pt/GN and (**b**) UV-Pt@TiO_2.

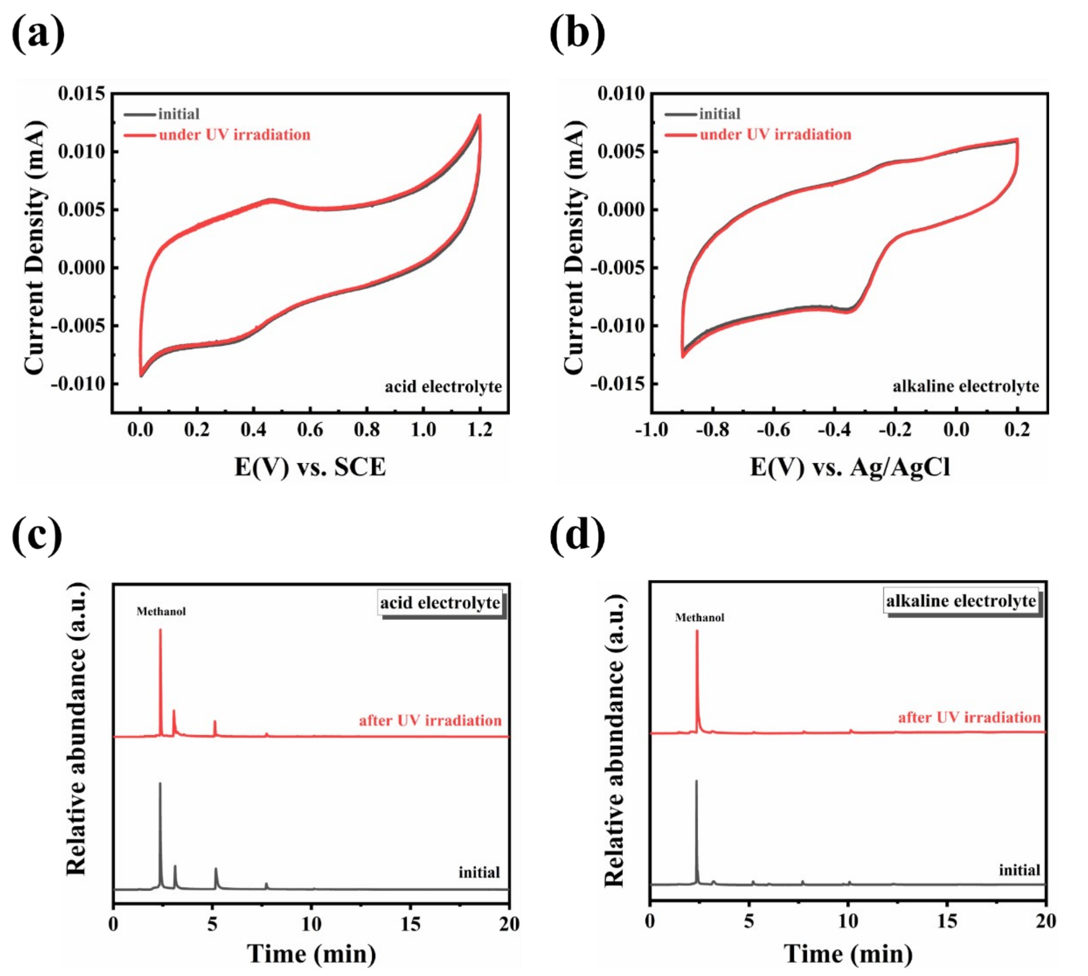

Fig. S8 CV curves of methanol oxidation without or with UV irradiation in (**a**) 0.5 M

H_2SO_4+ 1 M CH_3OH solution and (**b**) 1 M KOH+ 1 M CH_3OH solution. Typical GC spectra of methanol electrolyte before and after UV irradiation : (**c**) acid electrolyte and (**d**) alkaline electrolyte.

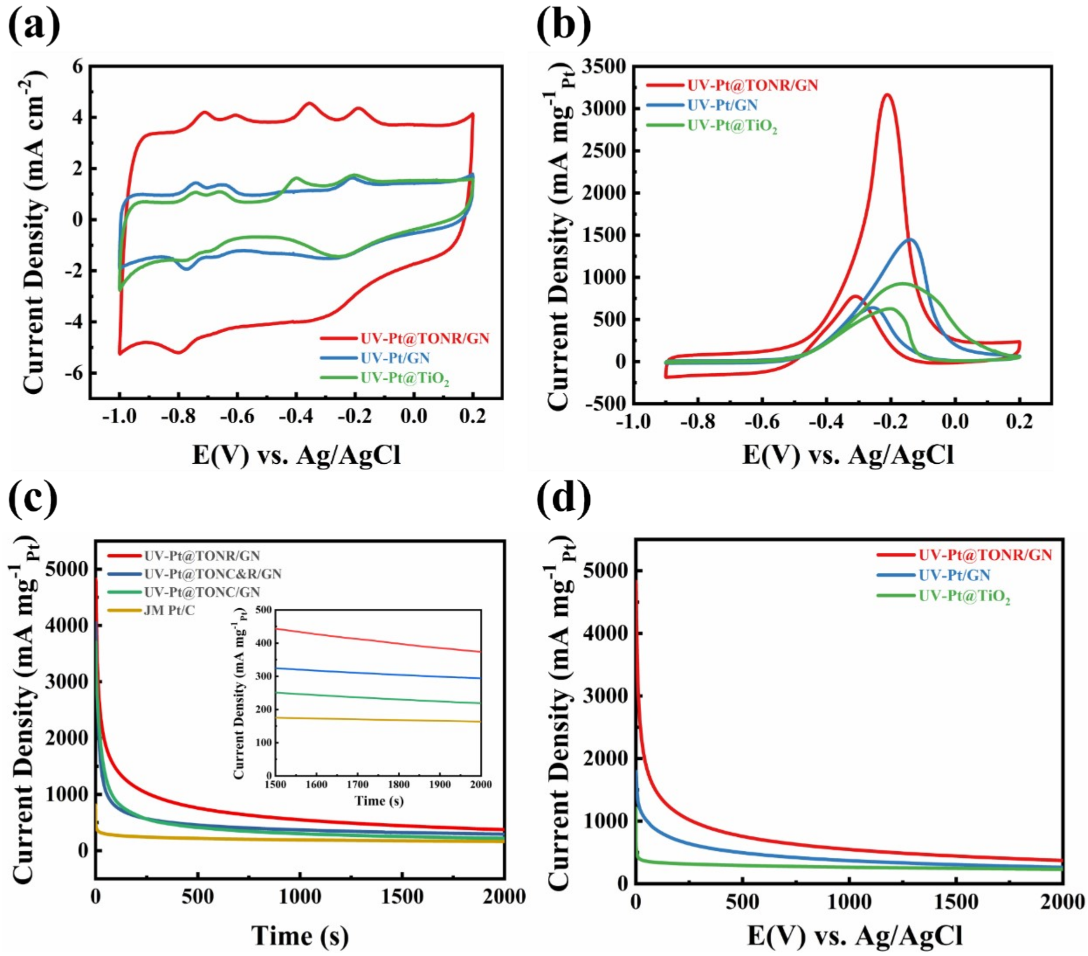

Fig. S9 (**a**) CV curves, (**b**) MOR measurements and (**c,d**) 2000s current−time (i−t) measurements of the synthesized catalysts in alkaline media.

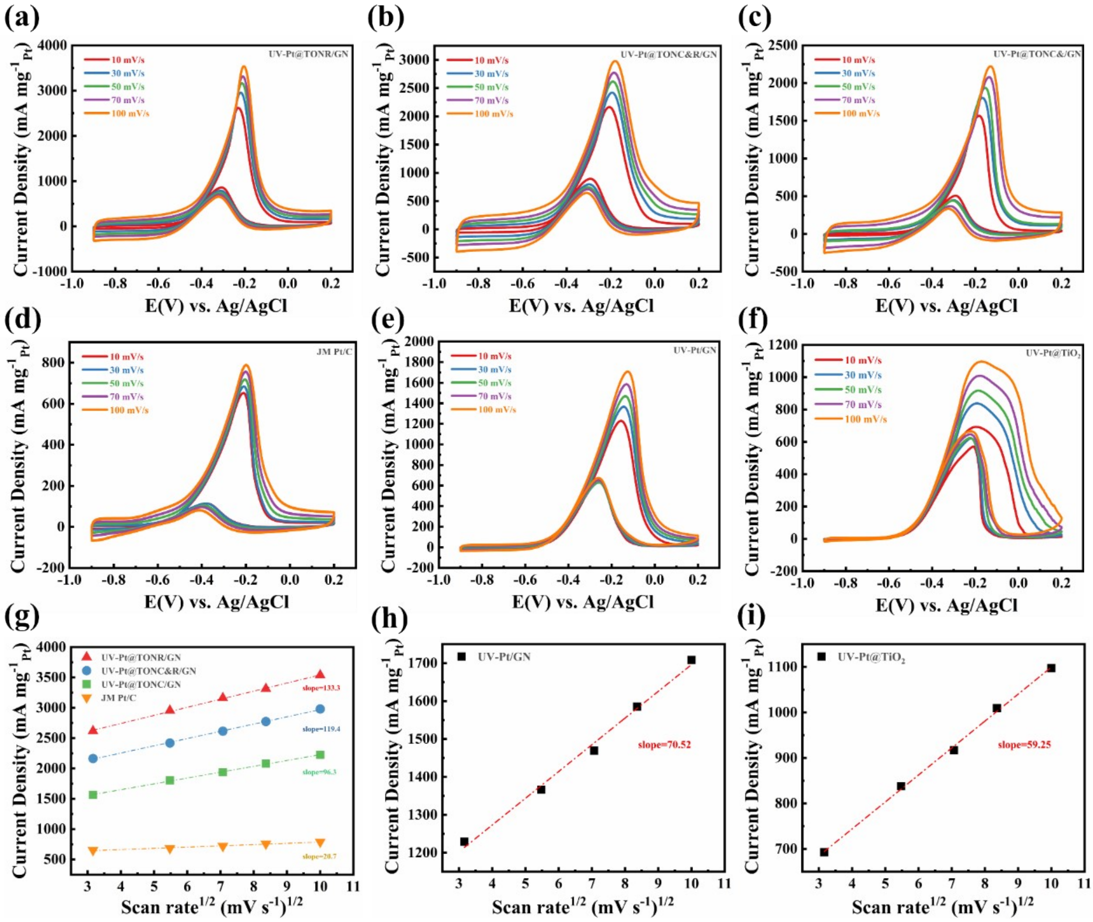

Fig. S10 CV curves of (**a**) UV-Pt@TONR/GN, (**b**) UV-Pt@TONC&R/GN, (**c**) UV-Pt@TONC/GN, (**d**) JM Pt/C, (**e**) UV-Pt/GN and (**f**) UV-Pt@TiO_2 at various scan rates and (**g-i**) corresponding linear relationship between peak current density and the square root of sweep rate in 1 M KOH + 1 M CH_3OH solution.

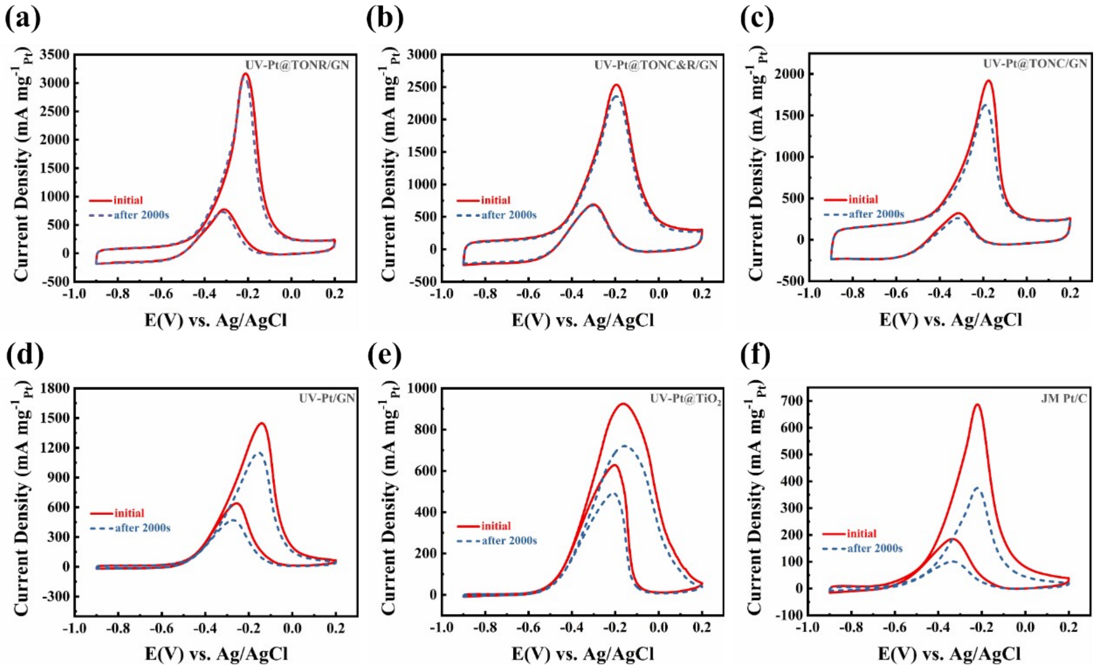

Fig. S11 CV curves of variously prepared catalysts before and after 2000 s i-t test in 1 M KOH + 1 M CH_3OH solution.

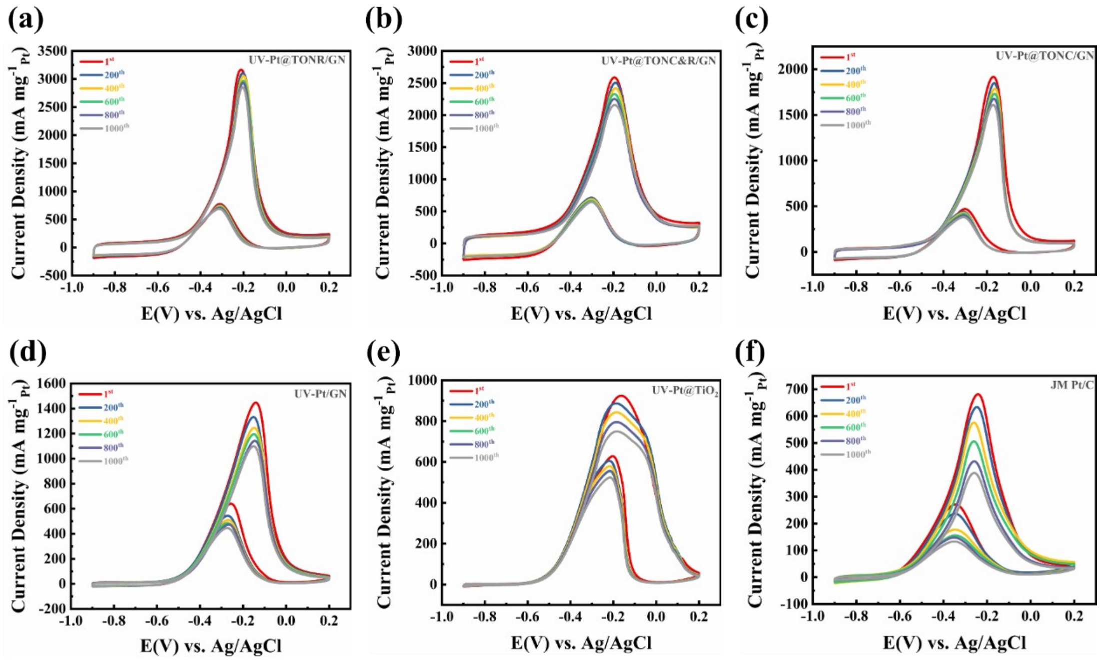

Fig. S12 MOR CV curves of (**a**) UV-Pt@TONR/GN, (**b**) UV-Pt@TONC&R/GN, (**c**) UV-Pt@TONC/GN, (**d**) UV-Pt/GN, (**e**) UV-Pt@TiO_2 and (**f**) JM Pt/C sweep for 1000 cycles in 1 M KOH + 1 M CH_3OH solution.

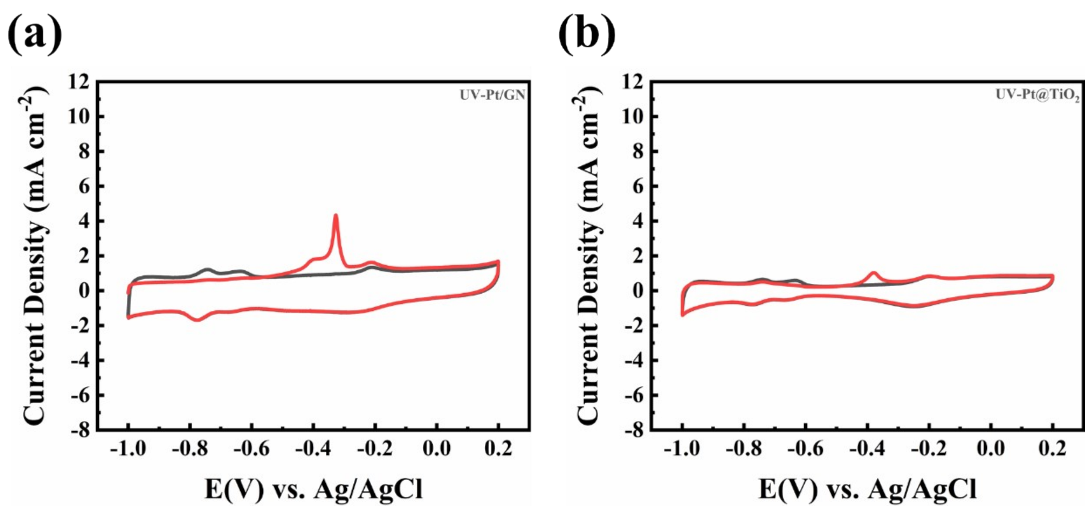

Fig. S13 CO-stripping voltammetry measurements of (a) UV-Pt/GN and (b) UV-Pt@TiO_2 in 1 M KOH.

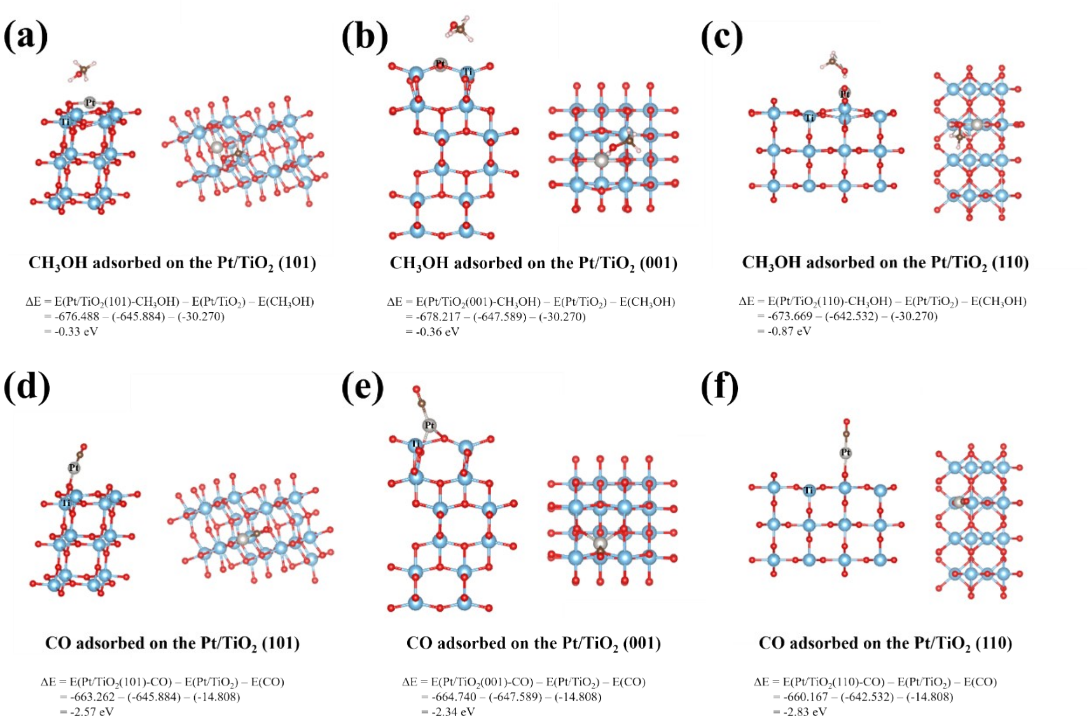

Fig. S14 Structures of adsorbed CH_3OH on (**a**) Pt/TiO_2(101), (**b**) Pt/TiO_2(001), (**c**) Pt/TiO_2(110) and CO on (**d**) Pt/TiO_2(101), (**e**) Pt/TiO_2(001), and (**f**) Pt/TiO_2 (110) surfaces and corresponding adsorption energies.

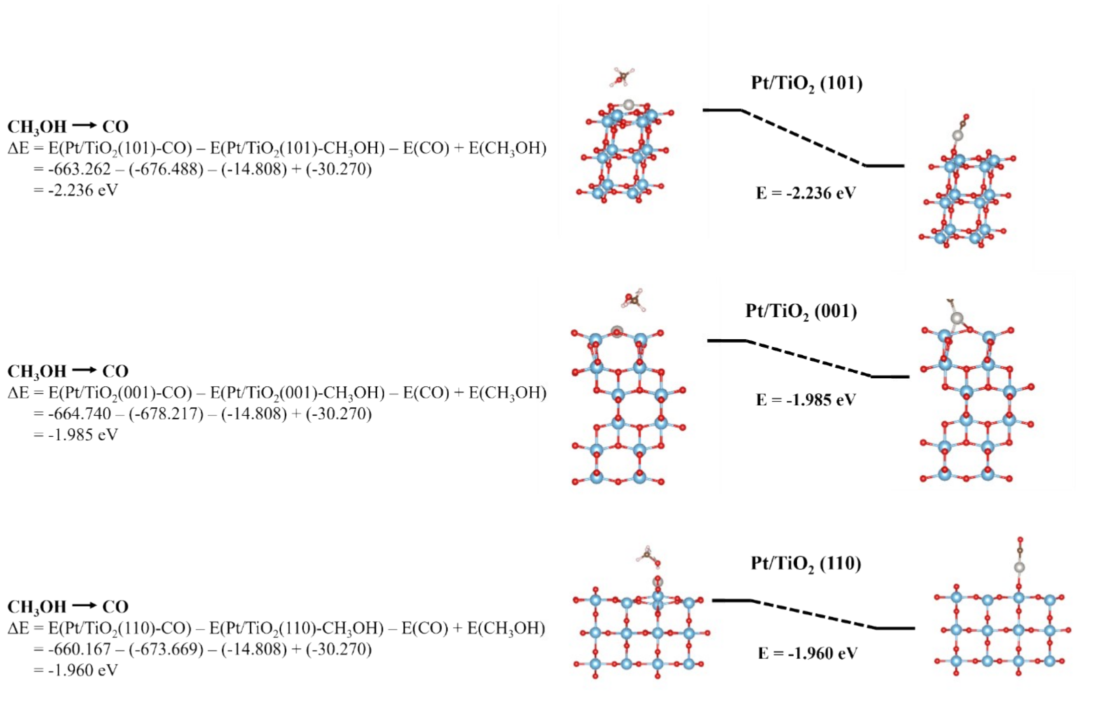

Fig. S15 Calculated formation energies obtained from the difference of the binding energies of CH_3OH and CO on Pt/TiO_2(101), Pt/TiO_2(001) and Pt/TiO_2(110) surfaces.

References

1. G. Chen, Z. Dai, L. Sun, L. Zhang, S. Liu, H. Bao, J. Bi, S. Yang and F. Ma, *J. Mater. Chem. A*, 2019, **7**, 6562-6571.
2. L. Jin, H. Xu, C. Chen, H. Shang, Y. Wang, C. Wang and Y. Du, *ACS Appl. Mater. Interfaces.*, 2019, **11**, 42123-42130.
3. C. Zhai, M. Sun, L. Zeng, M. Xue, J. Pan, Y. Du and M. Zhu, *Appl. Catal. B.*, 2019, **243**, 283-293.
4. Z. Zhang, Z. Luo, B. Chen, C. Wei, J. Zhao, J. Chen, X. Zhang, Z. Lai, Z. Fan, C. Tan, M. Zhao, Q. Lu, B. Li, Y. Zong, C. Yan, G. Wang, Z. J. Xu and H. Zhang, *Adv. Mater.*, 2016, **28**, 8712-8717.
5. Z. Gu, D. Bin, Y. Feng, K. Zhang, J. Wang, B. Yan, S. Li, Z. Xiong, C. Wang, Y. Shiraishi and Y. Du, *Appl. Surf. Sci.*, 2017, **411**, 379-385.
6. W. Huang, H. Wang, J. Zhou, J. Wang, P. N. Duchesne, D. Muir, P. Zhang, N. Han, F. Zhao, M. Zeng, J. Zhong, C. Jin, Y. Li, S. T. Lee and H. Dai, *Nat. Commun.*, 2015, **6**, 10035.
7. J. Ding, W. Hu, L. Ma, M. Gan, F. Xie, W. Zhan and W. Lu, *J. Power Sources*, 2021, **481**, 228888.
8. W. Yao, X. Jiang, M. Li, Y. Li, Y. Liu, X. Zhan, G. Fu and Y. Tang, *Appl. Catal. B.*, 2021, **282**, 119595.
9. C. Li, Y. Qu, L. Du, G. Chen, S. Lou, Y. Gao and G. Yin, *ACS Sustain. Chem. Eng.* , 2019, **7**, 8597-8603.
10. L. Huang, X. Zhang, Q. Wang, Y. Han, Y. Fang and S. Dong, *J. Am. Chem. Soc.*, 2018, **140**, 1142-1147.
11. Y. Kwon, Y. Kim, J. W. Hong, Y. Whang, S. Kim, D. H. Wi, H. R. Byon and S. W. Han, *J. Mater. Chem. A*, 2020, **8**, 25842-25849.
12. S. Wu, J. Liu, Y. Ye, Z. Tian, X. Zhu and C. Liang, *ACS Appl. Energy Mater.*, 2019, **2**, 5577-5583.