Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Thermally Driven Interfacial Diffusion Synthesis of Nitrogen-Doped Carbon Confined Trimetallic Pt_3CoRu Composites for Methanol Oxidation Reaction

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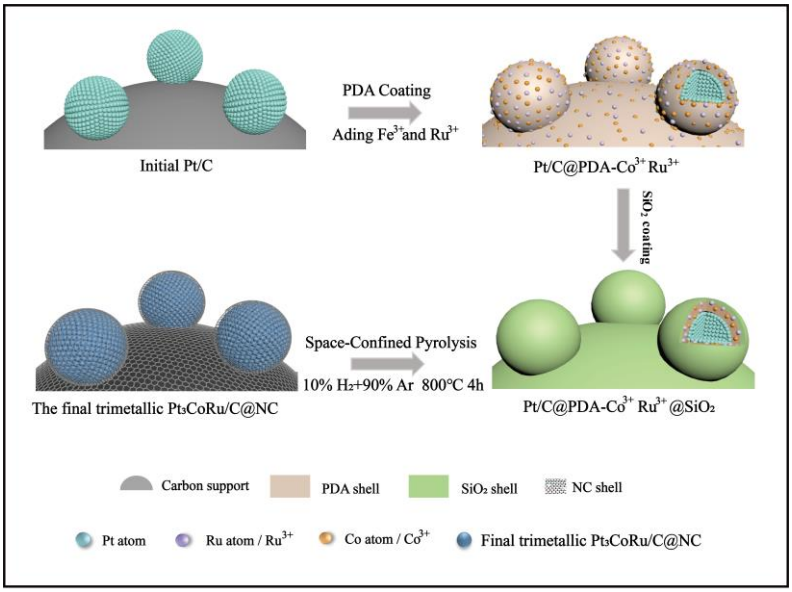


Figure S1. Schematic fabrication of trimetallic Pt_3CoRu/C@NC catalyst based on thermally driven interfacial diffusion alloying method.

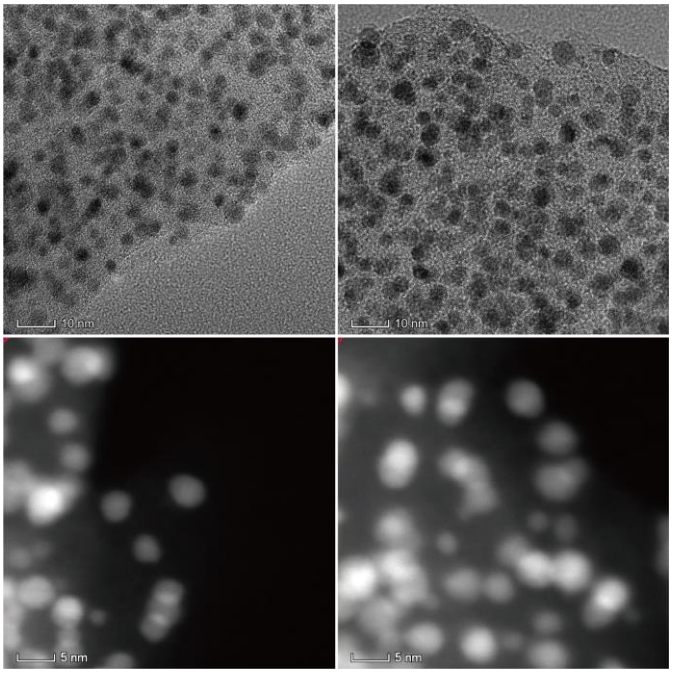


Figure S2. The TEM and HR-TEM images of the prepared $Pt_3CoRu/C@NC$ sample.

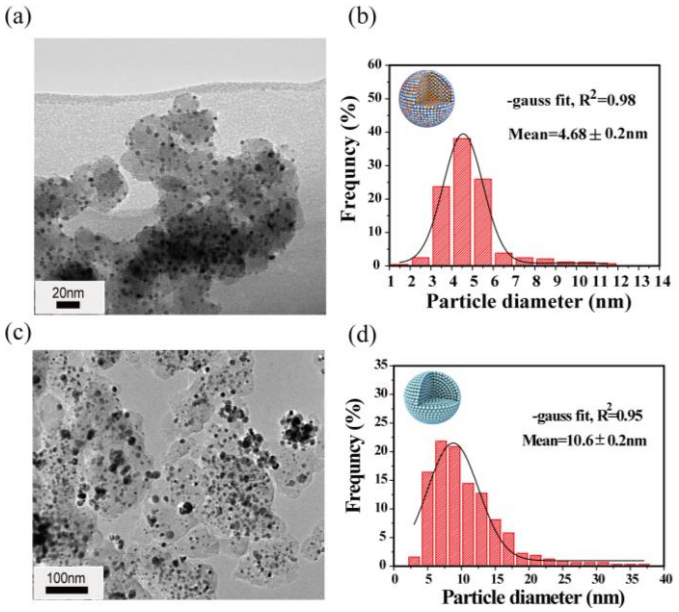


Figure S3. TEM images and the corresponding particle size statistics of the $Pt_3CoRu/C@NC$ and commercial Pt/C catalysts after high-temperature annealing.

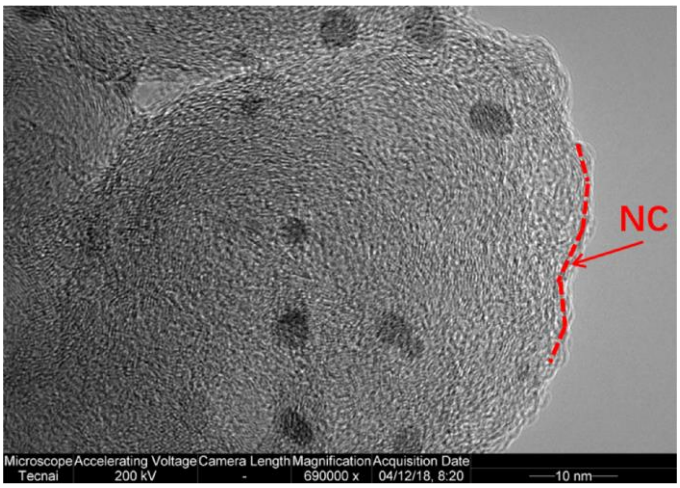


Figure S4. The HRTEM images of the $Pt_3CoRu/C@NC$ catalysts.

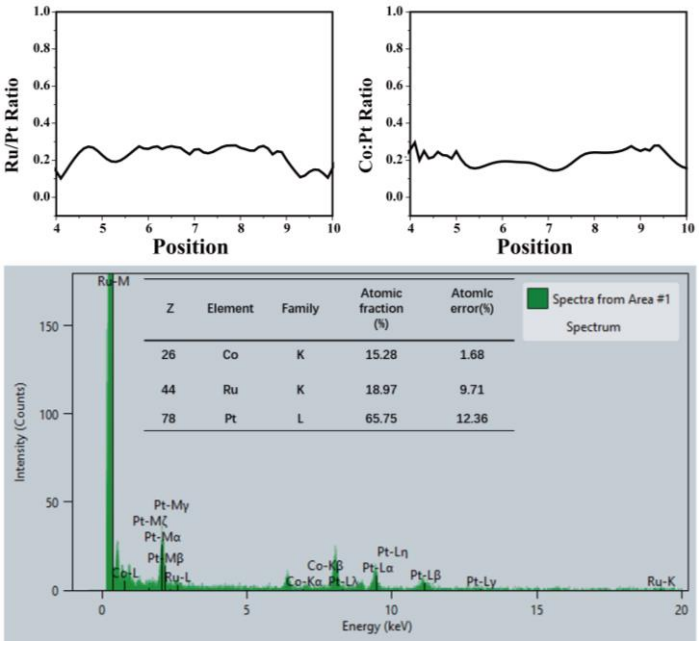


Figure S5. The Ru/Pt and Co/Pt atomic ratio from EELS and the corresponding EDX profile and atomic fraction of the $Pt_3CoRu/C@NC$ NP.

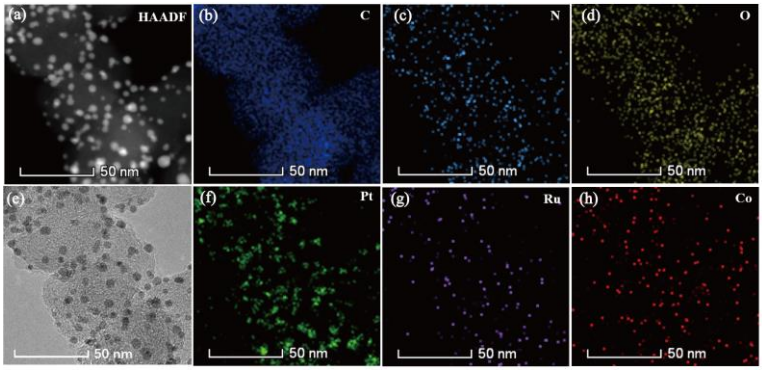
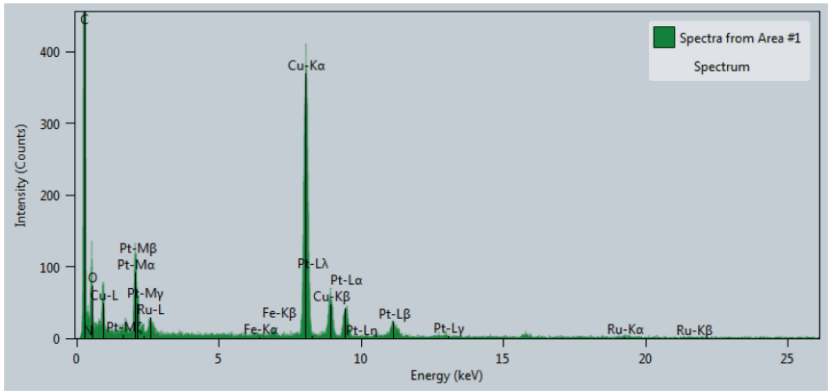


Figure S6. HAADF-STEM images of the $Pt_3CoRu/C@NC$ catalysts (a) and the corresponding elemental mapping (b-h).



Z	Element	Family	Atomic Fraction(%)	Atomic Error(%)	Mass Fraction(%)	Mass Error(%)	Fit Error(%)
6	C	K	86.12	9.43	57.01	5.12	6.85
7	N	K	1.24	0.15	0.04	0.12	0.06
8	O	K	2.12	0.47	1.90	0.40	4.58
29	Cu	K	9.14	1.55	30.25	4.39	0.87
26	Co	K	0.04	0.01	0.11	0.02	15.85
44	Ru	K	0.39	0.07	1.88	0.32	10.63
78	Pt	L	0.95	0.13	8.82	1.07	1.12

Figure S7. The EDX profile and corresponding atomic fraction of the $Pt_3CoRu/C@NC$ catalyst.

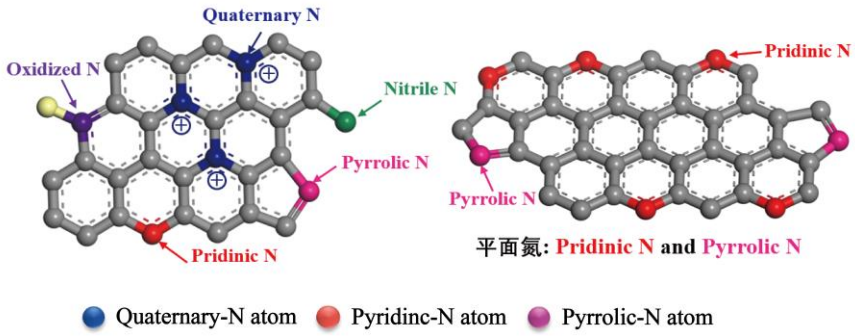


Figure S8. The illustration of the corresponding pyrrolic-N and pyridinic-N quaternary-N respectively.

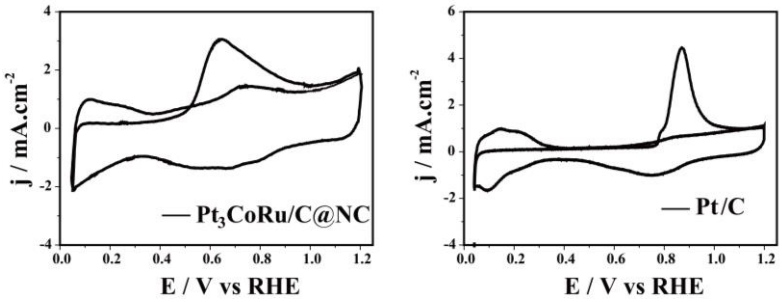


Figure S9. The detailed CO stripping curves of the $Pt_3CoRu/C@NC$ and commercial Pt/C catalysts.

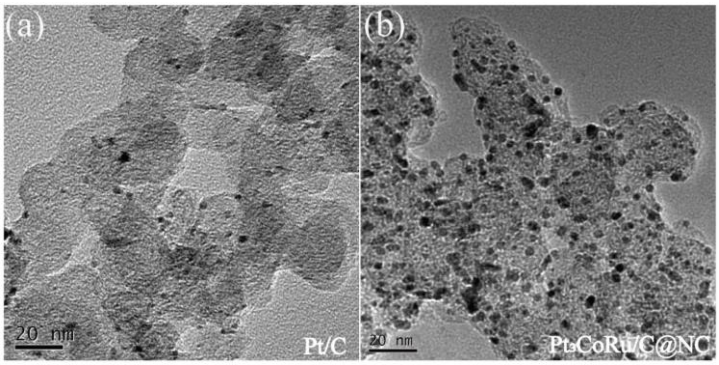


Figure S10. The TEM images of the Pt/C and $Pt_3CoRu/C@NC$ catalyst after under a constant potential of 0.75VRHE for 6000s.

Catalysts	I_f:I_b	Onset Potential(v)of CO oxidation (vsRHE)	Peak currents from CV curves		Electrolytes	References
			MA (A/mg pt)	SA (mA/cm^2)		
Fe@(PtRu) NPs	----	0.295 vs NHE	0.819	----	0.1 M $HClO_4$+1 M Methanol	1
PtRuFe NWs	----	0.41	----	2.4	0.1 M $HClO_4$ + 0.5 M Methanol	2
PtPdRu spheres	0.97	----	0.294	----	0.5 M $HClO_4$ + 0.5 M Methanol	3
FePtPd NWs	1.09	----	0.489	-----	0.1 M $HClO_4$ + 0.2 M Methanol	4
$Pt_4Ru_4Fe_2$/C	----	0.4	0.11	1.31	1 M H_2SO_4 + 1 M methanol	5
$Pt_5Ru_3Fe_2$/C	----	0.3	0.107	1.22	1 M H_2SO_4 + 1 M Methanol	5
Au/Ag/Pt	----	----	0.98	1.33	1 M H_2SO_4 + 1 M Methanol	6
PtRuCu/C dendrites	1.32	0.47	1.13	1.20	0.1 M $HClO_4$ + 1 M Methanol	7
Pt_3CoRu/C@NC	2.50	0.35	0.97	1.60	0.1 M $HClO_4$ + 0.5 M Methanol	This work

Table S1. A brief comparison of the MOR electrochemical activity of the catalysts reported in the currently literature to the trimetallic Pt_3CoRu/C@NC catalyst.

Reference:

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(2) Megan E. Scofield, Christopher Koenigsmann, L. Wang, H. Q. Liu, Stanislaus S. Wong, Tailoring the composition of ultrathin, ternary alloy PtRuFe nanowires for the methanol oxidation reaction and formic acid oxidation reaction. *Energy. Environ. Sci.* 8 (2015) 350.

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(5) K. R. Lee, M. K. Jeon, S. I. Woo, Composition optimization of PtRuM/C (M = Fe and Mo) catalysts for methanol electro-oxidation via combinatorial method. *Appl. Catal. B: Environ.* 91 (2009) 428-433.

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(7) S. F. Xue, W. T. Deng, F. Yang, J. L. Yang, Ibrahim. Saana. Amiinu, D. P. He, H. L. Tang, S. C. Mu. Hexapod PtRuCu Nanocrystalline Alloy for Highly Efficient and Stable Methanol Oxidation, *ACS Catal.* 8 (2018) 7578-7584.