

Supporting Information

Solvent-free melting-assisted pyrolysis strategy applied on the Co/N co-doped porous carbon catalyst

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Synthesis of 5-(4-carboxyphenyl)-10,15,20-triphenyl cobalt porphyrins The cobalt porphyrin was prepared based on a reported method.³⁷ Benzaldehyde (5.57 g, 52.5 mmol) and p-carboxybenzaldehyde (2.63 g, 17.5 mmol) dissolved in 180 mL propionic acid were loaded in a three-neck flask, then heated to reflux under magnetic stirring. Following that, the solution (30 ml) containing newly evaporated pyrrole (4.69 g, 70.0 mmol) was added with a constant pressure drop funnel and kept refluxing for 1 h. Subsequently, 100 mL deionized (DI) water was added after the mixture was cooled down to ambient temperature and then refrigerated overnight. After that, the resulting product was collected by filtration, washing and purification via column chromatography and denoted as CPTPP. 1.00 g of the obtained CPTPP and 100 mL N, N-dimethyl formamide (DMF) were introduced into a 250 mL three-necked flask under magnetically stirring and heated to reflux. Then, 2.7 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added step by step, and kept stirring and 100 mL DI water was added when cooled to room temperature. 5-(4-carboxyphenyl)-10,15,20-triphenyl cobalt porphyrin was obtained by extraction, washing and drying at 80 °C.

Synthesis of KIT-6 4.0 g of P123 was dissolved in 144 g of DI water and 7.9 g of concentrated HCl (35%) and then stirred at 35 °C until P123 was entirely dissolved. 4.0 g of butanol was introduced under stirring at 35 °C. After stirring for 1 h, 8.6 g of TEOS was added in the solution, and kept stirring at 35 °C for 24 h. Following that, the mixture was transferred to a Teflon-lined autoclave and heated at 100 °C for another 24 h. The resulting

white precipitates were filtered, and washed with DI water, and dried at 100 °C for 24 h. Finally, the mesoporous KIT-6 was obtained after heated at 550 °C in air for 5 h.

Materials Tetraethoxysilane (TEOS, 98% purity), EO-PO-EO triblock copolymer (P123, $M_w = 5800$), n-butyl alcohol, hydrochloric acid, p-carboxybenzaldehyde, benzaldehyde, propionic acid, pyrrole, methyl alcohol, ethanol, N, N-dimethyl formamide (DMF), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), dichloromethane (CH_2Cl_2), ethylbenzene, sucrose, p-ethyltoluene, p-bromoethylbenzene, 4-ethyl biphenyl, benzyl ether, propylene benzene, isopropyl benzene, indene, tetrahydronaphthalene, diphenylmethane, fluorene and brominated fluorene were obtained from commercial sources and used without further purification.

Characterization Using a NOVA 1000e from Quantachrome Instruments, N_2 adsorption-desorption analysis of the samples outgassed at 200 °C for 3 h were conducted at -196 °C and the relative pressure ranging from 0.05 to 0.98. The specific surface areas were calculated using the BET method. The pore size distribution plot was recorded from the desorption branch of the isotherm based on the BJH model. The surface morphology of the samples was investigated and the high angle annular dark field scanning TEM images (HAADF-STEM) were obtained on FEI Talos F200x with image corrector operating 300 kV. The X-ray powder diffraction (XRD) was performed on a Bruker D8 Advance analyzer with Ni-filtered Cu K α radiation (40 kV, 40 mA). Raman was analyzed on a Mono Vista

2560 Spectrometer with a laser at 532 nm (2.33 eV). X-ray photoelectron spectra (XPS) measurements were taken on an Escalab 520Xi system using Al K α radiation (1486.6 eV).

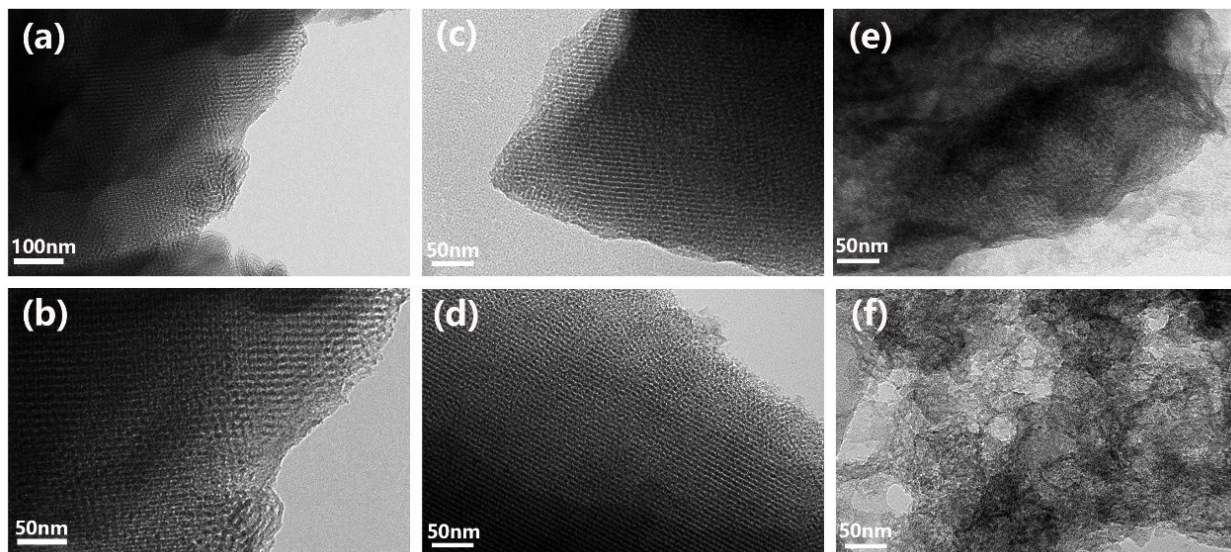


Figure S1. The TEM analysis of different regions within (a, b) KIT-6; (c) Co-N-C-600/PCMK; (d) Co-N-C-800/PCMK; (e) Co-N-C-900/PCMK; (f) Co-N-C-1000/PCMK.

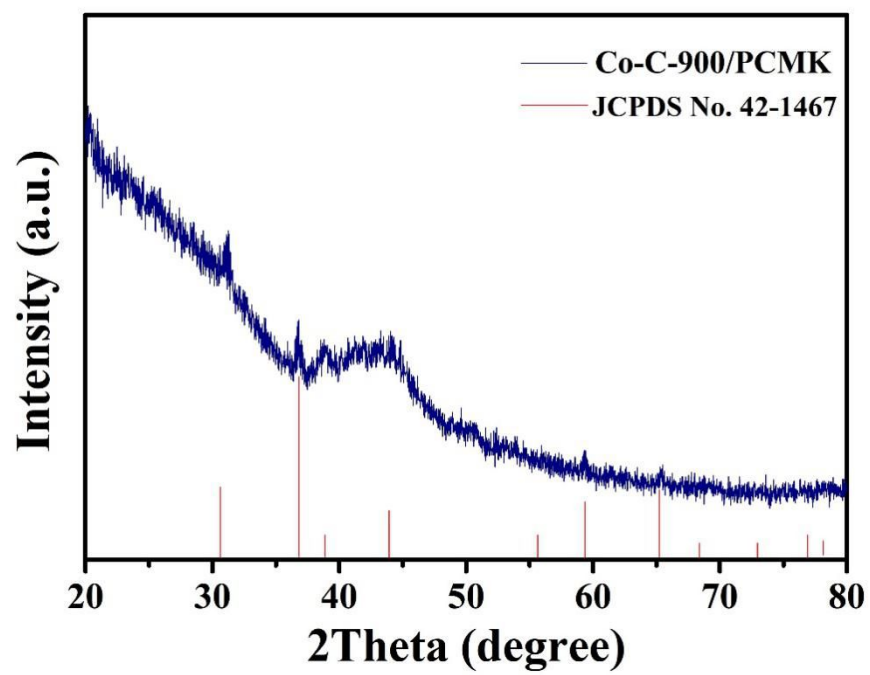


Figure S2. Wide-angle powder XRD patterns of the Co-C-900/PCMK catalyst.

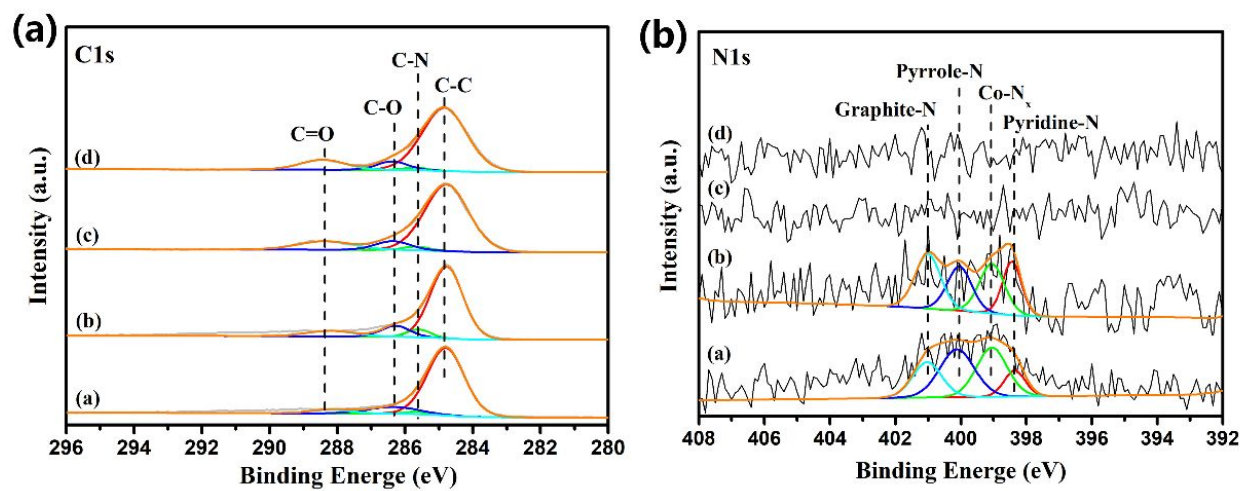


Figure S3. N and C high-resolution XPS spectra of as-prepared catalysts. (a) Co-N-C-600/PCMK; (b) Co-N-C-800/PCMK; (c) Co-N-C-900/PCMK; (d) Co-N-C-1000/PCMK

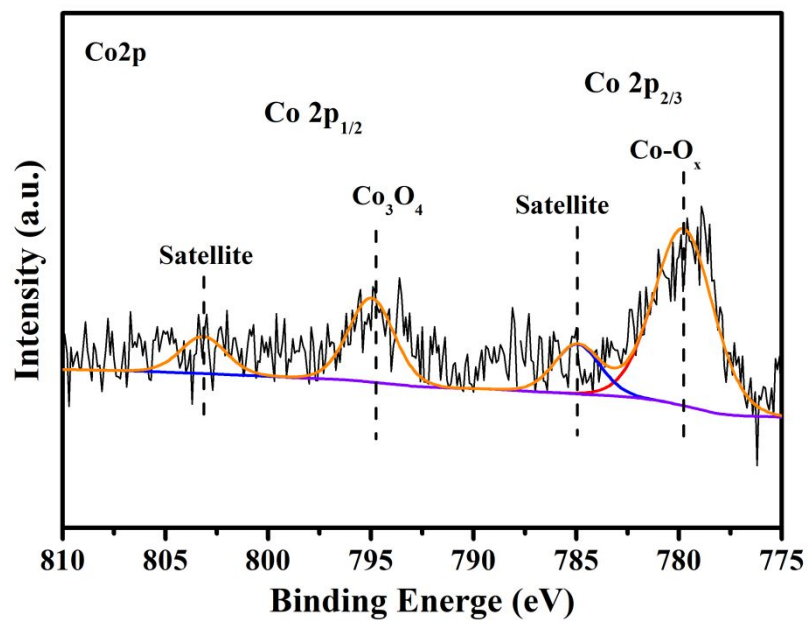


Figure S4. High-resolution XPS spectra of the Co-C-900/PCMK catalyst.

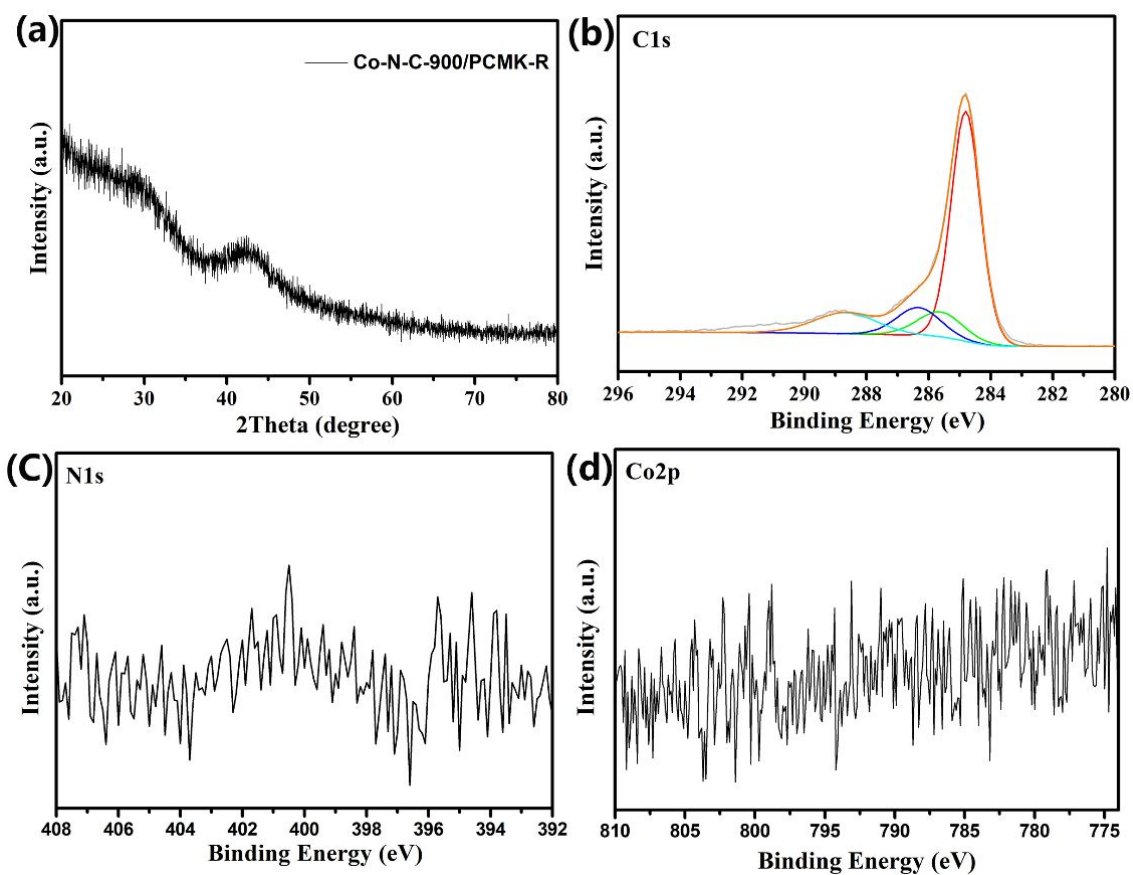


Figure S5. (a) XRD spectrum and (b-d) High-resolution XPS spectra of the reused Co-N-C-900/PCMK catalyst.

Table S1. Nitrogen adsorption and desorption test data.

entry	Sample	S (m ² /g)			Dp(nm)	Vtotal (cc/g)
		Total	S(micro)	S(meso)		
1	KIT-6	724	188	536	4.53	0.82
2	0.05-Co-N-C-600/PCMK-0.5	966	652	314	3.10	0.75
3	0.05-Co-N-C-700/PCMK-0.5	811	460	351	3.42	0.69
4	0.05-Co-N-C-800/PCMK-0.5	881	301	580	4.30	0.95
5	0.05-Co-N-C-900/PCMK-0.5	977	458	519	3.69	0.90
6	0.05-Co-N-C-1000/PCMK-0.5	1002	390	612	4.11	1.03
7	Co-C-900/PCMK-0.5	869	214	655	4.71	1.02
8	N-C-900/PCMK-0.5	651	157	494	4.59	0.75
9	C-900/PCMK-0.5	949	309	640	4.34	1.03
15	0.05-Co-N-C-600/PCMK-0.5-R	598	266	332	3.92	0.59

S: t-plot surface area; S(micro): micro surface area; S(meso): meso surface area; Dp: average pore diameter; Vtotal: total pore volume.

Table S2. The performance of selective oxidation of ethylbenzene with reused Co-N-C-T/PCMK^a.

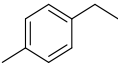
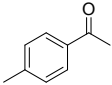
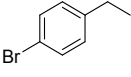
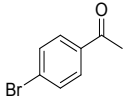
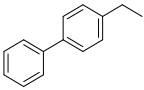
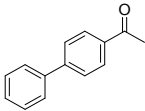
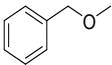
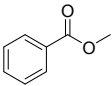
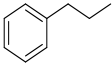
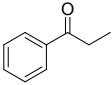
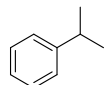
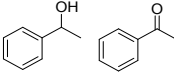



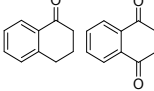
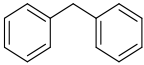
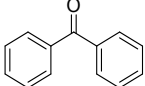
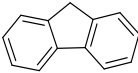
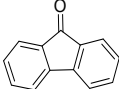
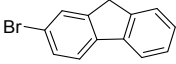
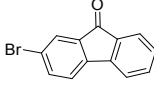
Entry	Run	Conv./%	Sel./%
1	R1	96	99
2	R2	88	94
3	R3	~65	78
4 ^b	R6	82	85
5 ^c	r5	~90	93

a: Reaction conditions: 1 mmol substrate, 15 mg catalyst, 3 mL H₂O, 3.5 mmol TBHP (70 wt% in water), 80 °C, 12 h.

b: Reaction conditions: The catalyst which has been used for 5 times is calcined again at high temperature and react at the same reaction conditions.

c: Reaction conditions: 1 mmol substrate, 15 mg catalyst, 3 mL H₂O, 3.5 mmol TBHP (70 wt% in water), 80 °C, 24 h.

Table S3. Catalytic oxidation several of substrates by Co-N-C-900/PCMK.

entry	substrate	product	Conv. [%]	Sel. [%]
1			95	93
2			98	94
3			97	87
4			>99	86
5			89	84
6		 1: 3.5	95	92
7			88	85
8		 1: 2.7	92	96
9			>99	>99
10			>99	92
11			98	90

Reaction conditions: substrate (1.0 mmol), TBHP (3.5 mmol, 75 wt% in water), catalyst (15 mg), H₂O (3.0 mL), 353 K, 12 h; the conversion and yield were determined by GC.