

Supporting information

Pt nanoparticles supported on porous sheath TiO₂ wrapped carbon nanotubes for selective glycerol electro-oxidation into tartronate

Chaohui Guan^a, Jiefei Li^b, Tao Chen^a, Liang Lv^a, Junfeng Du^a, Shuai Zhang^a, Hang Wei^a, Haibin Chu^{*a}

^a*College of Chemistry and Chemical Engineering, Inner Mongolia Key Laboratory of Rare Earth Catalysis, Inner Mongolia Engineering and Technology Research Center for Catalytic Conversion and Utilization of Carbon Resource Molecules, Inner Mongolia University, Hohhot 010021, China.*

^b*School of Petrochemical Engineering, Shenyang University of Technology, Liaoyang 111003, China.*

Corresponding author.

E-mail address: chuhb@imu.edu.cn (H. Chu).

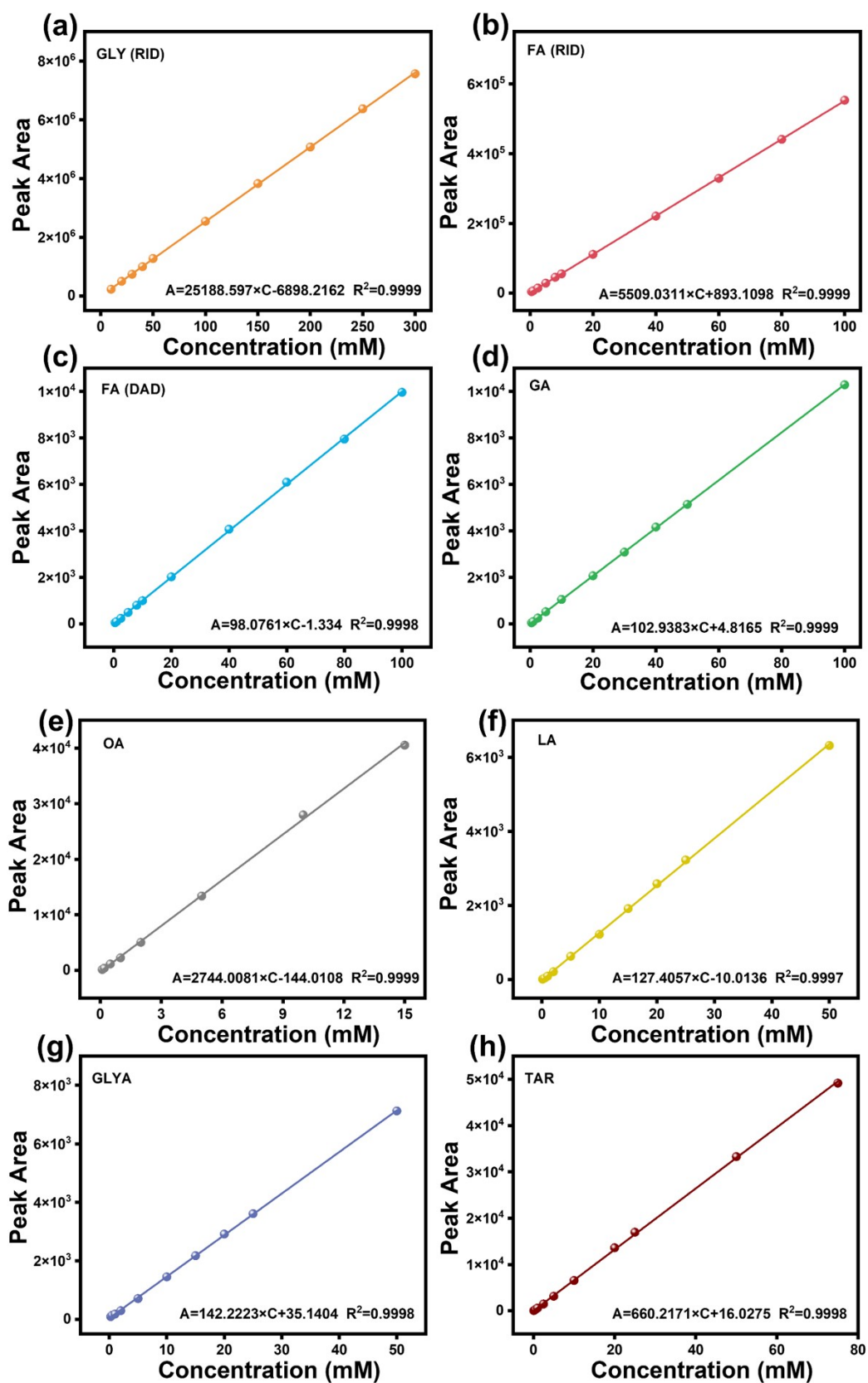


Fig. S1 The standard curves and corresponding linear fitting equations with correlation coefficients. (a) Glycerol and (b) FA with RID. (c) FA, (d) GA, (e) OA, (f) LA, (g) GLYA, and (h) TAR with DAD.

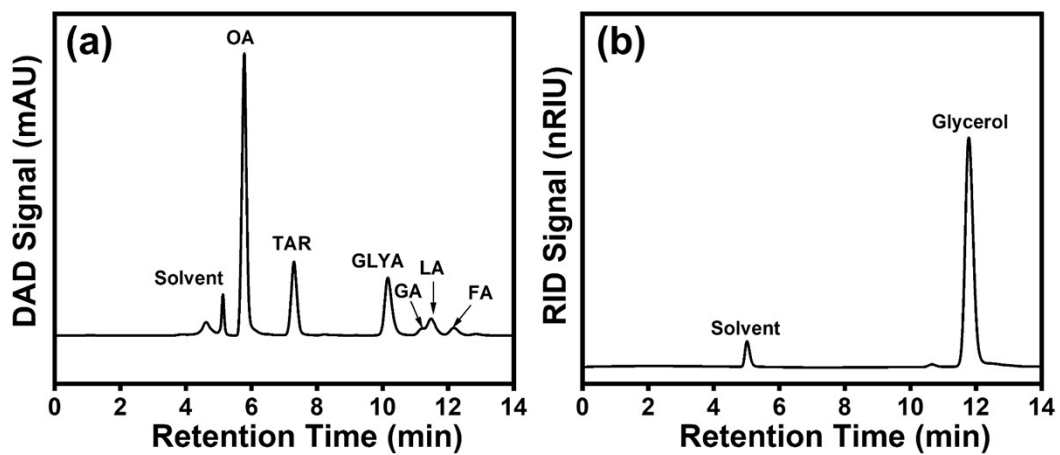


Fig. S2 HPLC chromatograms of (a) different products detected by DAD and (b) glycerol detected by RID.

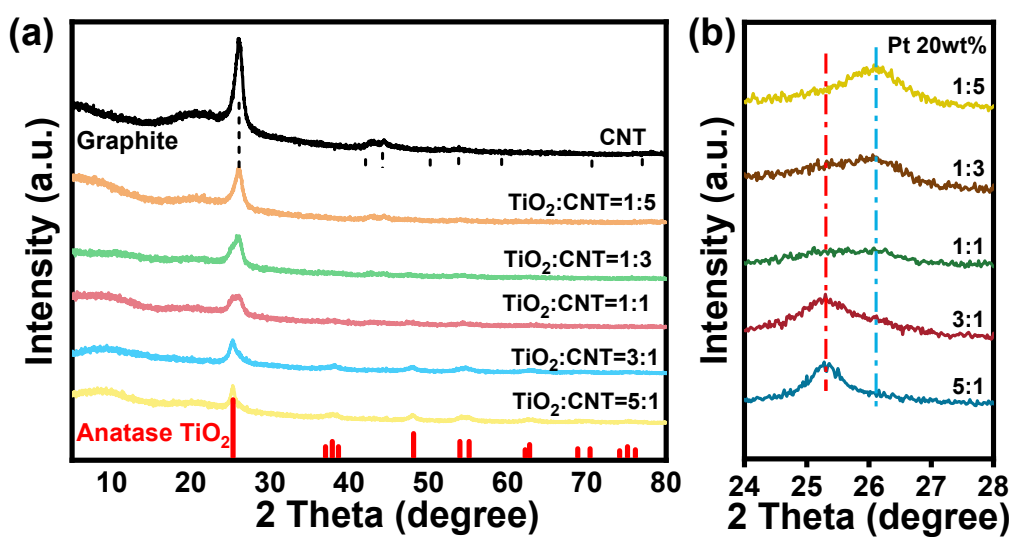


Fig. S3 XRD patterns of (a) different ratios TiO₂/CNT supports and (b) Partial enlarged XRD patterns of Pt-TiO₂/CNT catalysts with varying ratios of TiO₂/CNT.

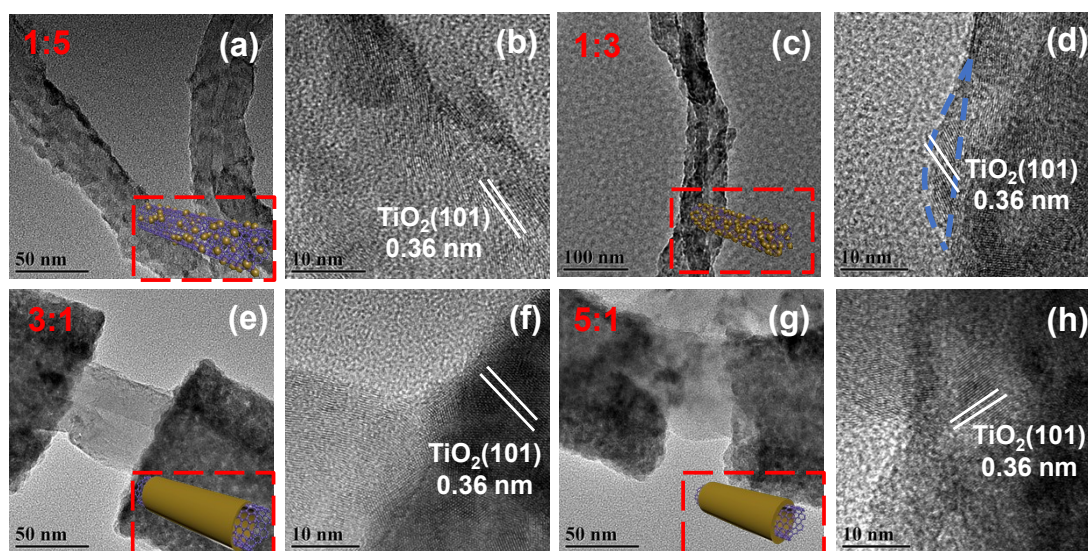


Fig. S4 TEM images of different ratios TiO_2/CNT supports with different magnification, **(a,b)** 1:5, **(c,d)** 1:3, **(e,f)** 3:1, **(g,h)** 5:1.

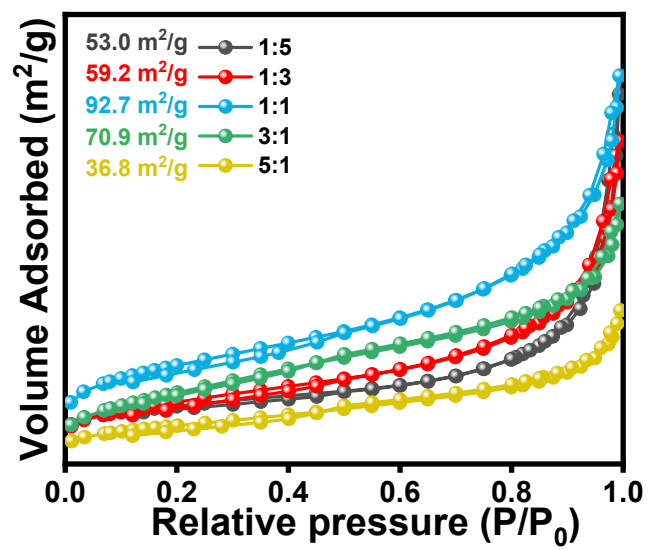


Fig. S5 N₂-adsorption-desorption isotherms of the supports with different ratios TiO₂/CNT.

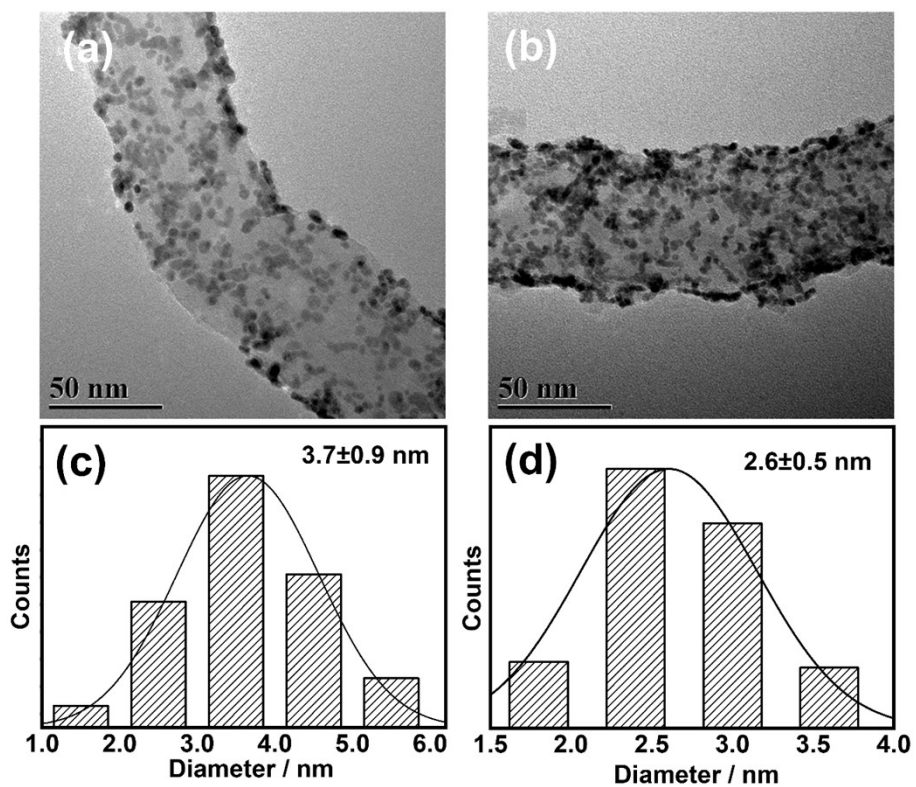


Fig. S6 The TEM images and corresponding size histograms of Pt nanoparticles of **(a,c)** Pt/CNT and **(b,d)** Pt-TiO₂/CNT.

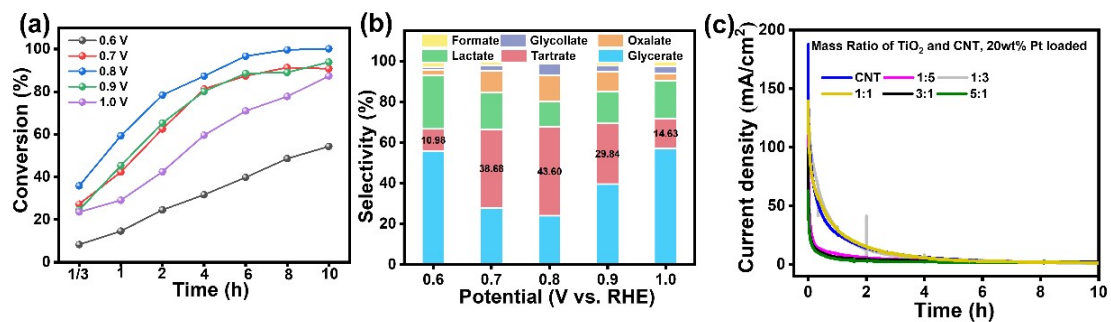


Fig. S7 (a) The glycerol conversion and (b) Selectivity of TAR after 10 h over Pt-TiO₂/CNT with different potential. (c) Amperometric i-t curve of Pt particles supported on TiO₂/CNT with different TiO₂:CNT ratios. **Condition:** 0.1 M glycerol with 1.0 M KOH at 60 °C and 0.8 V vs. RHE.

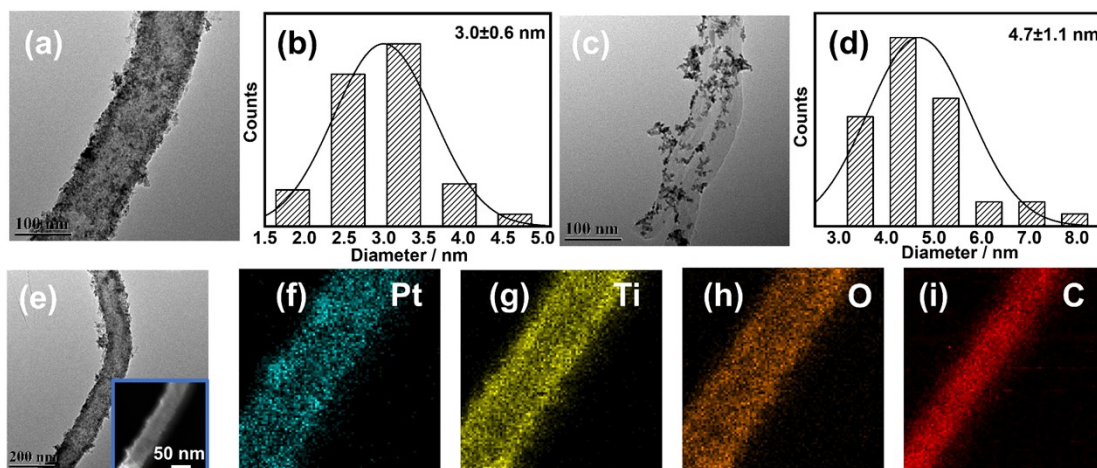


Fig. S8 TEM images of (a) Pt-TiO₂/CNT and (c) Pt/CNT after the glycerol oxidation reaction, with (b, d) corresponding size histograms of Pt particles. (e) TEM image and (f-i) the corresponding elemental mappings of Pt-TiO₂/CNT.

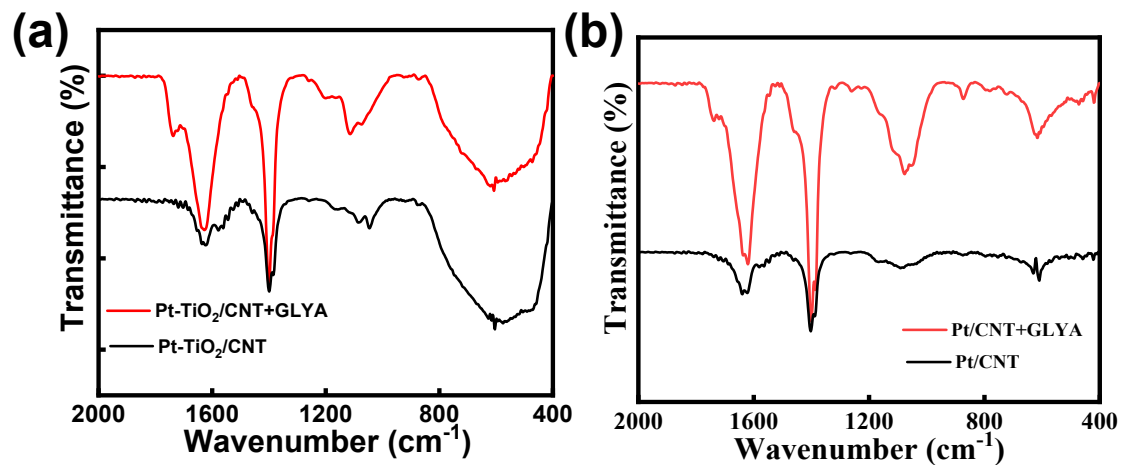


Fig. S9 IR spectra of the GLYA treated (a) Pt-TiO₂/CNT and (b) Pt/CNT

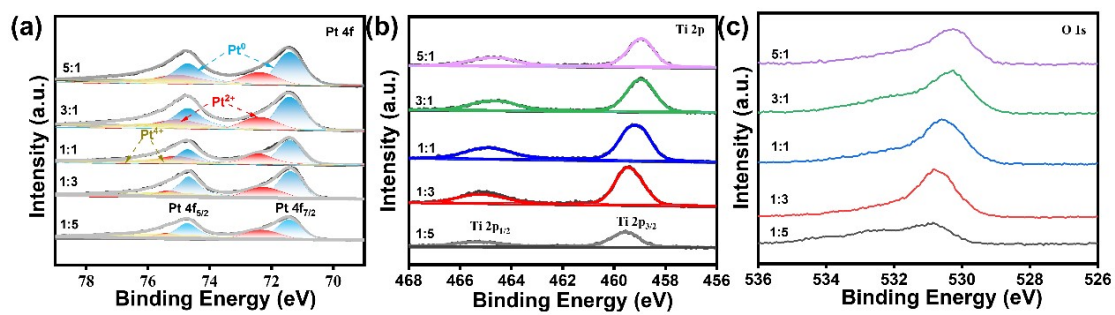


Fig. S10 XPS spectra of different catalysts. (a) Pt 4f, (b) Ti 2p, (c) O 1s.

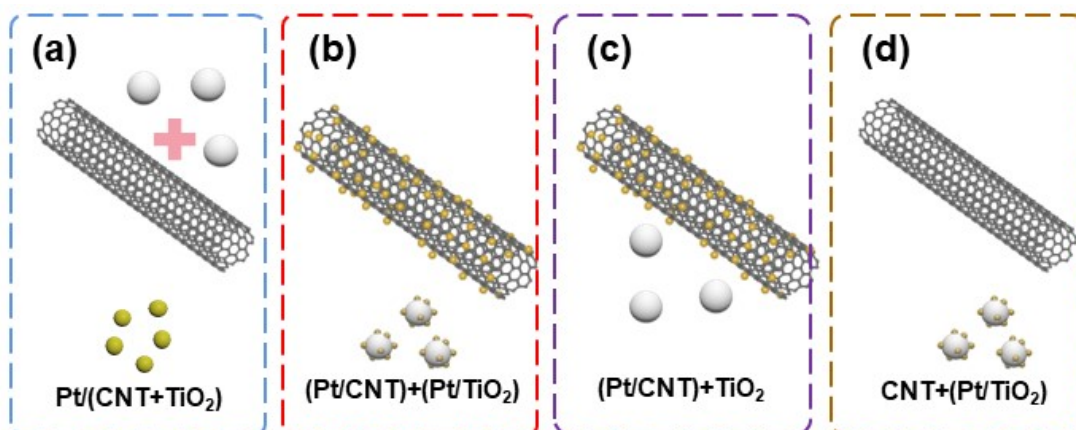


Fig. S11 Schematic diagram of catalysts with different combination of mechanical mixing. **(a)** TiO₂ and CNT are fully ground and mixed. **(b)** The Pt/CNT and Pt/TiO₂ are synthesized firstly, then Pt/CNT and Pt/TiO₂ are fully ground and mixed. **(c)** The Pt/CNT is synthesized firstly, then Pt/CNT and TiO₂ are fully ground and mixed. **(d)** The Pt/TiO₂ is synthesized firstly, then CNT and Pt/TiO₂ are fully ground and mixed

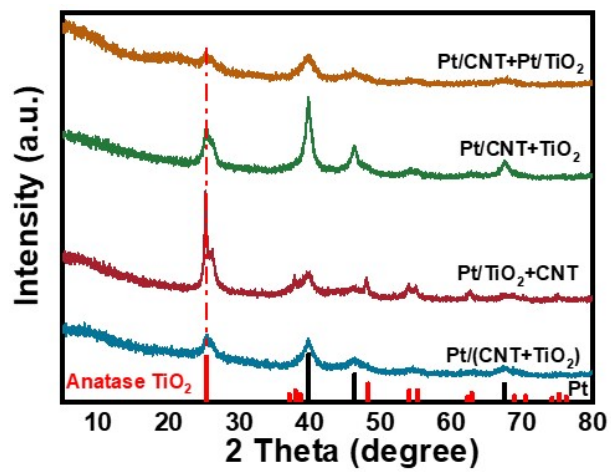


Fig. S12 XRD patterns of catalysts with different combination methods.

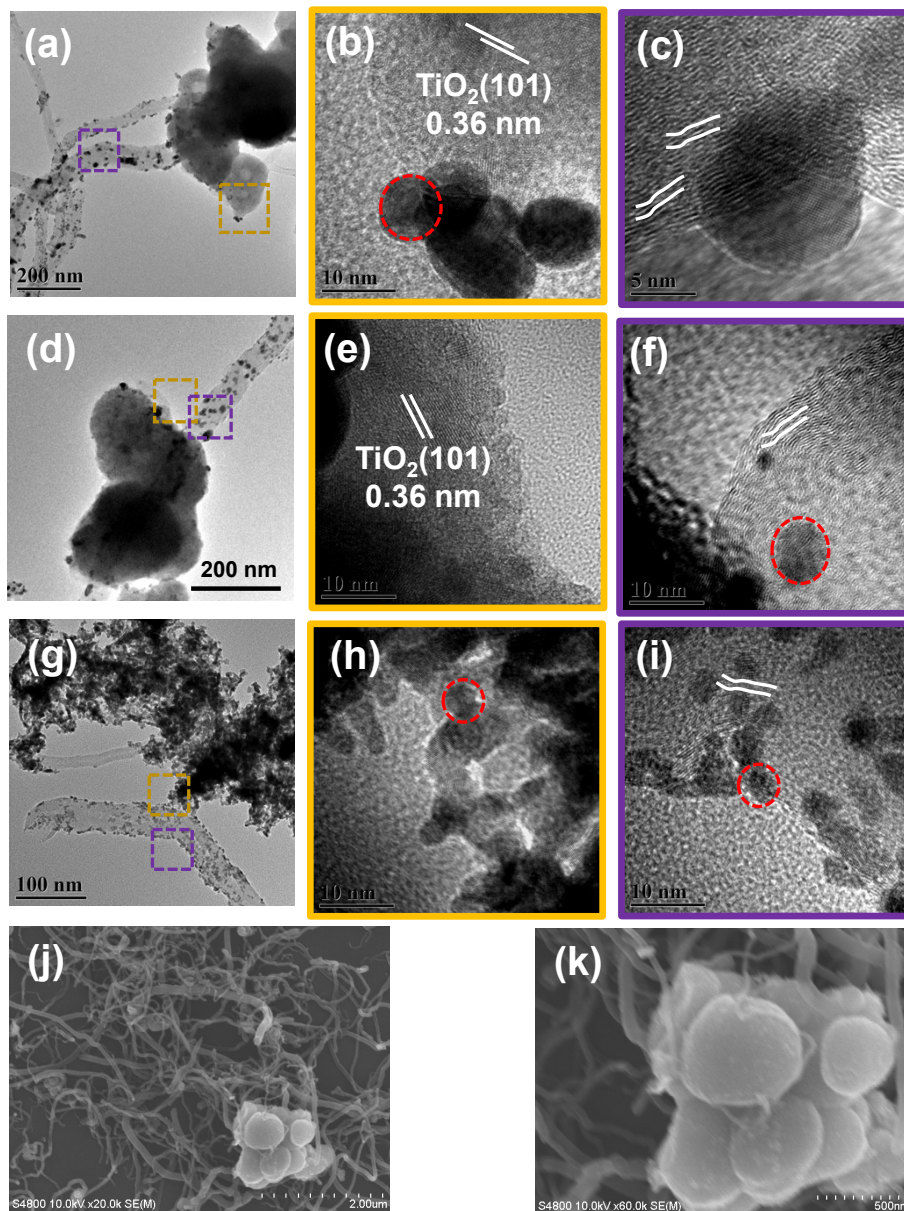


Fig. S13 TEM images of different combination catalysts with different magnification. **(a-c)** (Pt/CNT)+(Pt/TiO₂), **(d-f)** (Pt/CNT)+TiO₂, **(g-i)** Pt/(TiO₂+CNT), and **(j,k)** SEM images of (Pt/TiO₂)+CNT with different magnification. Note: The dotted boxes of different colors correspond to the solid boxes respectively.

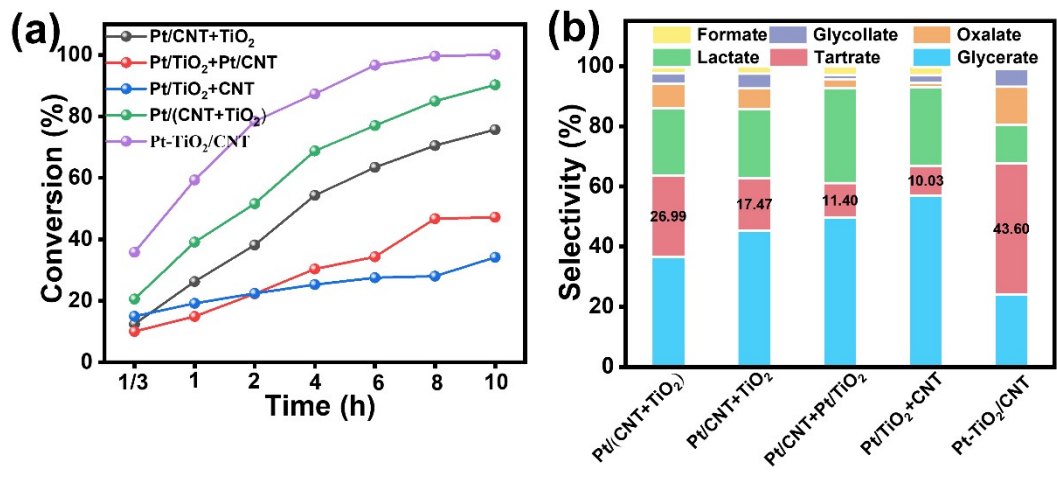


Fig. S14 Performance of different combination catalysts in glycerol oxidation. **(a)** The conversion of glycerol. **(b)** The selectivity of TAR after 10 h.

Table S1. ICP data of Pt-CNT and Pt-TiO₂/CNT

Sample	Pt%
Pt-CNT	18.9
Pt-TiO ₂ /CNT	18.8

Table S2. Glycerol oxidation over noble-metal catalysts

Catalyst	Electrolyte/Temperature	Potential/Time	Conv. (%)	Sel. of TAR. (%)	Ref.
Pt-TiO ₂ /CNT	0.1 M glycerol+1.0 M KOH, 60°C	0.8 V vs. RHE, 24h	~100	52.5	This work
Au-P4P/G	0.5 M glycerol +0.5 M KOH, RT*	0.1 V vs. Ag/AgCl, 2h	15	15	1
Au/C	2 M KOH+1 M glycerol,50 °C	0.3 V,1h	7.2	19	2
RA-Au/Ni foam	1 M KOH+0.1 M glycerol	1.0 V vs.RHE,2h	68.7	10.8	3
CuAu/C	0.5 M glycerol +0.5 M KOH, RT	0.1 V vs. Ag/AgCl,2h	-	17.6	4
AuPt	0.5 M glycerol +1.0 M KOH, RT	0.9 V vs. RHE, 12h	55.1	13	5
Pt/C	0.1 M glycerol +2.0 M KOH, 60°C	0.3 V vs. SHE/AEM,2h	63.7	34	6
Pt/FeNC	0.1 M glycerol+1.0 M KOH,60 °C	0.9 V vs. RHE,12h	100	50.8	7
Pt ₉ Bi/C	0.5 M glycerol +2.0 M KOH, RT	0.7 V vs.RHE,4h	-	10.9	8
Pt ₂ Rh ₁ /C	0.1 M glycerol +0.1 M HClO ₄ ,60°C	0.45 V vs.SCE,8h	90	40.3	9
Pt _{0.95} -Bi _{0.05} /TiN/HNWS/CC	1 M KOH+0.05 M glycerol, RT	0.45 V vs.RHE,8h	87	14.1	10
Pd/CNT	5 wt% glycerol +2.0 M KOH,60°C	102 mA, 3.3h	15	15	11
Pd-(Ni-Zn)/C	2 M KOH+5wt% glycerol	20 mA/cm ² ,10.2h	55.5	28.1	12
PdAg ₃ /CNT	1.0 M glycerol +4.0 M KOH,50°C	0.1 V vs.SHE, 2h	43	13.7	13
Au/C-NC	0.1 M glycerol+8.0 M KOH,60 °C	<0.45 V vs. RHE, 12h	89.2	69.3	14
Au/C	1 M glycerol+2 M KOH,60 °C	0.4 V vs. RHE,19h	35	78	15

*: RT—Room Temperature

References

1. Wang, H.; Thia, L.; Li, N.; Ge, X.; Liu, Z.; Wang, X., Selective electro-oxidation of glycerol over Au supported on extended poly(4-vinylpyridine) functionalized graphene. *Appl. Catal., B*, 2015, 166, 25-31.
2. Xin, L.; Zhang, Z.; Wang, Z.; Li, W., Simultaneous Generation of Mesoxalic Acid and Electricity from Glycerol on a Gold Anode Catalyst in Anion-Exchange Membrane Fuel Cells. *ChemCatChem*, 2012, 4, 1105-1114.
3. Kim, D.; Oh, L. S.; Tan, Y. C.; Song, H.; Kim, H. J.; Oh, J., Enhancing Glycerol Conversion and Selectivity toward Glycolic Acid via Precise Nanostructuring of Electrocatalysts. *ACS Catal.*, 2021, 11, 14926-14931.
4. González-Cobos, J.; Baranton, S.; Coutanceau, C., Development of Bismuth-Modified PtPd Nanocatalysts for the Electrochemical Reforming of Polyols into Hydrogen and Value-Added Chemicals. *ChemElectroChem*, 2016, 3, 1694-1704.
5. Dai, C.; Sun, L.; Liao, H.; Khezri, B.; Webster, R. D.; Fisher, A. C.; Xu, Z. J., Electrochemical production of lactic acid from glycerol oxidation catalyzed by AuPt nanoparticles. *J. Catal.*, 2017, 356, 14-21.
6. Zhang, Z.; Xin, L.; Li, W., Electrocatalytic oxidation of glycerol on Pt/C in anion-exchange membrane fuel cell: Cogeneration of electricity and valuable chemicals. *Appl. Catal., B*, 2012, 119, 40-48.
7. Li, J.; Jiang, K.; Bai, S.; Guan, C.; Wei, H.; Chu, H., High productivity of tartronate from electrocatalytic oxidation of high concentration glycerol through facilitating the intermediate conversion. *Appl. Catal., B*, 2022, 317, 121784.
8. Garcia, A. C.; Birdja, Y. Y.; Tremiliosi-Filho, G.; Koper, M. T. M., Glycerol electro-oxidation on bismuth-modified platinum single crystals. *J. Catal.*, 2017, 346, 117-124.
9. Huang, L.; Sun, J.-Y.; Cao, S.-H.; Zhan, M.; Ni, Z.-R.; Sun, H.-J.; Chen, Z.; Zhou, Z.-Y.; Sorte, E. G.; Tong, Y. J.; Sun, S.-G., Combined EC-NMR and In Situ FTIR Spectroscopic Studies of Glycerol Electrooxidation on Pt/C, PtRu/C, and PtRh/C. *ACS Catal.*, 2016, 6, 7686-7695.
10. Liu, L.; Liu, B.; Xu, X.; Jing, P.; Zhang, J., Heterogeneous Pt-Bi hybrid nanoparticle decorated self-standing hollow TiN nanowire as an efficient catalyst for glycerol electrooxidation. *J. Power Sources*, 2022, 543, 231836.
11. Fashedemi, O. O.; Miller, H. A.; Marchionni, A.; Vizza, F.; Ozoemena, K. I., Electro-oxidation of ethylene glycol and glycerol at palladium-decorated FeCo@Fe core-shell nanocatalysts for alkaline direct alcohol fuel cells: functionalized MWCNT supports and impact on product selectivity. *J. Mater. Chem. A*, 2015, 3, 7145-7156.
12. Marchionni, A.; Bevilacqua, M.; Bianchini, C.; Chen, Y. X.; Filippi, J.; Fornasiero, P.; Lavacchi, A.; Miller, H.; Wang, L.; Vizza, F., Electrooxidation of Ethylene Glycol and Glycerol on Pd-(Ni-Zn)/C Anodes in Direct Alcohol Fuel Cells. *ChemSusChem*, 2013, 6, 518-528.
13. Benipal, N.; Qi, J.; Liu, Q.; Li, W., Carbon nanotube supported PdAg nanoparticles for electrocatalytic oxidation of glycerol in anion exchange membrane fuel cells. *Appl. Catal., B*, 2017, 210, 121-130.
14. Qi, J.; Xin, L.; Chadderton, D. J.; Qiu, Y.; Jiang, Y.; Benipal, N.; Liang, C.; Li, W., Electrocatalytic

selective oxidation of glycerol to tartronate on Au/C anode catalysts in anion exchange membrane fuel cells with electricity cogeneration. *Appl. Catal., B*, 2014, 154-155, 360-368.

15. Zhang, Z.; Xin, L.; Qi, J.; Chadderton, D. J.; Sun, K.; Warsko, K. M.; Li, W., Selective electro-oxidation of glycerol to tartronate or mesoxalate on Au nanoparticle catalyst via electrode potential tuning in anion-exchange membrane electro-catalytic flow reactor. *Appl. Catal., B*, 2014, 147, 871-878.