

Ultralow Platinum Catalysts for High Performance Fuel Cells: *in Situ* Encapsulation
of platinum atoms and CoPt₃ into 3D hollow nanoshells

Jingjing Zhang, Pingwen Ming, Bing Li, Cunman Zhang*

Clean Energy Automotive Engineering Center and School of Automotive Studies,
Tongji University, Shanghai 201804, China

* Corresponding author.

E-mail addresses: libing210@tongji.edu.cn (B. Li)

1. Experimental Section

1.1 Chemical and Electrocatalyst preparation

Analytical grade cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Methanol, Ethanol were obtained from Sinopharm Chemical Reagents, China. 2-Methylimidazole was obtained from Aladdin Reagents Ltd. NaBH_4 was obtained from Sinopharm Chemical Reagents, China. PtCl_2 was obtained from Shanghai Macklin Biochemical Ltd. The commercial Pt/C (20%) catalyst was purchased from Johnson Matthey. Nafion (5wt%) was acquired from Sigma-Aldrich. All of the chemicals used in this experiment were analytical grade and used without further purification.

1.2 Synthesis of ZIF-67

2-methylimidazole (2.5 g) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 g) were dissolved in 50 mL methanol respectively to form two solutions, and stirred them vigorously for five minutes at room temperature to obtain homogeneous solutions. Then, the first solution was added into the second solution under stirring, and the final mixture was stirred constantly at 25 °C for 1 h and stationary for 12 h to form ZIF-67. The obtained product was collected by centrifugation and washed ethanol for three times, which disperse in ethanol and waited for use.

1.3 Synthesis of Co@NC

The as-prepared ZIF-67 was pyrolyzed under an H_2 &Ar (H_2 5%) atmosphere in a tube furnace. The samples were calcined at 350 °C (1.5 h) with a rate of 2 °C min^{-1} , furthermore, further, the samples were calcined at 700 °C with a rate of 2 °C min^{-1} and maintained at 700 °C for 3.5 h. Then naturally cooling to room temperature.

1.4 Synthesis of PtCl_2 @ZIF-67

20 mL PtCl₂ solution (1 mg/mL) was added to a fresh dispersion of ZIF-67. After agitated stirring at room temperature for 1 h, 3 mL NaHB₄ (1 mg/mL) was added dropwise under stirring. the as-obtained products were centrifuged, and finally freeze-dried for overnight.

1.5 Preparation of Pt SAs/CoPt₃@NC

The as prepared PtCl₂@ZIF-67 was pyrolyzing under an H₂/Ar (H₂ 5%) atmosphere in a tube furnace. The sample was heated to 350 °C (1.5 h) with a rate of 2 °C min⁻¹, further, the samples were calcined at 700 °C with a rate of 2 °C min⁻¹ and maintained at 700 °C for 3.5 h. Then naturally cooling to room temperature.

1.6 Materials characterization

The morphologies of catalysts and the changes after the durability test were analyzed by transmission electron microscopy (TEM). The crystallinity of the Pt SAs/CoPt₃@NC and Co@NC-700 catalysts were determined by X-ray diffraction (XRD). Raman spectroscopy was employed to measure the graphitization degrees in carbon materials and analyze their structural changes. The bulk compositions of Pt SAs/CoPt₃@NC catalysts were characterized by inductively coupled plasma mass spectrometry (ICP-MS). Scanning electron microscopy (SEM) was employed to analyze the sample shape of Pt SAs/CoPt₃@NC. The specific surface areas and pore size distributions of carbon supports were obtained by Brunauer-Emmett-Teller (BET) analysis with high-purity N₂ as filling gas after degassing at 200 °C for 8 h.

1.7 Fabrication of MEAs

The slurry was prepared by dispersing catalyst and 5% Nafion solution into water and

isopropanol (volume ratio of 1:1). This slurry was sprayed onto a membrane of 25 cm² (GORE, thickness of 10 μm), and then the gas diffusion layers (25BC, SGL) were fixed to both sides of the as-sprayed membrane to produce MEAs. The MEAs were fabricated using the Pt SAs/CoPt₃/NC catalysts and the commercial 20wt% Pt/C(JM) catalyst in the cathode and anode, respectively, and two controls were obtained using Pt SAs/CoPt₃/NC in the cathode and only Pt/C (JM) in both electrodes. The Pt loadings of the cathode and anode in all of the MEAs are 0.03 and 0.015 mgPt cm⁻².

1.8 Electrochemical Evaluation

The electrochemical tests of supports and catalysts were conducted by a rotating disc electrode (RDE) technique. The catalyst of 2 mg was added to a Nafion/ethanol solution of 1 mL (the mass ratio of Nafion solution/ethanol is 1:30) to obtain the catalyst ink. Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and 30000 cycles of durability testing (in 0.1M HClO₄ solution) were employed to estimate electrochemical activity and durability of catalysts.

1.9 Single-Cell and High Potential Durability Tests of MEAs

All MEAs performed the same single-cell tests. The operating conditions of polarization curves was as follows: the cell temperature, relative humidity (RH), back pressure (relative to the atmosphere), and H₂/air stoichiometric ratio (excess coefficient) are 80 °C, 80%, 120 kPa, and 1.7:3.0, respectively. The operating conditions of the durability test were as follows: the cell temperature and RH were 80 °C and 100%, respectively, and the cathode and anode were supplied with N₂ and H₂ of 0.2 NLPM.

2.0 Pt SAs@NC

2-methylimidazole (2.5 g) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 g) were dissolved in 50 mL methanol respectively to form two solutions, and stirred them vigorously for five minutes at room temperature to obtain homogeneous solutions. Then, the first solution was added into the second solution under stirring, and the final mixture was stirred constantly at 25 °C for 1 h and stationary for 12 h to form ZIF-8, the obtained product was collected by centrifugation. 20 mL PtCl_2 solution (1 mg/mL) was added to a fresh dispersion of ZIF-8. After agitated stirring at room temperature for 1 h, 3 mL NaHB_4 (1 mg/mL) was added dropwise under stirring. the as-obtained products were centrifuged, and finally freeze-dried for overnight ($\text{PtCl}_2@\text{ZIF-8}$). The as prepared $\text{PtCl}_2@\text{ZIF-8}$ was pyrolyzing under an N_2 atmosphere in a tube furnace. The samples were calcined at 910 °C with a rate of 2 °C min^{-1} and maintained at 910 °C for 3.5 h. Then naturally cooling to room temperature. According to Figure 3, we have successfully synthesized single-atom Pt.

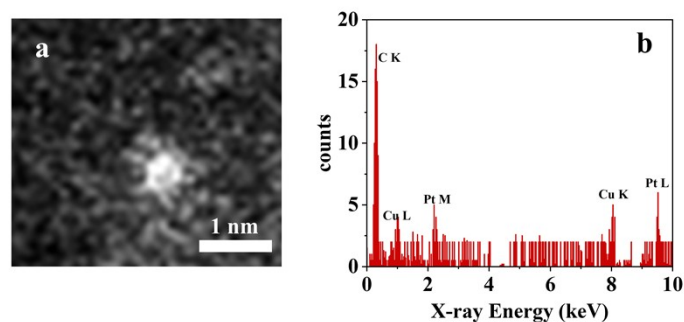


Figure S1. Pt SAs@NC catalyst. a) HAADF-STEM images. b) EDXS spectrum.

2.1 Pt₃Co@ NC

Synthesis of Pt₃Co according to previous literature method¹, The obtained Pt₃Co for the next-stage usage.

ZIF-8 samples were calcined at 910 °C with a rate of 2 °C min^{-1} and maintained at 910 °C for 3.5 h. Then naturally cooling to room temperature. NC (20 mg) was ultrasonically dispersed in 15 mL of isopropanol for 1 hour, followed by the addition of 10 mL of cyclohexane containing Pt₃Co nanoparticles, and then ultrasonicated for another 0.5 hours. The as-prepared slurry was subjected to centrifugation at 10000 rpm for 5 min and dried in a vacuum oven at 70 °C for 2 hours to obtain the Pt₃Co@ NC

catalyst. According to Figure S2, we have successfully synthesized the active species CoPt_3 .

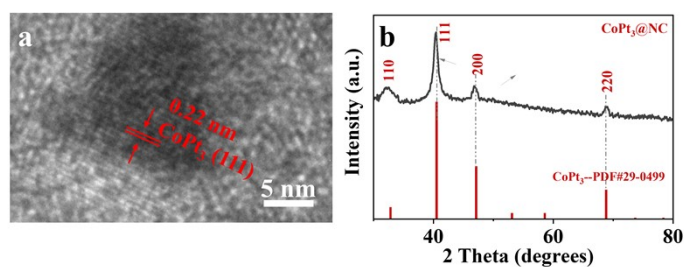


Figure S2. $\text{CoPt}_3@NC$ catalyst. a) HRTEM images. b) XRD spectrum.

2.2 $\text{Co}@NC$

2-methylimidazole (2.5 g) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 g) were dissolved in 50 mL methanol respectively to form two solutions, and stirred them vigorously for five minutes at room temperature to obtain homogeneous solutions. Then, the first solution was added into the second solution under stirring, and the final mixture was stirred constantly at $25\text{ }^\circ\text{C}$ for 1 h and stationary for 12 h to form ZIF-67. The obtained product was collected by centrifugation. The as-prepared ZIF-67 was pyrolyzed under an $\text{H}_2\&\text{Ar}$ (H_2 5%) atmosphere in a tube furnace. The samples were calcined at $350\text{ }^\circ\text{C}$ (1.5 h) with a rate of $2\text{ }^\circ\text{C min}^{-1}$, furthermore, further, the samples were calcined at $700\text{ }^\circ\text{C}$ with a rate of $2\text{ }^\circ\text{C min}^{-1}$ and maintained at $700\text{ }^\circ\text{C}$ for 3.5 h. Then naturally cooling to room temperature. According to Figure S3, we have successfully synthesized cobalt nanoparticles.

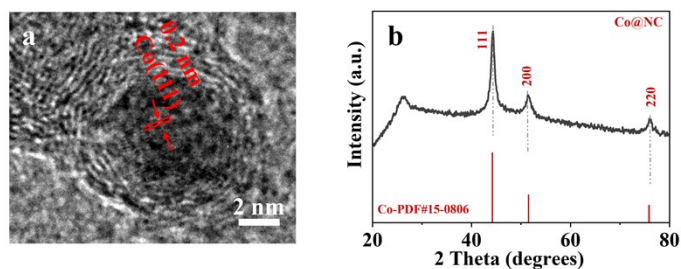


Figure S3. $\text{Co}@NC$ catalyst. a) HRTEM images. b) XRD spectrum.

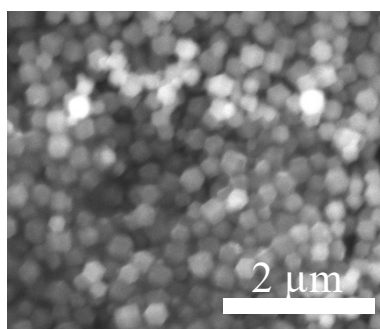


Figure S4. SEM of ZIF-67.

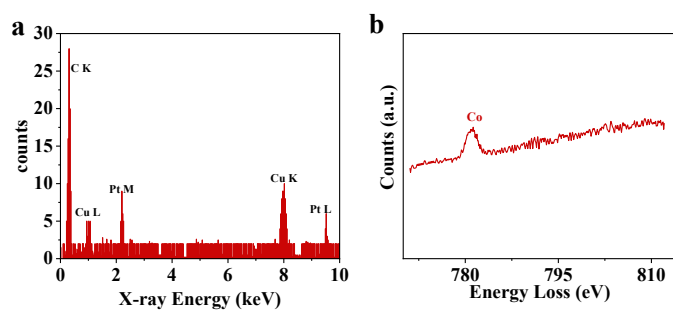


Figure S5. a) EDXS spectrum. b) EELS spectrum.

Table S1. the ICP-MS analysis for Pt element in Pt SAs/CoPt₃@NC.

element	ICP-MS (wt%)
Pt	3.2

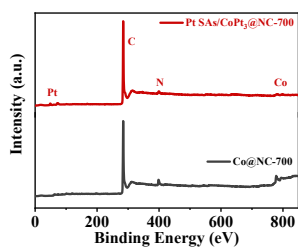


Figure S6. The XPS spectra of Pt SAs/CoPt₃@NC-700 and Co@NC-700 catalysts.

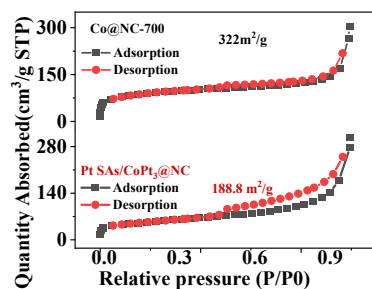


Figure S7. N_2 adsorption–desorption isotherms of the Pt SAs/ $CoPt_3@NC$ and $Co@NC$ catalysts.

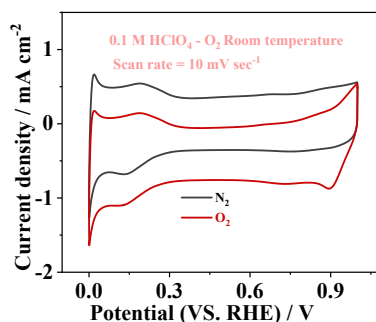


Figure S8. CV profiles of Pt SAs/ $CoPt_3@NC-700$ catalyst (black and red curves indicate CV curves recorded in N_2 - and O_2 -saturated 0.1 M $HClO_4$ solution, respectively).

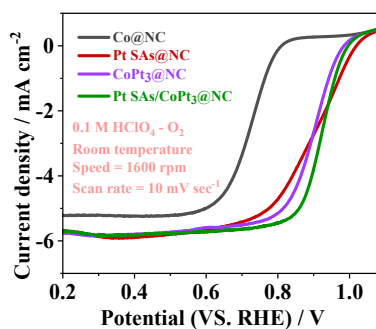


Figure S9. Positive-going ORR polarization curves of $Co@NC$, $Pt\ SAs@NC$, $CoPt_3@NC$, and $Pt\ SAs/CoPt_3@NC$ catalysts in O_2 -saturated 0.1 M $HClO_4$ solution.

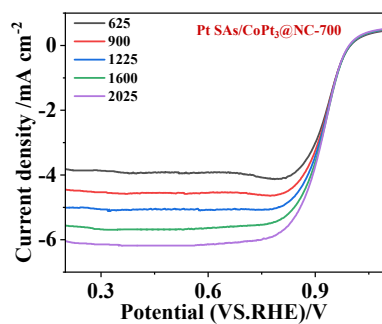


Figure S10. Koutecky–Levich plots of the Pt SAs/CoPt₃@NC.

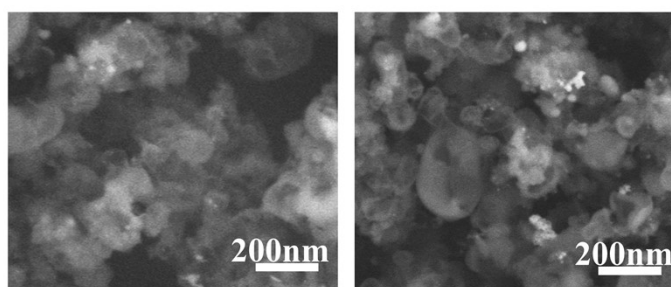


Figure S11. a, b) SEM images of Pt SAs/CoPt₃@NC-700 before and after 30000 cycles.

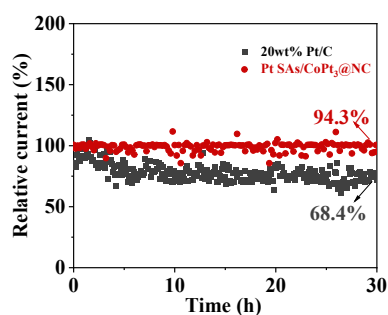


Figure S12. Long-term i-t test performed of Pt SAs/CoPt₃@NC-700 and 20wt% Pt/C in 0.1 M HClO₄.

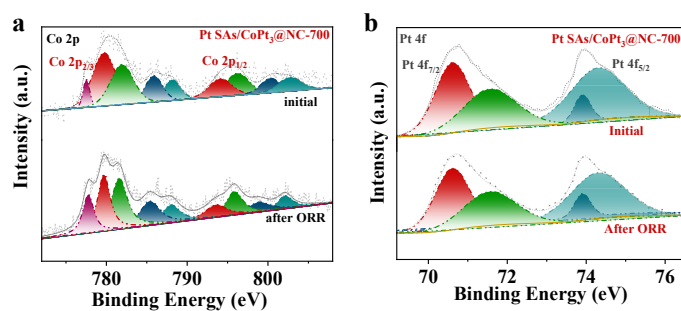


Figure S13. (a) Co 2p and (b) Pt 4f spectrums of Pt SAs/CoPt₃@NC-700 before and after ORR stability test.

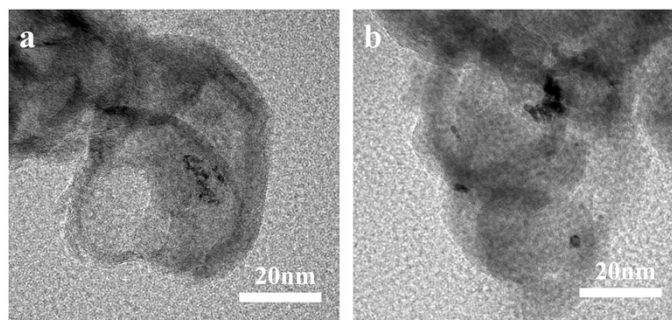


Figure S14. a, b) TEM images of Pt SAs/CoPt₃@NC-700 before and after 30000 cycles.

Table S2. Comparison of the ORR activity of Pt SAs/CoPt₃@NC with various recently reported Pt-based catalysts and advanced catalysts.

Catalysts	electrolyte	Half-wave potential (V vs. RHE)	Pt loading (ugPt cm ⁻²)	References
Pt SAs/CoPt ₃ @NC	0.1 M HClO ₄	0.928	13	This work
Pt/C	0.1 M HClO ₄	0.908	51	This work
PtCo ₃ -H600	0.1 M HClO ₄	0.905	12	2
Pt/CNTs	0.1 M HClO ₄	0.85	20	3
PtBi/C	0.1 M HClO ₄	0.886	10	4
PtA@FeSA-N-C	0.1 M HClO ₄	0.923	13	5
PtFe/C	0.1 M HClO ₄	0.893	19.99	6
Pt/40Co-NC-900	0.1 M HClO ₄	0.92	60	7
PtCu NSs/C,	0.1 M HClO ₄	0.893	18.9	8
PtFe-Fe ₂ C	0.1 M HClO ₄	0.91	26.52	9
Pd@PtCu	0.1 M HClO ₄	0.89	15	10
Pt@Co SAs-ZIF-NC	0.1 M HClO ₄	0.917	25.5	12
PtDs/gdsDNA/rGO	0.1 M HClO ₄	0.9	14.14	13
Co _{1.08} Fe _{3.34} @NGT	0.1 M HClO ₄	≈0.8	\	14
Pt _n /gDNA-GO	0.1 M HClO ₄	0.9	11.31	15

Table S3. Pt 4f peak position and proportion (%) of Pt⁰ and Pt^{δ+} in Pt SAs/CoPt₃@NC.

Pt SAs/CoPt ₃ @NC			
Pt ⁰ 4f(eV)	7/2	70.6	18.9%
	5/2	/	
Pt ^{δ+} 4f(eV)	7/2	71.3	21.1%
	5/2	74.1 and 74.6	27.0% and 32.8%

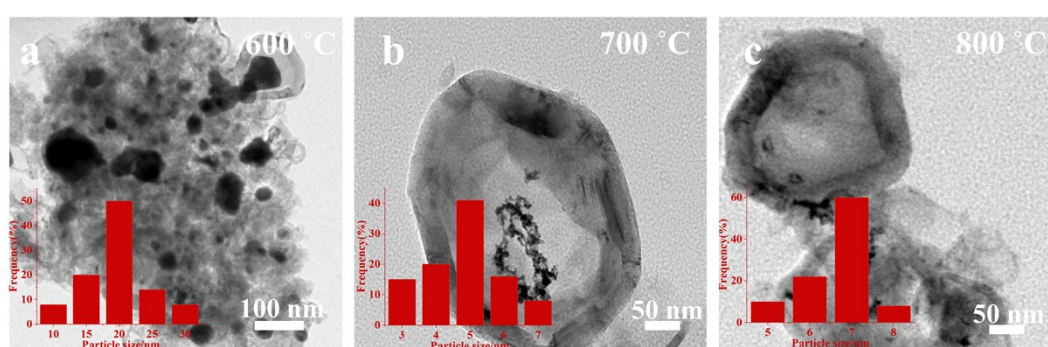


Figure S15. TEM image and particle size distribution image. a) Pt SAs/CoPt₃@NC-600; b) Pt SAs/CoPt₃@NC-700 and c) Pt SAs/CoPt₃@NC-800.

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