

Manipulating the Surface Composition of Pt-Ru Bimetallic Nanoparticles to Control the Methanol Oxidation Reaction Pathway

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Experiment Section

Chemicals and materials

Commercial Pt/C catalyst (JM, 20 wt% Pt). Antimony trichloride (RuCl₃, 99%), 4-(2-ethylamino) benzene-1,2-diol (C₈H₁₁O₂N, 90%, purchased from adamas-beta). Tetraethyl orthosilicate (Si(OC₂H₅)₄, 98%), Tris (hydroxymethyl) aminomethane (C₄H₁₁NO₃, 99.5%), Nafion (5% in a mixture of lower aliphatic alcohols and water). High-pure Milli-Q H₂O (18.2MΩ, TOC<2ppb) was used to make all the solutions.

Synthesis of series Pt₁Ru_x/C@NC samples

The Pt₁Ru_x/C@NC catalysts was prepared according to our previous reported method with some modification. In a typical synthesis, 100 mg commercial Pt/C powder (JM, 20 wt. % Pt) was dispersed in 20 mL ethanol solution, the solution was then stirred ultrasonically at room temperature for 30min to achieve homogeneous dispersion, the 20 mL deionized water was added to 20ml ethanol solution. The mixture solution was also stirred ultrasonically at room temperature for 30min, and then adding 40 mg dopamine (PDA) which dissolved in 10 mL Tris-HCl (50 mM, pH≈8.5)

solution. The mixture was stirred for 16 h at room temperature. The obtained nanocomposite (Pt/C-PDA) was gathered by centrifugation and washing with deionized water and then dried at 80°C for 8 h. The obtained Pt/C-PDA was stirred with RuCl₃ solutions in deionized water to form Pt/C-PDA-Ru³⁺ suspension. After 12 h stirring, adding 2 mL TEOS and 2 mL HCl (PH=3) solution to the pre-prepared Pt/C-PDA-Ru³⁺ suspension and the admixture was mixed at room temperature for 30min to receive a uniform mixture. The uniform mixture was moved to glass petri dishes and allowed to slowly evaporate in open circumstances until the composite films (Pt/C-PDA-Ru³⁺-SiO₂) formed. For pyrolysis of the Pt/C-PDA-Ru³⁺-SiO₂, the solid films were heated at a rate of 10°C/min to 700°C and maintained for 4 h under flowing 8%H₂/92%Ar to obtain the PtRu-SiO₂ alloy series composites. After slowly cooling the sample to room temperature, the PtRu-SiO₂ alloy composites were etched by 0.3M HF to removal the surface silica shells. The resulting products were washed with anhydrous alcohol and deionized water and finally dried under vacuum at 60 °C for 24 h. The final catalyst of Pt₁Ru_{0.5}/C@NC, Pt₁Ru₁/C@NC and Pt₁Ru₂/C@NC catalysts were prepared by adding the 20ul, 40ul, and 80ul 0.26g_{Ru}/ml RuCl₃ solutions, respectively.

Characterization

Physical Characterization X-ray diffraction (XRD) patterns were recorded on a XRD6000 using Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) at a step rate of 2°/s. Low-resolution transmission electron microscopy (TEM) was carried out on a FEI Tecnai G220S-TWIN instrument operating at 120 kV. High-resolution transmission electron microscopy (HRTEM), Atomically resolved Aberration-corrected high-angle annular dark-field scanning TEM (ACHAADF-STEM) in combination with energy-dispersive X-ray spectroscopy (EDX) were carried out on the Aberration-Corrected TEM FEI Titan 80-300 instrument operating at accelerating voltage of 80-300 kV (Spherical Aberration: $\leq 2\mu\text{m}$, Adjustable; TEM Information limit: $\leq 0.08\text{nm}$; STEM Resolution: $\leq 0.136\text{nm}$; EELS Energy Resolution: $\leq 0.7\text{eV}$). XPS was acquired using a Kratos XSAM800 spectrometer equipped with monochromatic Al X-ray source (Al KR, 1.4866 keV), the vacuum in the analysis chamber was maintained at 10^{-7} Pa, and the binding energy was calibrated by using 284.6 eV as the C 1s peak energy. The concentration of Pt and Ru in the as-prepared catalysts was determined by the inductively coupled plasma mass spectrometry (Thermo Fisher Scientific, iCAP6300 ICP-MS)

Electrochemical measurements

All electrochemical experiments were performed on the electrochemical workstation of Autolab PGSTAT302N at room temperature ($25\pm 1^\circ\text{C}$), using a three electrodes electrochemical setup with a rotating disk electrode (RDE) system in a standard three-electrode cell. The cell associated of a glassy carbon working electrode (GC electrode, 5mm in diameter, PINE: AFE3T050GC), an Ag/AgCl (3M KCl) reference electrode and a graphite rod counter electrode. All potentials in this work were given relative to the reversible hydrogen electrode (RHE). Specifically, the potential measured with a Ag/AgCl electrode can be related by $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.267 \text{ V}$. The working electrodes were prepared by applying catalyst ink onto GC disk electrodes. In brief, the 2mg electrocatalyst was dispersed in ethanol and ultrasonicated for 30 min to form a uniform catalyst ink. A total of 10 μL of well-dispersed catalyst ink was applied onto a pre-polished GC disk. After drying at room temperature, a drop of 0.01 wt% Nafion solution was applied onto the surface of the catalyst layer to form a thin protective film. The prepared electrodes were dried at room temperature before electrochemical tests. Before electrochemical measurements, all the electrodes were pretreated by cyclic voltammetry (CV) at potential between 0.05 V to 0.9 V at a sweep rate of 50 mV/s for 30 cycles to remove any surface contamination in 0.1M HClO₄. The methanol oxidation reaction (MOR) was conducted by CV at 0-1.2V for 20 cycles in N₂-saturated 0.1 M HClO₄ solution containing 0.5M CH₃OH. The CO stripping were conducted in N₂-saturated 0.1 M HClO₄ solution which was purged with CO before the measurement at 10 mV/s. Chronoamperometry was carried out at the constant potential of 0.7 V in 0.1M HClO₄ + 0.5 M CH₃OH. The electrochemical surface area (ECSA) of Pt in the catalysts using the following equation (E1):

$$ECSA = Q_{co} / 0.42 [Pt] \quad (\text{E1})$$

where Q_{co} is the charge due to the integrated area of the CO dissolved peak, 0.42 mC/cm is the electrical charge associated with monolayer adsorption of hydrogen on Pt, and [Pt] is the loading of Pt on the working electrode.

Here we choose (111) crystal plane as the computational crystal plane. L is the lattice parameter and d represent the interplanar spacing of the selected crystal faces. The induced strain variation was approximately calculated by the Debye-Scherrer equation and Bragg's law, details calculated by the following equations (E2-E3):

$$L = 1/2d \quad (\text{E2})$$

$$L_2 \text{Strain}\% = (L_2 - L_1 / L_1)\% \quad (\text{E3})$$

Among which, L_2 strain% is the percentage change of the lattice parameter of the studied catalyst (PtRu/C@NC) when compared to standard sample 1 (Pt/C), L_1 represents the lattice parameter of the Pt/C, and L_2 is the lattice parameter of the researched PtRu/C@NC sample.

$$C(\text{nm}) = \frac{0.9\delta}{B(2\theta) \cdot \cos(\theta)} \quad (\text{E4})$$

C is the interplanar spacing of the selected crystal plane, B is the half width of the selected crystal plane, 2θ is the angle corresponding to the selected crystal plane, and δ is the wavelength of the Cu target, which is generally 1.5456 nm.

***In situ* Fourier transform infrared-diffuse reflection spectrum (FTIRs)**

The external potential in the experiment was realized by potentiostat. The instrument of React IR TM 15 the detection frequency was 1Hz with the indexing value of 4cm^{-1} was used to acquisition reaction signal. The mass spectrometry signal was 20 points per second. All the spectra are presented in the form of absorption spectra. The electrochemical properties and electrocatalytic behavior of the catalysts in a simple three-electrode system (see Chapter 1.4 for details). The *in-situ* FTIRs recorded simultaneously with the chronoamperometric (CA) test in the 0.1M HClO_4 +0.5M CH_3OH solution. Before *In situ* FTIR measurement, the catalyst was activated in N_2 saturated 0.1M HClO_4 solutions for 30 cycles (to ensure steady-state reactivity). The infrared background spectra are collected at the same time. After that, the electrolyte 0.1M HClO_4 solution switched to N_2 saturated 0.1M HClO_4 +0.5M CH_3OH solution. Chronoamperometric at constant potential of 0.05V, 0.1V, 0.3V, 0.5V, 0.7V, 0.85V were conducted, simultaneous recording the *in-situ* FTIR spectrum under chronoamperometric on a constant potential of the homemade PtRu catalyst after 10s, 50s, 100s, 200s, 300s.

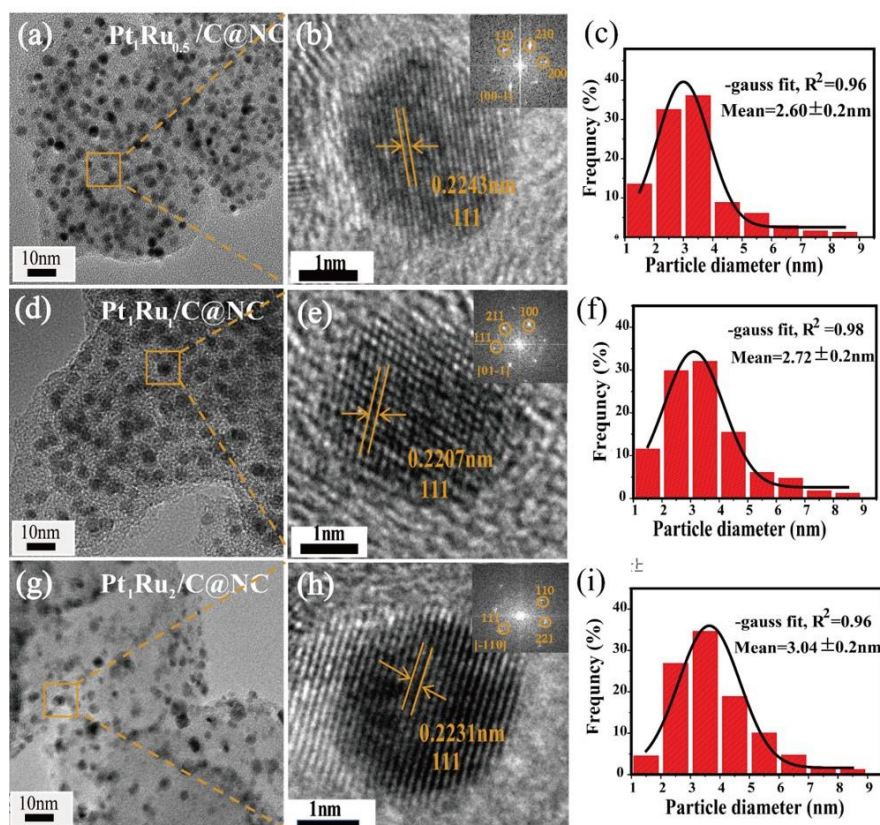


Figure S1. The HRTEM images and its corresponding FFT images as well as the corresponding statistical particle size of Pt₁Ru_{0.5}@NC/C (a-c), Pt₁Ru₁@NC/C (d-f) and Pt₁Ru₂@NC/C (g-i) catalysts, respectively.

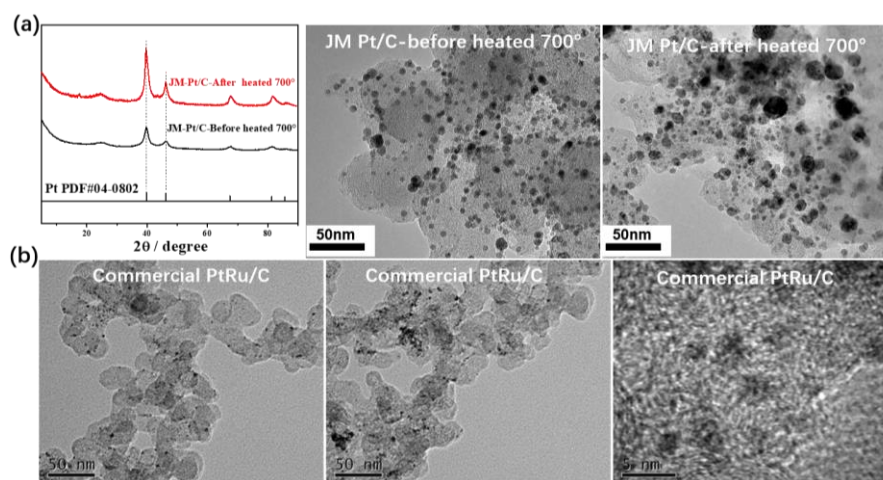


Figure S2. (a) The XRD and corresponding TEM curves of commercial Pt/C catalysts before and after high temperature annealing. (b) The TEM and HRTEM images of commercial PtRu/C catalysts.

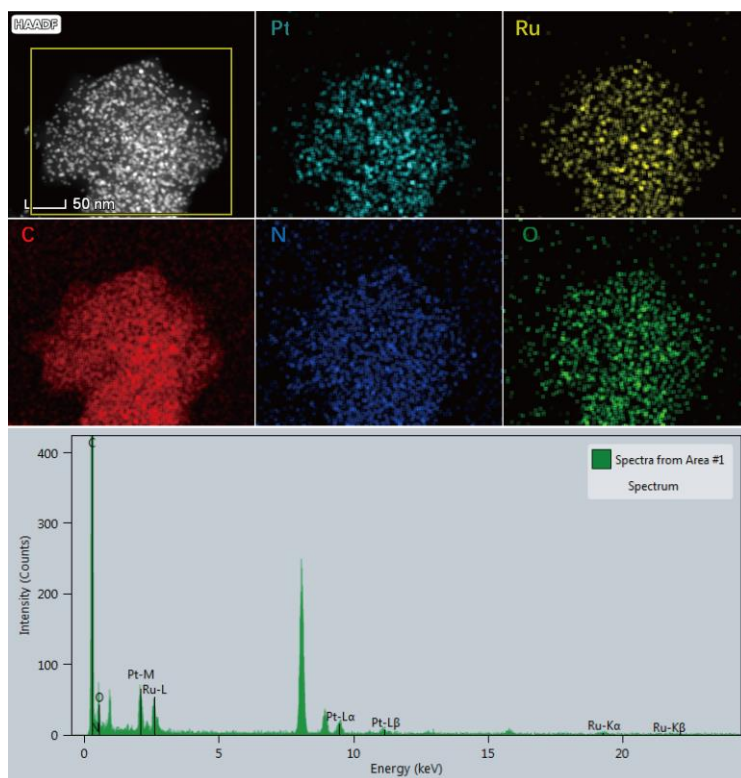


Figure S3. HAADF-TEM image and the corresponding elemental mapping as well as the EDX profile of the Pt₁Ru₁@NC/C catalysts.

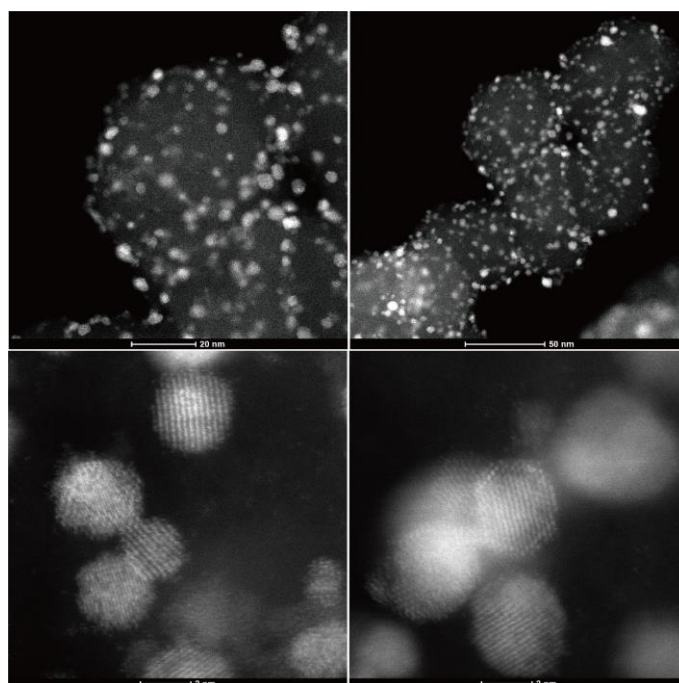


Figure S4. More detailed aberration-corrected HAADF-STEM images of Pt₁Ru₁@NC/C catalysts

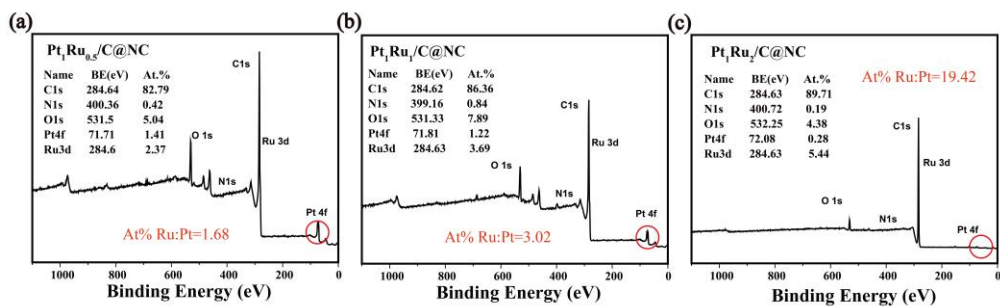


Figure S5. The elemental compositions of Pt₁Ru_{0.5}@NC/C (a), Pt₁Ru₁@NC/C (b) and Pt₁Ru₂@NC/C (c) catalysts performed in XPS.

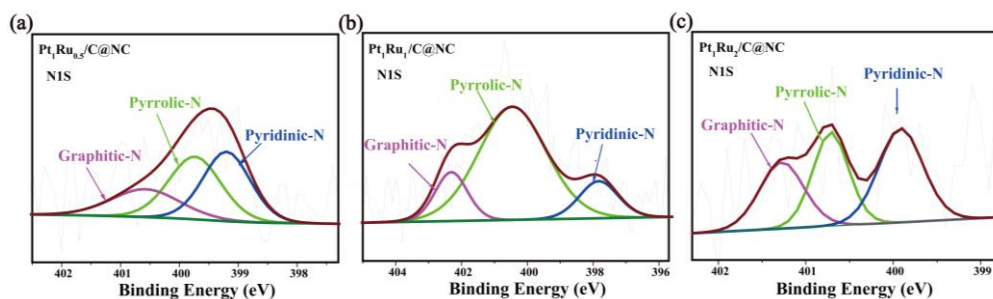


Figure S6. The N 1s of Pt₁Ru_{0.5}@NC/C (a), Pt₁Ru₁@NC/C (b) and Pt₁Ru₂@NC/C (c) catalysts.

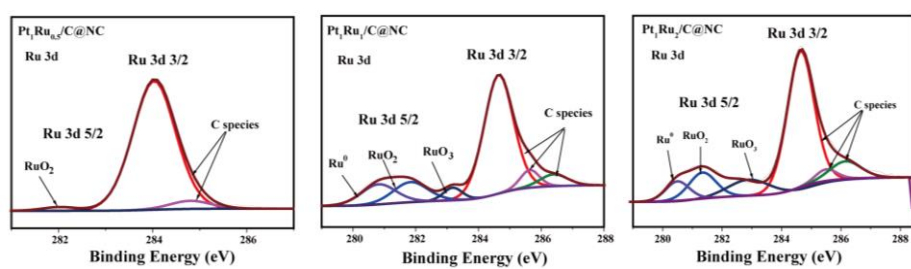


Figure S7. The Ru 3d of Pt₁Ru_{0.5}@NC/C, Pt₁Ru₁@NC/C and Pt₁Ru₂@NC/C catalysts.

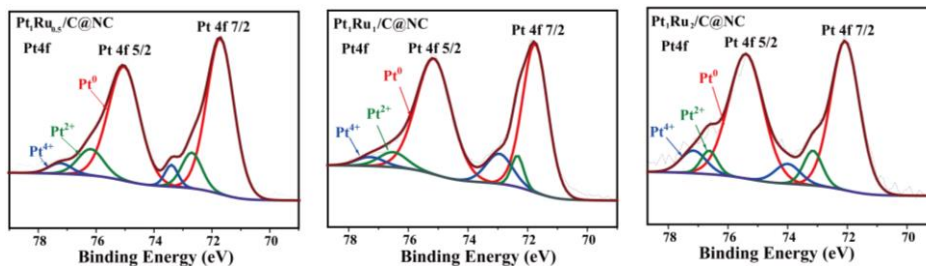
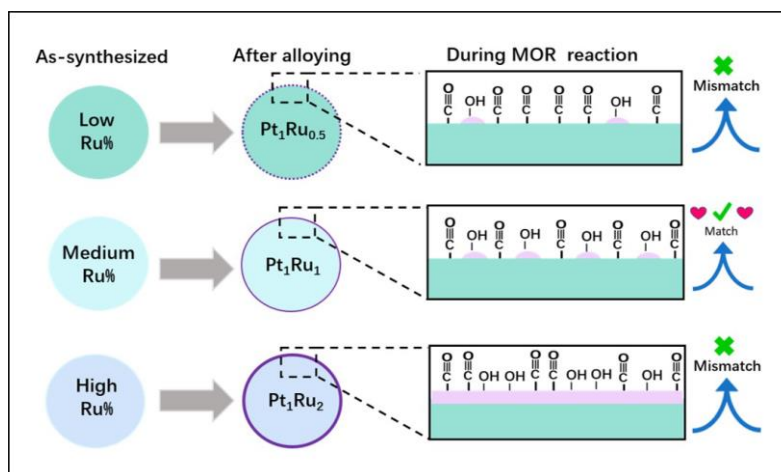


Figure S8. The Pt 4f of $\text{Pt}_1\text{Ru}_{0.5}@NC/C$, $\text{Pt}_1\text{Ru}_1@NC/C$ and $\text{Pt}_1\text{Ru}_2@NC/C$ catalysts.



Scheme S1. Schematic illustration of surface evolution and bimetallic synergy in PtRu alloy nanoparticles with different Ru percentage content. Low Ru% represent the low molar feeding of Ru^{3+} to Pt ($\text{Pt}_1\text{Ru}_{0.5}@NC/C$), medium Ru% means the catalyst of $\text{Pt}_1\text{Ru}_1@NC/C$, High Ru% represent the of $\text{Pt}_1\text{Ru}_2@NC/C$ catalyst. Pt is shown in blue; Ru and RuO_x are depicted in purple.

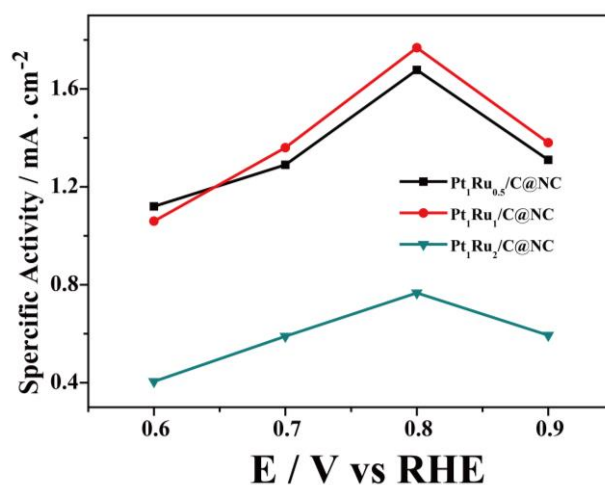


Figure S9. The relationship between specific activity normalized to Pt surface area with the MOR electrocatalytic activity of the $\text{Pt}_1\text{Ru}_{0.5}@NC/C$, $\text{Pt}_1\text{Ru}_1@NC/C$ and $\text{Pt}_1\text{Ru}_2@NC/C$ catalysts.

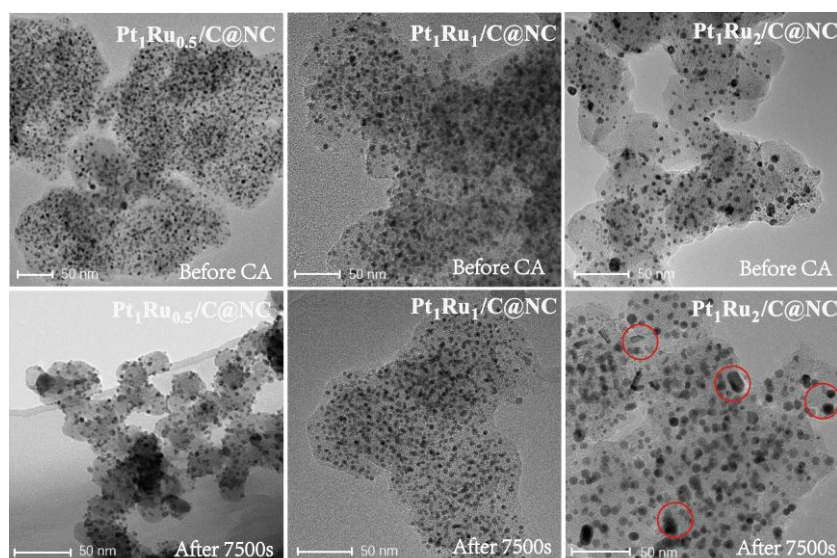


Figure S10. The TEM images of $\text{Pt}_1\text{Ru}_{0.5}\text{@NC/C}$, $\text{Pt}_1\text{Ru}_1\text{@NC/C}$ and $\text{Pt}_1\text{Ru}_2\text{@NC/C}$ catalysts before and after the CA test.

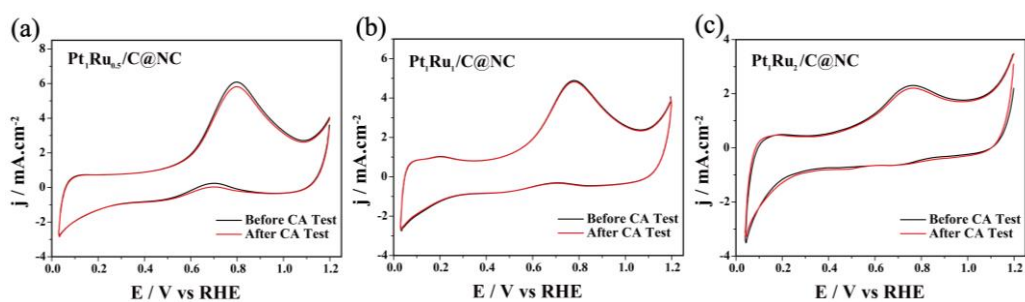
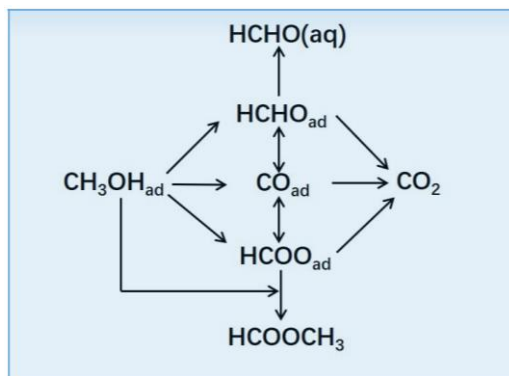


Figure S11. CV curves of $\text{Pt}_1\text{Ru}_{0.5}\text{@NC/C}$ (a), $\text{Pt}_1\text{Ru}_1\text{@NC/C}$ (b) and $\text{Pt}_1\text{Ru}_2\text{@NC/C}$ (c) performed in 0.1 M HClO_4 + 0.5 M CH_3OH solution before and after the CA test.



Scheme S2. A simplified scheme for the complete electrooxidation of CH_3OH to CO_2 on Pt in acidic solutions.

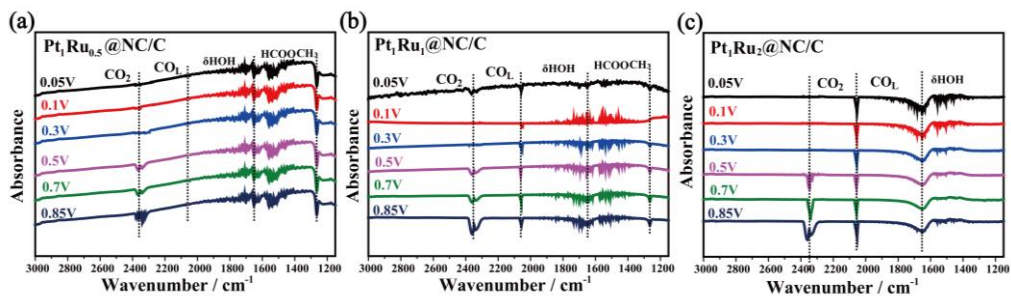


Figure S12. *In situ* FTIR spectra for methanol oxidation in 0.1 M HClO₄ + CH₃OH solution after 10s on Pt₁Ru_{0.5}@NC/C (a), Pt₁Ru₁@NC/C (c) and Pt₁Ru₂@NC/C.

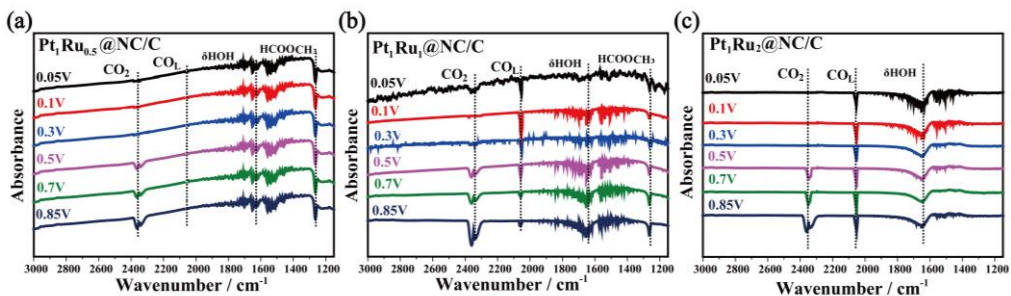


Figure S13. *In situ* FTIR spectra for methanol oxidation in 0.1 M HClO₄ + CH₃OH solution after 50s on Pt₁Ru_{0.5}@NC/C (a), Pt₁Ru₁@NC/C (c) and Pt₁Ru₂@NC/C.

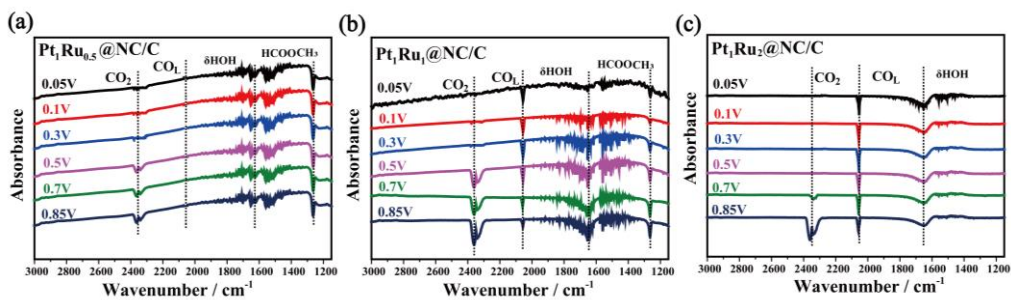


Figure S14. *In situ* FTIR spectra for methanol oxidation in 0.1 M HClO₄ + CH₃OH solution after 200s on Pt₁Ru_{0.5}@NC/C (a), Pt₁Ru₁@NC/C (c) and Pt₁Ru₂@NC/C.

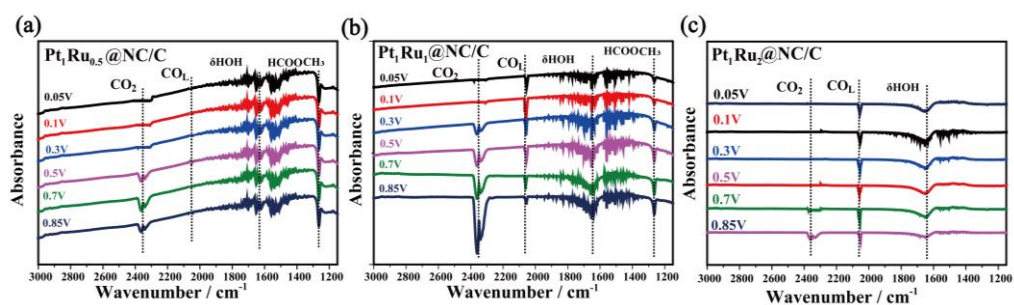


Figure S15. *In situ* FTIR spectra for methanol oxidation in 0.1 M HClO₄ + CH₃OH solution after 300s on Pt₁Ru_{0.5}@NC/C (a), Pt₁Ru₁@NC/C (c) and Pt₁Ru₂@NC/C.

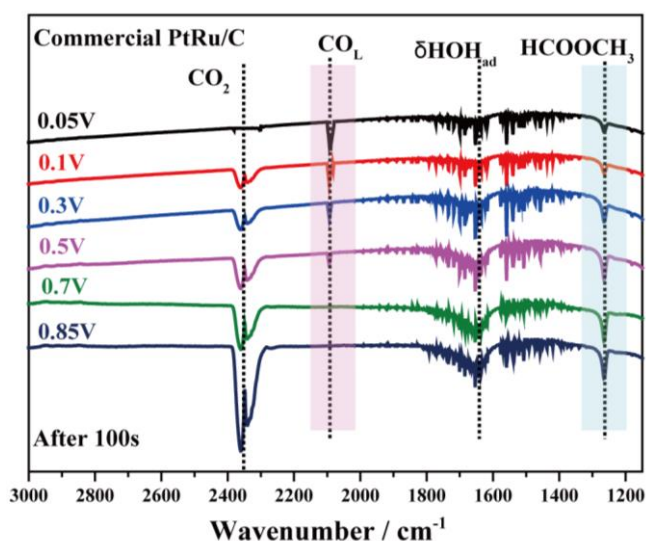


Figure S16. The In-situ FTIR spectra for methanol oxidation in 0.1 M HClO₄ + CH₃OH solution after 100s on commercial PtRu/C catalyst.

Catalysts	ICP (Before Stability test)		ICP (After Stability test)	
	Loading by weight%		Loading by weight%	
	Pt loading (wt%)	Ru loading (wt%)	Pt loading (wt%)	Ru loading (wt%)
Pt ₁ Ru _{0.5} /C@NC	7.3	0.8	7.1	0.7
Pt ₁ Ru ₁ /C@NC	6.3	2.1	6.2	2.0
Pt ₁ Ru ₂ /C@NC	4.6	3.9	4.3	3.7

Table S1. The elemental loadings of Pt₁Ru_{0.5}/C@NC, Pt₁Ru₁/C@NC and Pt₁Ru₂/C@NC catalysts by using ICP.

Catalysts	2 θ /degree	Lattice	Strain	Particle size	Particle size
	(111)	parameter (1/Å)	(%)	From XRD (nm)	From TEM (nm)
JM-Pt/C	39.763	0.2208	---	2.88	3.15
Pt ₁ Ru _{0.5} /C@NC	40.390	0.2241	1.49	2.27	2.60
Pt ₁ Ru ₁ /C@NC	40.465	0.2249	1.66	2.48	2.72
Pt ₁ Ru ₂ /C@NC	40.314	0.2233	1.13	2.96	3.04

Table S2. The detailed lattice parameter and induced strain variation as well as the NP sizes of Pt₁Ru_{0.5}@NC/C, Pt₁Ru₁@NC/C and Pt₁Ru₂@NC/C catalysts according the powder X-ray diffraction patterns.

Catalysts	Wt% form ICP	ECSA (m ² /g _{Pt})	<i>I</i> / <i>I</i> _b	Peak currents from CV curves	
				MA	SA
				(mA/ug _{Pt})	(mA/cm)
Pt ₁ Ru _{0.5} /C@NC	7.3	49	6.86	0.59	1.29
Pt ₁ Ru ₁ /C@NC	6.3	47	7.17	0.67	1.36
Pt ₁ Ru ₂ /C@NC	4.6	39	5.46	0.23	0.59

Table S3. The details of the electroactivity in Pt₁Ru_{0.5}/C@NC, Pt₁Ru₁/C@NC and Pt₁Ru₂/C@NC catalysts.

Catalysts	<i>I</i> / <i>I</i> _b	Onset	Peak currents from CV		Electrolytes	References
		Potential(v) of	curves			
		CO oxidation (vs RHE)	MA (A/mg _{Pt})	SA (mA/cm ²)		
PtRu/PPDA MWCNTs	---	0.15 (Vs SCE)	---	0.732	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	1
Porous Ru ₅₀ Pt ₅₀ /C	---	---	---	1.32	0.1 M HClO ₄ + 0.5 M CH ₃ OH	2
Pt ₁₃ Ru ₂₂	0.97	---	0.86	0.59	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ OH	3
PtRu NWs	---	---	0.36	1.16	0.1 M HClO ₄ + 0.5 M CH ₃ OH	4
Pt ₄ Ru ₄ Fe ₂ /C	---	0.40	0.11	1.31	1 M H ₂ SO ₄ + 1 M CH ₃ OH	5
Pt ₅ Ru ₃ Fe ₂ /C	---	0.30	0.107	1.22	1 M H ₂ SO ₄ + 1 M CH ₃ OH	5
Pt ₁ Ru _{0.5} /C@NC	6.86	0.36	0.59	1.29	0.1 M HClO ₄ + 0.5 M CH ₃ OH	This Work
Pt ₁ Ru ₁ /C@NC	7.17	0.35	0.67	1.36	0.1 M HClO ₄ + 0.5 M CH ₃ OH	This Work

Table S4. A brief comparison of the MOR electrochemical activity of the catalysts reported in the currently literature to the homemade Pt₁Ru_{0.5}/C@NC, Pt₁Ru₁/C@NC catalyst.

Reference:

- (1) Wu, B. H.; Zhu, J. J.; Li, X.; Wang, X. Q.; Chu, J.; Xiong, S. X. PtRu nanoparticles supported on p-phenylenediamine-functionalized multiwalled carbon nanotubes: enhanced activity and stability for methanol oxidation. *Ionics* **2019**, *25*, 181-189.
- (2) Zhao, W. Y.; Ni, B.; Yuan, Q.; He, P. L.; Gong, Y.; Gu, L.; Wang, X. Highly Active and Durable Pt₇₂Ru₂₈ Porous Nanoalloy Assembled with Sub-4.0 nm Particles for Methanol Oxidation. *Adv. Energy Mater.* **2017**, 1601593.
- (3) Kaplan, D.; Burstein, L.; Popov, I.; Peled, E. The Effect of Different Pt:Ru Surface Composition on Methanol-Oxidation Activity of Carbon-Supported PtRu/IrNi Catalysts, *J. Electrochem. Soc.* **2016**, *163*, 1004-1010.
- (4) Huang, L.; Zhang, X. P.; Wang, Q. Q.; Han, Y. J.; Fang, Y. X.; Dong, S. J. Shape-Control of PtRu Nanocrystals: Tuning Surface Structure for Enhanced Electrocatalytic Methanol Oxidation. *J. Am. Chem. Soc.* **2018**, *140*, 1142–1147.
- (5) Lee, K. R.; Jeon, M. K.; Woo, S. I. Composition optimization of PtRuM/C (M = Fe and Mo) catalysts for methanol electro-oxidation via combinatorial method. *Appl. Catal. B: Environ.* **2009**, *91*, 428-433.