

Supplementary Information

CeO₂ Nano-Nails Induced Interface Electronic Effect Boost Ethanol Oxidation

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Results and Discussion

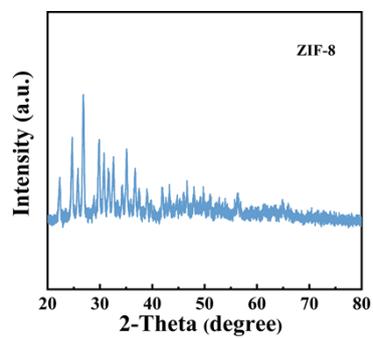


Figure S1. XRD images of ZIF-8.

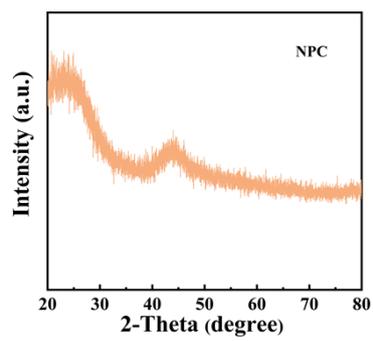


Figure S2. XRD images of NPC.

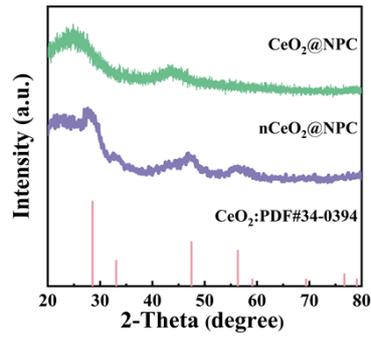


Figure S3. XRD images of nCeO₂@NPC with high Ce content and CeO₂@NPC with low Ce content.

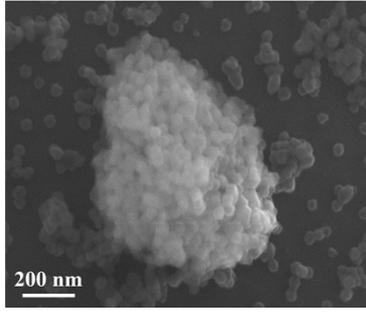


Figure S4. SEM images of ZIF-8.

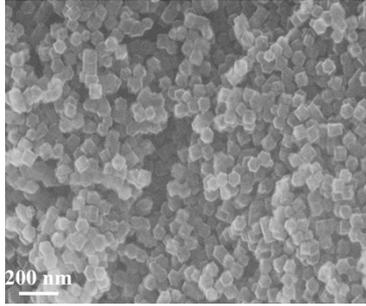


Figure S5. SEM images of NPC.

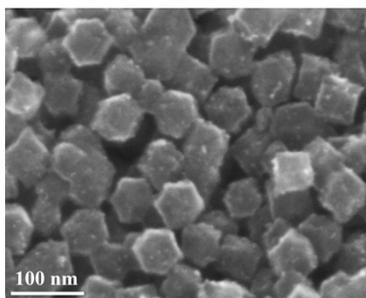


Figure S6. SEM images of nCeO₂@NPC.

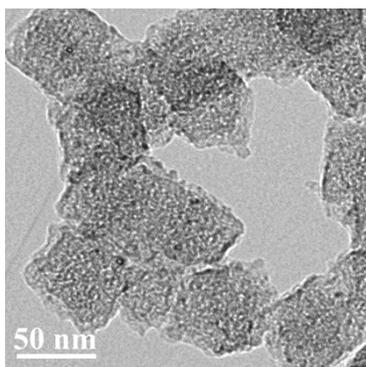


Figure S7. TEM images of $\text{CeO}_2@\text{NPC}$ with low Ce content.

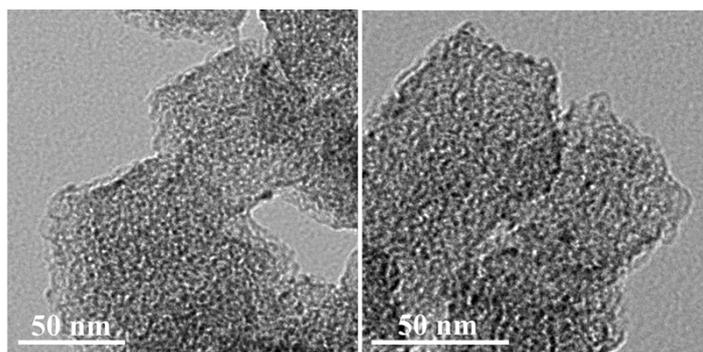


Figure S8. TEM images of nCeO₂@NPC with high Ce content.

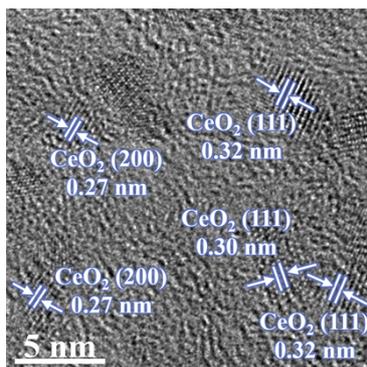


Figure S9. HRTEM images of nCeO₂@NPC.

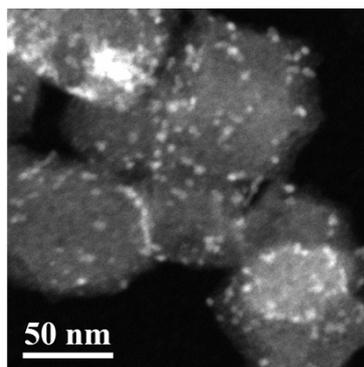


Figure S10. HAADF-STEM images of CeO₂@NPC with low Ce content.

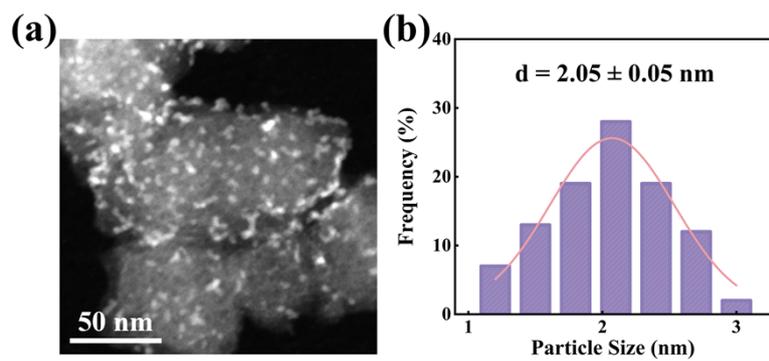


Figure S11. (a) HAADF-STEM images and (b) the corresponding particle size distribution of $n\text{CeO}_2@\text{NPC}$ with high Ce content.

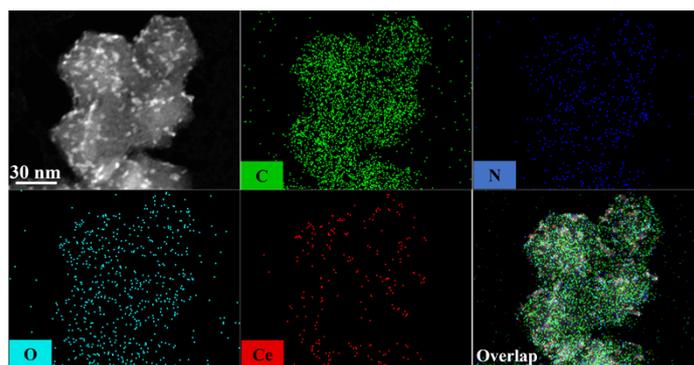


Figure S12. Elemental mappings of nCeO₂@NPC.

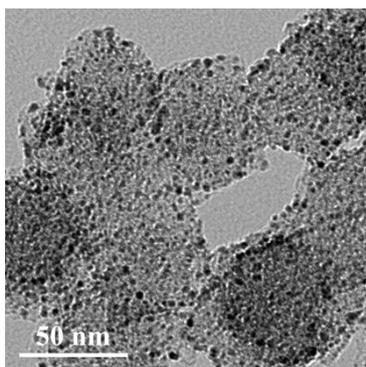


Figure S13. TEM images of Pt/nCeO₂@NPC.

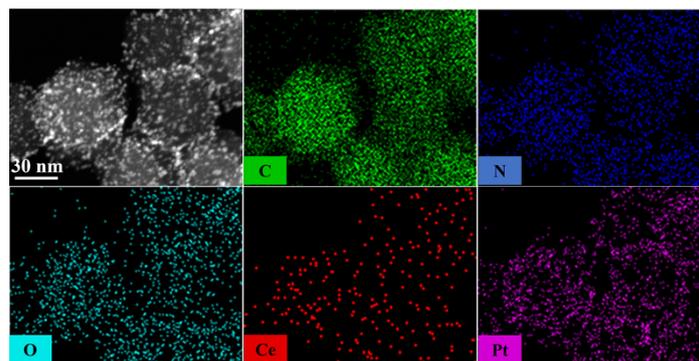


Figure S14. The EDS mapping of Pt/nCeO₂@NPC.

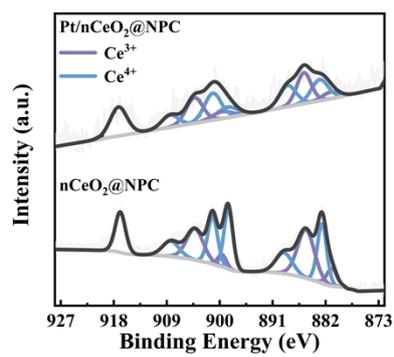


Figure S15. High-resolution Ce 3d XPS spectra of Pt/nCeO₂@NPC and nCeO₂@NPC.

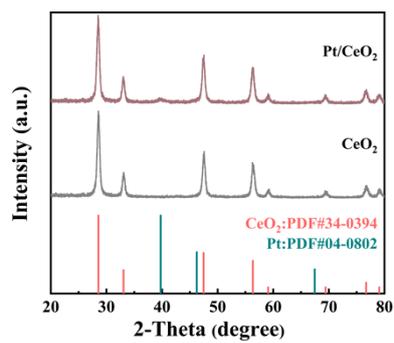


Figure S16. XRD patterns of Pt/CeO₂, and CeO₂.

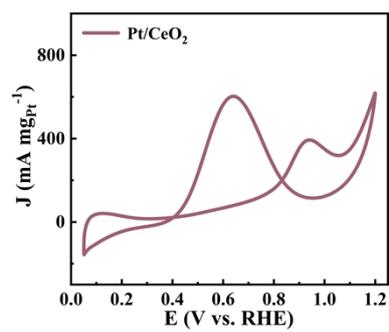


Figure S17. CV curve of EOR for Pt/CeO₂ in 0.5 M H₂SO₄ + 1 M CH₃CH₂OH solution.

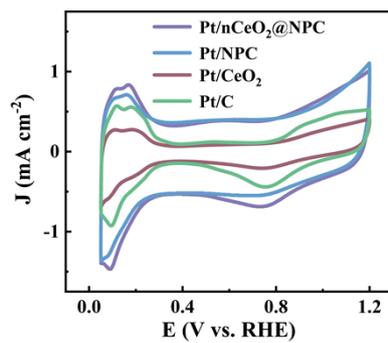


Figure S18. CV curves of Pt/nCeO₂@NPC, Pt/NPC, Pt/CeO₂, and Pt/C in 0.5 M H₂SO₄ solution with sweep rate of 50 mV s⁻¹.

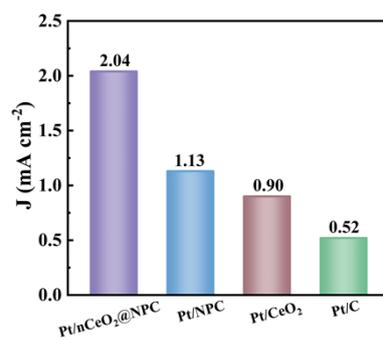


Figure S19. Comparison of specific activity of Pt/nCeO₂@NPC, Pt/NPC, Pt/CeO₂, and Pt/C.

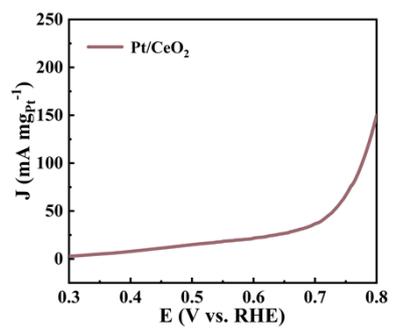


Figure S20. LSV curves of EOR for Pt/CeO₂ in 0.5 M H₂SO₄ + 1 M CH₃CH₂OH solution.

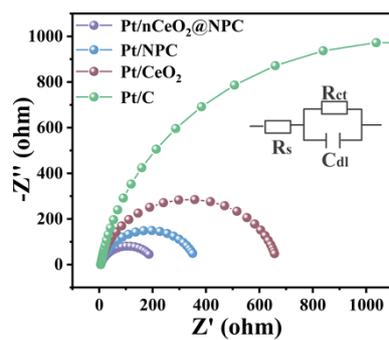


Figure S21. Nyquist plot at a potential of 0.7 V vs. RHE of Pt/nCeO₂@NPC, Pt/NPC, Pt/CeO₂, and Pt/C.

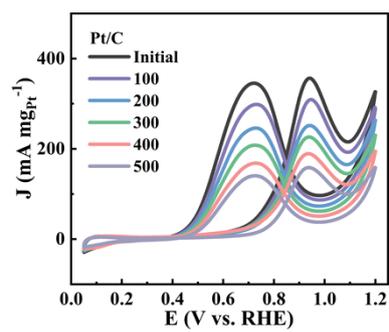


Figure S22. CV of Pt/C in N_2 -saturated $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{CH}_2\text{OH}$ solution at scan rate of 50 mV s^{-1} during the durability tests.

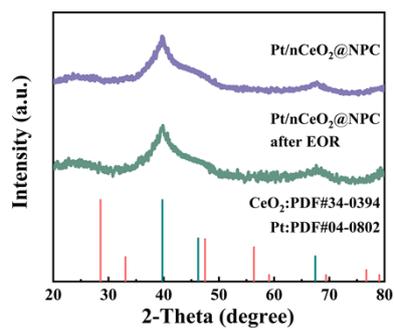


Figure S23. XRD patterns of Pt/nCeO₂@NPC before and after the ADT test.

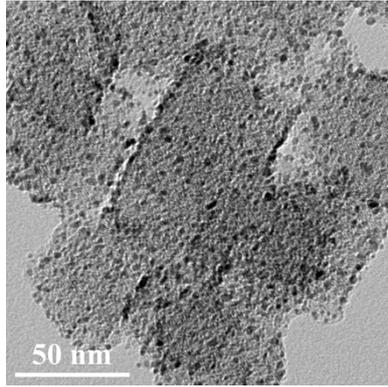


Figure S24. TEM image of Pt/nCeO₂@NPC after the ADT test.

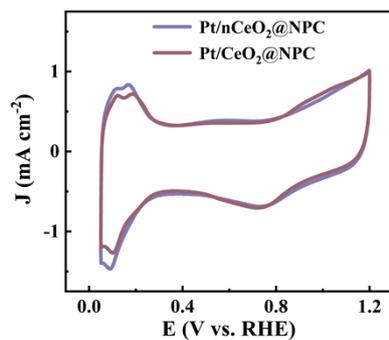


Figure S25. CV curves of Pt/nCeO₂@NPC, and Pt/CeO₂@NPC in 0.5 M H₂SO₄ solution with sweep rate of 50 mV s⁻¹.

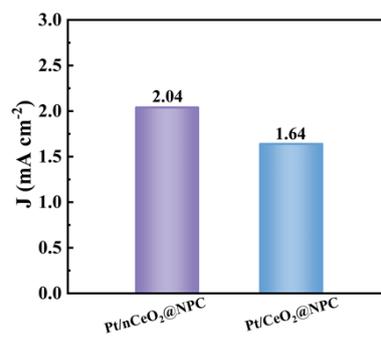


Figure S26. Comparison of specific activity of Pt/nCeO₂@NPC, and Pt/CeO₂@NPC.

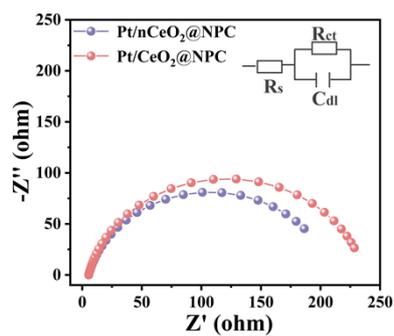


Figure S27. Nyquist plot at a potential of 0.7 V vs. RHE of $\text{Pt/nCeO}_2\text{@NPC}$, and $\text{Pt/CeO}_2\text{@NPC}$.

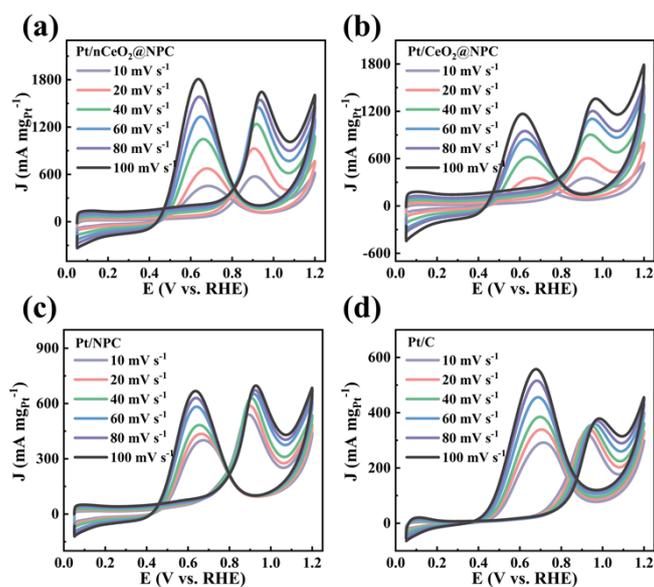


Figure S28. (a) CV curves of the Pt/nCeO₂@NPC catalyst at different scan rates (10, 20, 40, 60, 80, and 100 mV s⁻¹). (b) CV curves of the Pt/CeO₂@NPC catalyst at different scan rates (10, 20, 40, 60, 80, and 100 mV s⁻¹). (c) CV curves of the Pt/NPC catalyst at different scan rates (10, 20, 40, 60, 80, and 100 mV s⁻¹). (d) CV curves of the commercial Pt/C catalyst at different scan rates (10, 20, 40, 60, 80, and 100 mV s⁻¹).

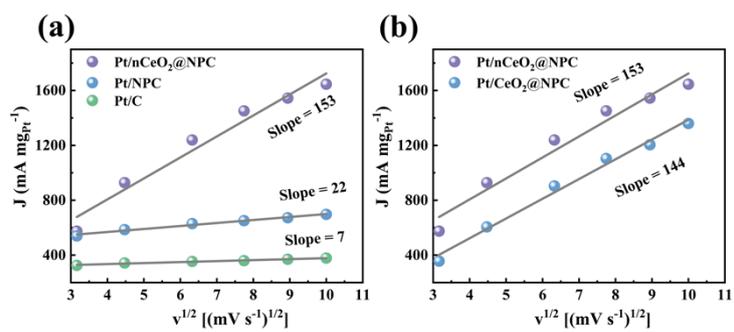


Figure S29. Linear relationship between mass activity and the square root of scan rate.

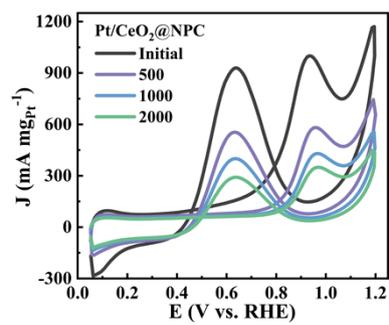


Figure S30. CV of Pt/CeO₂@NPC in N₂-saturated 0.5 M H₂SO₄ + 1 M CH₃CH₂OH solution at scan rate of 50 mV s⁻¹ during the durability tests.

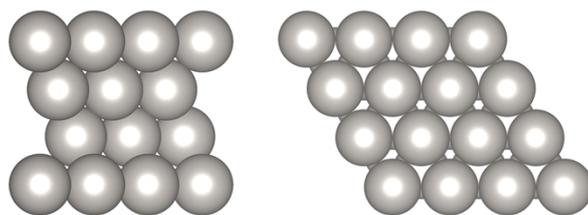


Figure S31. Structural models of Pt from multiple perspectives. Gray spheres represent Pt atoms.

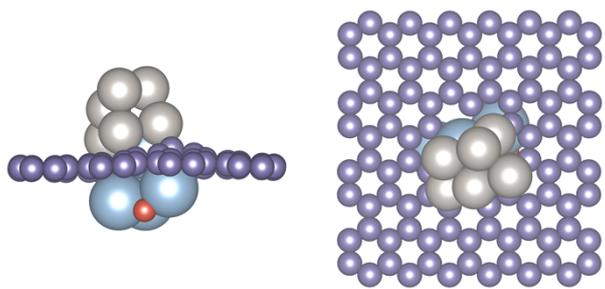


Figure S32. Structural models of Pt/CeO₂@NPC from multiple perspectives. Gray, purple, blue, and red spheres represent Pt, C, Ce, and O atoms, respectively.

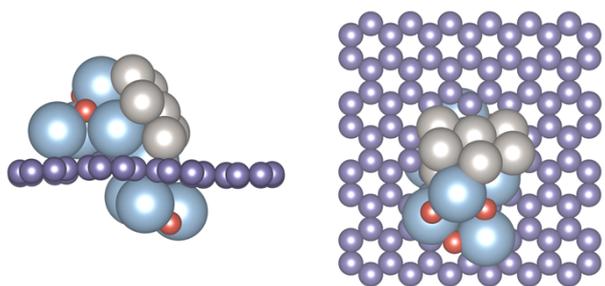


Figure S33. Structural models of Pt/nCeO₂@NPC from multiple perspectives. Gray, purple, blue, and red spheres represent Pt, C, Ce, and O atoms, respectively.

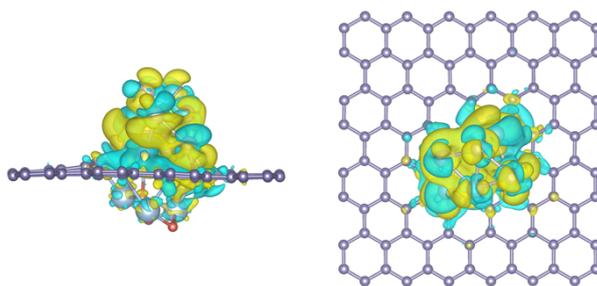


Figure S34. Charge density difference distribution of Pt/CeO₂@NPC. Gray, purple, blue, and red spheres represent Pt, C, Ce, and O atoms, respectively. The yellow area represents the region where charges accumulate, while the blue area represents the region where charges are depleted.

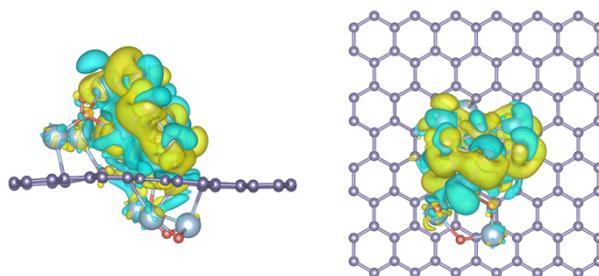


Figure S35. Charge density difference distribution of Pt/nCeO₂@NPC. Gray, purple, blue, and red spheres represent Pt, C, Ce, and O atoms, respectively. The yellow area represents the region where charges accumulate, while the blue area represents the region where charges are depleted.

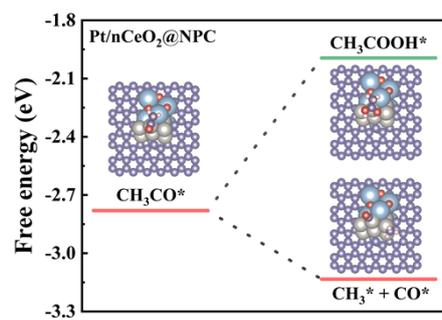


Figure S36. Free energy diagrams of C1 and C2 pathway on Pt/nCeO₂@NPC.

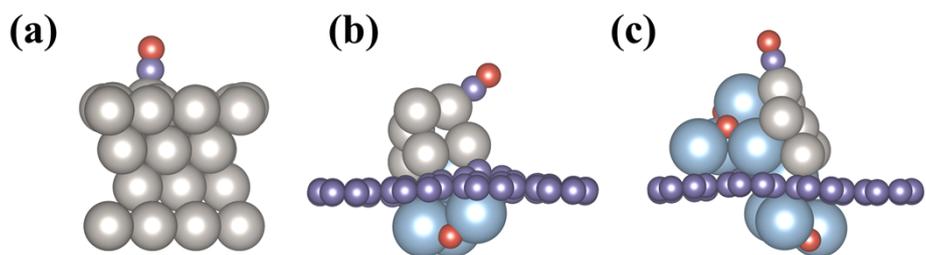


Figure S37. The adsorption model of CO* on (a) Pt (111), (b) Pt/CeO₂@NPC, and (c) Pt/nCeO₂@NPC. Gray, purple, blue, and red spheres represent Pt, C, Ce, and O atoms, respectively.

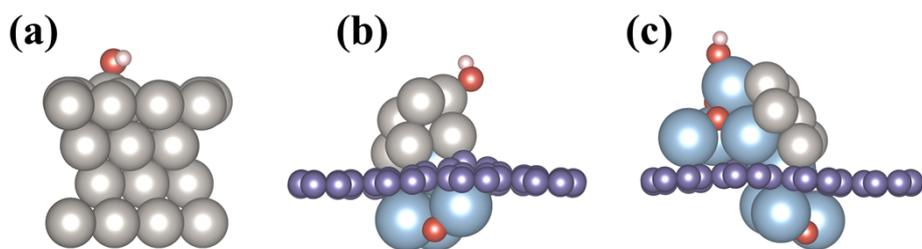


Figure S38. The adsorption model of OH* on (a) Pt (111), (b) Pt/CeO₂@NPC, and (c) Pt/nCeO₂@NPC. Gray, purple, blue, red, and pink spheres represent Pt, C, Ce, O, and H atoms, respectively.

Table S1. Elemental contents of as-prepared samples measured by ICP-MS.

Samples	Pt loading (wt.%)	Ce loading (wt.%)
Pt/CeO ₂ @NPC	11.12	6.11
Pt/nCeO ₂ @NPC	10.10	3.72
Pt/NPC	16.70	/
Pt/CeO ₂	12.26	60.31

Table S2. Surface Species Percent of Pt/nCeO₂@NPC, Pt/NPC and nCeO₂@NPC.

Samples	Ce ³⁺ /(Ce ⁴⁺ + Ce ³⁺)
Pt/nCeO ₂ @NPC	45.86
Pt/NPC	/
nCeO ₂ @NPC	34.05

Table S3. FT-EXAFS fitting parameters of Pt/nCeO₂@NPC, Pt/NPC and Pt foil.

Sample	Path	S ₀ ²	CN	R(Å)	ΔE ₀ (eV)	σ ² (Å ²)
Pt foil	Pt-Pt	0.8	12	2.76	8.4	0.004
Pt/NPC	Pt-N	0.8	1.1	1.93	6.1	0.003
	Pt-Pt	0.8	7.3	2.72	6.1	0.008
Pt/nCeO ₂ @NPC	Pt-O	0.8	0.9	2.04	7.3	0.003
	Pt-N	0.8	0.9	1.92	7.3	0.003
	Pt-Pt	0.8	6.8	2.73	7.3	0.007

Table S4. Comparison of mass activity and specific activity normalized to the mass of all metals

Samples	Mass activity (mA mg _{Metal} ⁻¹)	Specific activity (mA cm ⁻²)
Pt/CeO ₂ @NPC	645	1.1
Pt/nCeO ₂ @NPC	1004	1.5
Pt/NPC	639	1.13
Pt/CeO ₂	67	0.15
Pt/C	355	0.52

Table S5. EIS data of Pt/nCeO₂@NPC, Pt/CeO₂@NPC, Pt/NPC, Pt/CeO₂, and Pt/C for EOR in N₂-saturated 0.5 M H₂SO₄+1 M CH₃CH₂OH.

Samples	R _s (Ω)	R _{ct} (Ω)
Pt/nCeO ₂ @NPC	5.46	204
Pt/CeO ₂ @NPC	5.49	232
Pt/NPC	5.54	361
Pt/CeO ₂	5.95	662
Pt/C	6.14	2270

Table S6. The performance comparisons with the reported work.

Samples	Mass activity (mA mg _{Pt} ⁻¹)	
Pt/nCeO ₂ @NPC	1374	This work
Pt-0.5SnO _x /NCNC	1187	1
NiRuPt/Ti _{0.9} Ir _{0.1} O ₂ - C	720.75	2
Pt/N-Ti ₃ C ₂ T _x	435.35	3
Pt-Bi/RGO	384	4
H-PtSn/SnO _x /CNT-2	825	5

- 1 Z. Zhang, Q. Wu, K. Mao, Y. Chen, L. Du, Y. Bu, O. Zhuo, L. Yang, X. Wang and Z. Hu, Efficient Ternary Synergism of Platinum/Tin Oxide/Nitrogen-Doped Carbon Leading to High-Performance Ethanol Oxidation, *ACS Catal.*, 2018, **8**, 8477-8483.
- 2 H. Q. Pham and T. T. Huynh, Integrating Low Pt-Based Ternary NiRuPt Nanoalloy on Hybrid TiO₂-Based Oxide–Carbon Composite for Enhanced Ethanol Oxidation, *The Journal of Physical Chemistry Letters*, 2023, **14**, 4631-4637.
- 3 T. T. Huynh, Q. Huynh, A. Q. K. Nguyen and H. Q. Pham, Strong Component-Interaction in N-doped 2D Ti₃C₂T_x-Supported Pt Electrocatalyst for Acidic Ethanol Oxidation Reaction, *Adv. Sustainable Syst.*, 2025, **9**, 2400995.
- 4 Y. C. Sekhar, V. Vinothkumar, H. S. Rao, L. S. Sarma, J. Oh and T. H. Kim, Synergistic effects of platinum-bismuth nanoalloys on reduced graphene oxide for superior methanol and ethanol oxidation in acidic medium, *Int. J. Hydrogen Energy*, 2024, **81**, 471-480.
- 5 Z. Zheng, Q. Jiang, X. Cheng, X. Han, Q. Kuang and Z. Xie, Platinum-Tin/Tin Oxide/CNT Catalysts for High-Performance Electrocatalytic Ethanol Oxidation, *Chemistry – A European Journal*, 2022, **28**, e202103521.

Table S7. Surface Species Percent of Pt/nCeO₂@NPC and Pt/CeO₂@NPC.

Samples	Ce ³⁺ /(Ce ⁴⁺ + Ce ³⁺)
Pt/nCeO ₂ @NPC	45.86
Pt/CeO ₂ @NPC	38.80