Supplementary Information

Construction of Hollow Porous Carbon Sphere@CoP/Nitrogen Doped Carbon Supported Platinum Catalyst for high performance methanol oxidation

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1 Experimental Section

1.1 Chemicals and materials

Cetyltrimethyl ammonium bromide (CTAB), resorcinol (R), formaldehyde (F), tetraethylorthosilicate (TEOS), ammonia solution (25%, NH_4OH), Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, purity 99%), ethylene glycol (EG) and hydrofluoric acid (HF) were purchased from Chuandong Chemical Reagent Company (Chengdu, China). 2-methylimidazole (Hmim) and polyvinyl pyrrolidone (PVP) were received from Aladdin Chemical Co., Ltd. Hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, 99.9%) was purchased from the First Regent Factory (Shanghai, China). Nafion solution was purchased from Dupont China Holding Co., Ltd.

1.2 Electrochemical measurement.

Cyclic voltammetry (CV) measurements were recorded from -0.2 V to 1.0 V in N_2 saturated 0.5 M H_2SO_4 solution with a scan rate of 50 mV s^{-1}, the catalytic activity of the catalysts was investigated in N_2 saturated 0.5 M H_2SO_4 containing 1 M CH_3OH solution at a scan rate of 50 mV s^{-1}. To estimate the stability of the catalysts, chronoamperometry was performed in solution of 1.0 M CH_3OH containing 0.5 M H_2SO_4 solution for 7200 s. Electrochemical impedance spectroscopy (EIS) was performed at frequencies range between 0.01 Hz and 100 kHz, to evaluate tolerance to CO of the catalyst, CO stripping voltammetry was measured, the potential range and scan rate are the same as CV measurement. Firstly, absorption of CO was tested

in CO saturated 0.5 M H_2SO_4 solution for 20 min, and then N_2 was used to clean the electrolyte for 20 min to remove remained CO in the solution.

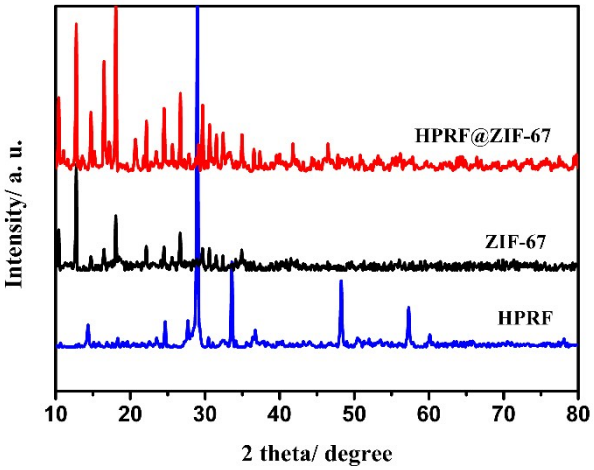


Fig. S1. XRD patterns of HPRF, ZIF-67 and HPRF@ZIF-67.

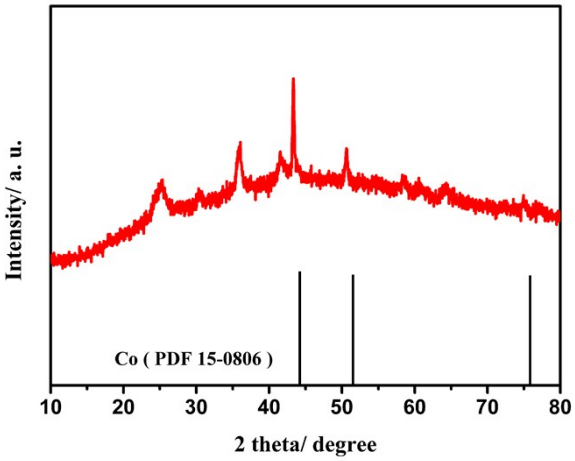
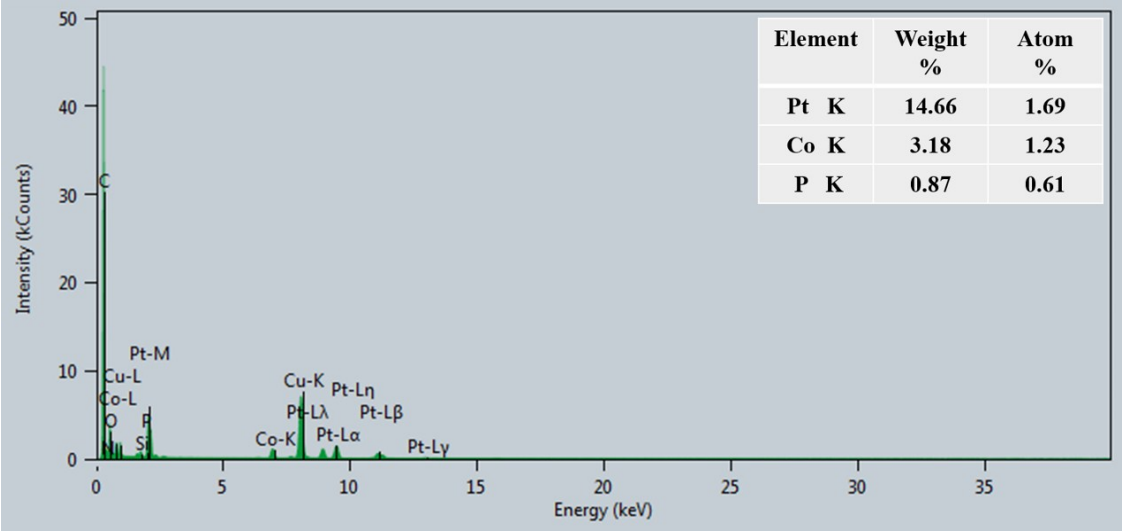


Fig. S2. XRD patterns of HPCS@Co/NC



Element	Weight %	Atom %
Pt K	14.66	1.69
Co K	3.18	1.23
P K	0.87	0.61

Fig. S3. EDS spectrum and the corresponding element contents of Pt-HPCS@CoP/NC catalyst.

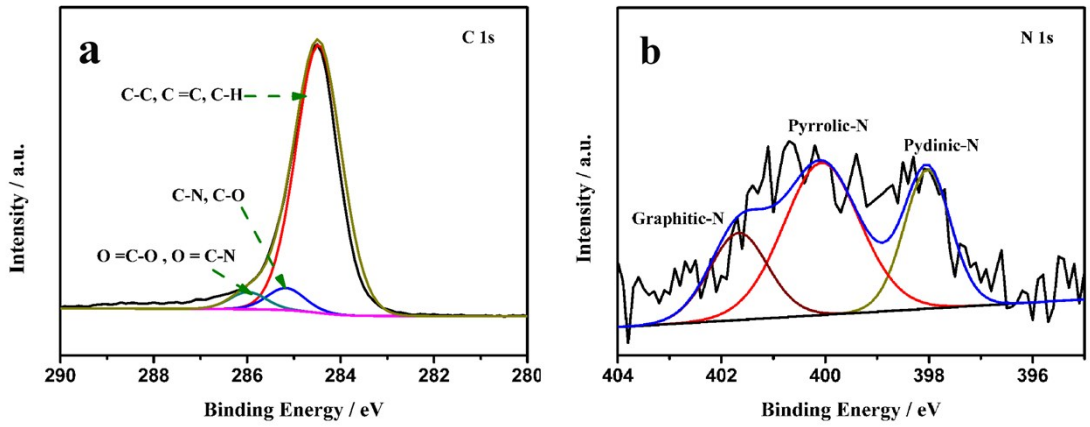


Fig. S4. XPS spectra of C 1s (a) and N 1s (b).

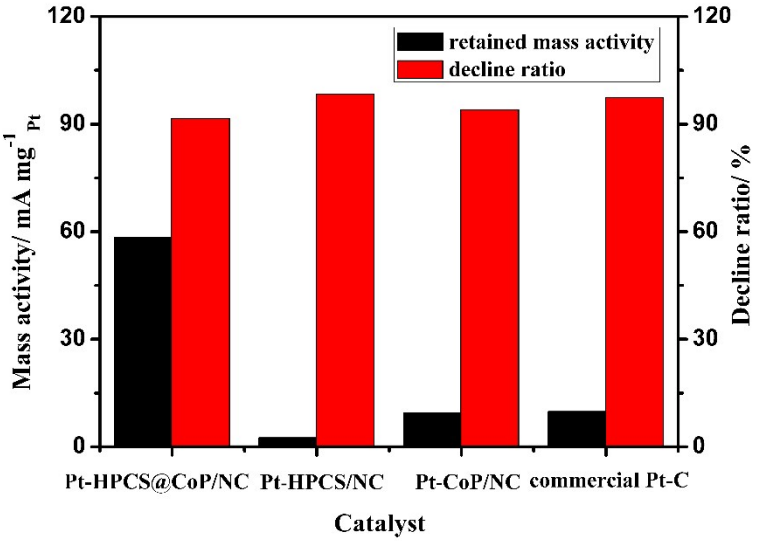


Fig. S5. The retained mass activities and corresponding activity decline ratio of all the catalysts after 7200 s.

Table S1. Results of the fit of the Pt 4f spectra, values give in % of the total intensity.

Samples	Pt (0)		Pt (II)	
	Binding energy (eV)	Ratio (%)	Binding energy (eV)	Ratio (%)
Pt-HPCS@CoP/NC	71.60	35.12	70.79	19.34
	74.90	33.26	73.97	12.27
Pt-HPCS/NC	71.50	35.03	70.52	15.89
	74.80	32.60	73.48	16.48

	71.10	34.86	73.36	18.03
Pt-CoP/NC				
	74.40	30.23	71.97	16.88
	71.43	28.55	72.22	25.66
Commercial Pt-C				
	74.73	28.18	75.59	17.67