

Pt-based nanoparticles decorated by phosphorus-doped CuWO_4 to enhance methanol oxidation activity

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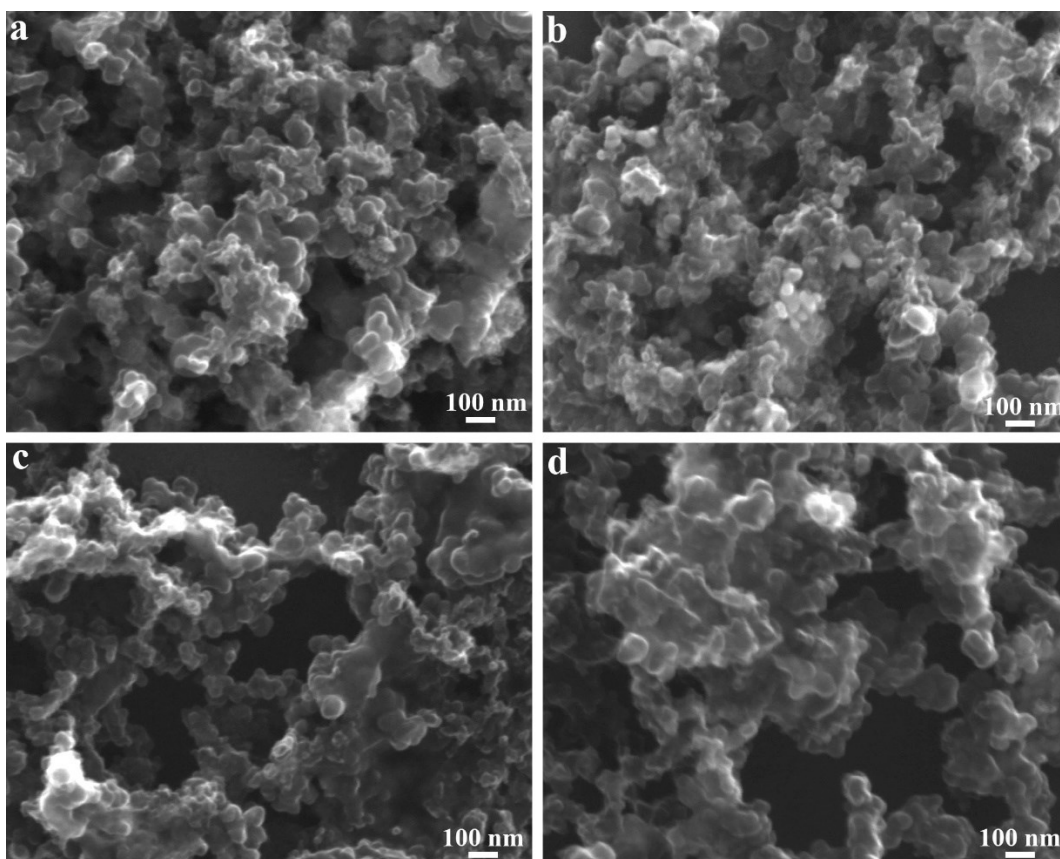


Figure. S1. SEM patterns of $\text{CuWO}_4 \cdot 2\text{H}_2\text{O}/\text{C}$ (a), $\text{C}/\text{P-CuWO}_4$ (b) and $\text{Cu}(\text{OH})_2/\text{C}$ (c), $\text{C}/\text{P-CuO}$ (d), respectively.

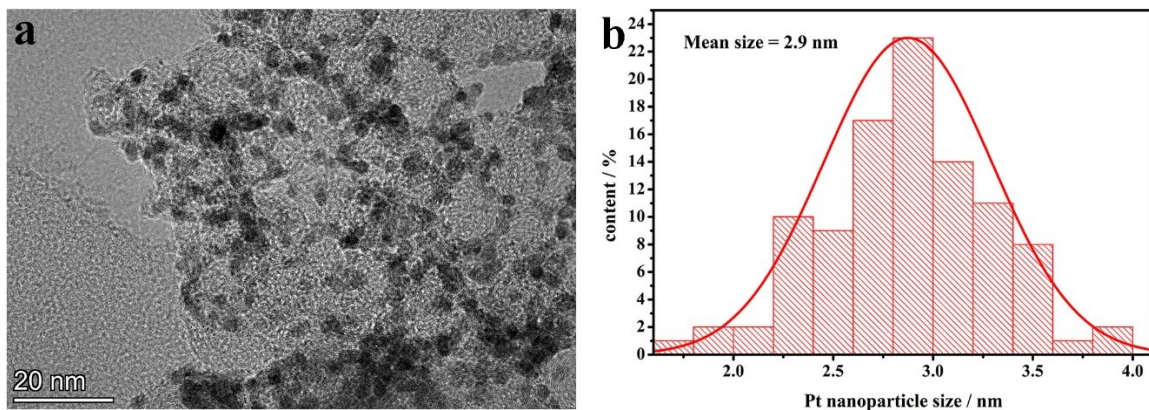


Figure. S2. TEM patterns and mean size of Pt NPs of Pt/C-CuWO₄

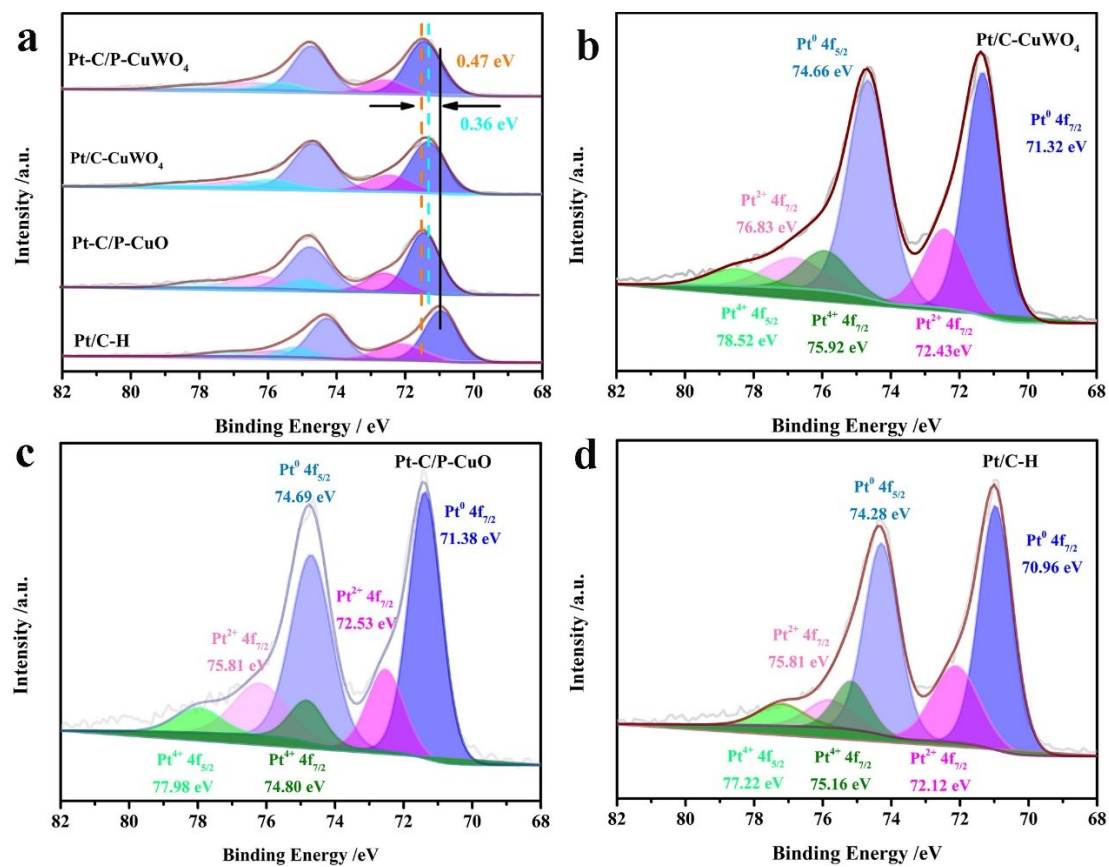


Figure. S3 XPS spectra XPS survey spectra of catalysts (a) and Pt 4f spectra of Pt-C/P-CuWO₄(b), Pt/C-CuWO₄ (c), Pt-C/P-CuO(d), Pt-C/P-WO₃(e) and Pt/C-H (f), respectively.

Table S1: The fitting results and surface components of the Pt 4f spectra for catalysts.

samples	Pt ⁰		Pt ²⁺		Pt ⁴⁺	
	Binding	Relative ratio	Binding	Relative	Binding	Relative
	Energy	%	Energy	ratio	Energy	ratio
	(eV)		(eV)	%	(eV)	%
Pt-C/P-CuWO ₄	71.43	70.30	72.67	18.5	75.72	11.2
	74.81		76.51		78.26	
Pt/C-CuWO ₄	71.32	68.06	72.43	20.6	75.92	11.34
	74.66		76.83		78.52	
Pt-C/P-CuO	71.38	66.08	72.53	23.25	74.80	10.68
	74.69		76.20		77.98	
Pt/C-H	70.96	66.24	72.12	21.39	75.81	12.37
	74.28		75.16		77.22	

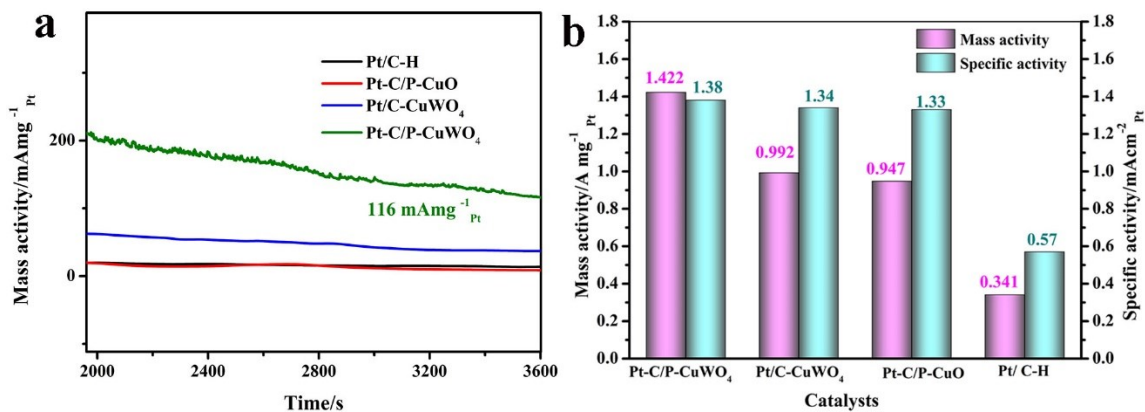


Figure. S4 Chronoamperometric curves of Pt-C/P@CuWO₄/C, Pt/C-CuWO₄, Pt-C/P-CuO and Pt/C-H catalysts in 0.5 M H₂SO₄ solution at a scan rate of 50 mV s⁻¹ (a), the mass activity and specific activity (b).

Table S2: Electro-chemic values in 0.5 M H₂SO₄ solution of four samples toward electrochemical active surface area (ECSA)

samples	ECSA (m ² ·g ⁻¹ _{Pt})	Specific activity (mA·cm ⁻² _{Pt})	Mass activity (mA·mg ⁻¹ _{Pt})
Pt-C/P-CuWO ₄	103.28	1.38	1422
Pt/C-CuWO ₄	73.87	1.34	992
Pt-C/P-CuO	71.13	1.33	947
Pt/C-H	59.70	0.57	341

Table S3: summarized this work and other reported accomplishments in methanol oxidation reaction.

samples	ECSA ($\text{m}^2 \cdot \text{g}^{-1} \text{Pt}$)	Mass activity ($\text{mA} \cdot \text{mg}^{-1} \text{Pt}$)	Conditions	References
Pt-C/P-CuWO ₄	103.28	1422	0.5 M H ₂ SO ₄ +1.0 M CH ₃ OH	This work
Pt-WO ₂ /WO ₃	-	694	0.5 M H ₂ SO ₄ +1.0 M CH ₃ OH	1
Pt/Fe ₃ O ₄ -SNG	162.06	1129	0.5 M H ₂ SO ₄ +0.5 M CH ₃ OH	2
Pt/NiCoP _x @NCNT-NG	54.2	857	0.5 M H ₂ SO ₄ +0.5 M CH ₃ OH	3
PtPdNiP TOMNs	57.1	1040	0.5 M H ₂ SO ₄ +1.0 M H ₃ OH	4
Pt/TiO ₂ /NDC	36.3	527	0.5 M HClO ₄ +1.0 M CH ₃ OH	5

References

1. Y. Zhou, X. C. Hu, X. H. Liu and H. R. Wen, *Chemical Communications*, 2015, **51**, 15297-15299.
2. J. Zhong, L. Wu, J. Lan, M. Waqas, M. Sun, Y. Fan, W. Chen, L. Liu and J. Yang, *International Journal of Hydrogen Energy*, 2020, **45**, 22929-22937.
3. J. Ding, W. Hu, L. Ma, M. Gan, F. Xie, W. Zhan and W. Lu, *Journal of Power Sources*, 2021, **481**, 228888.
4. Q. Zhou, J. Wu, Z. Pan, X. Kong, Z. Cui, D. Wu and G. Hu, *International Journal of Hydrogen Energy*, 2020, **45**, 33634-33640.
5. J. Zhang, J. Chen, F. Zhou, X. W. Zeng, A. Xing, B. Jia, B. Y. Fan, J. Wang and X. Y. Liu, *Journal of Electrochemical Energy Conversion and Storage*, 2021, **18**.