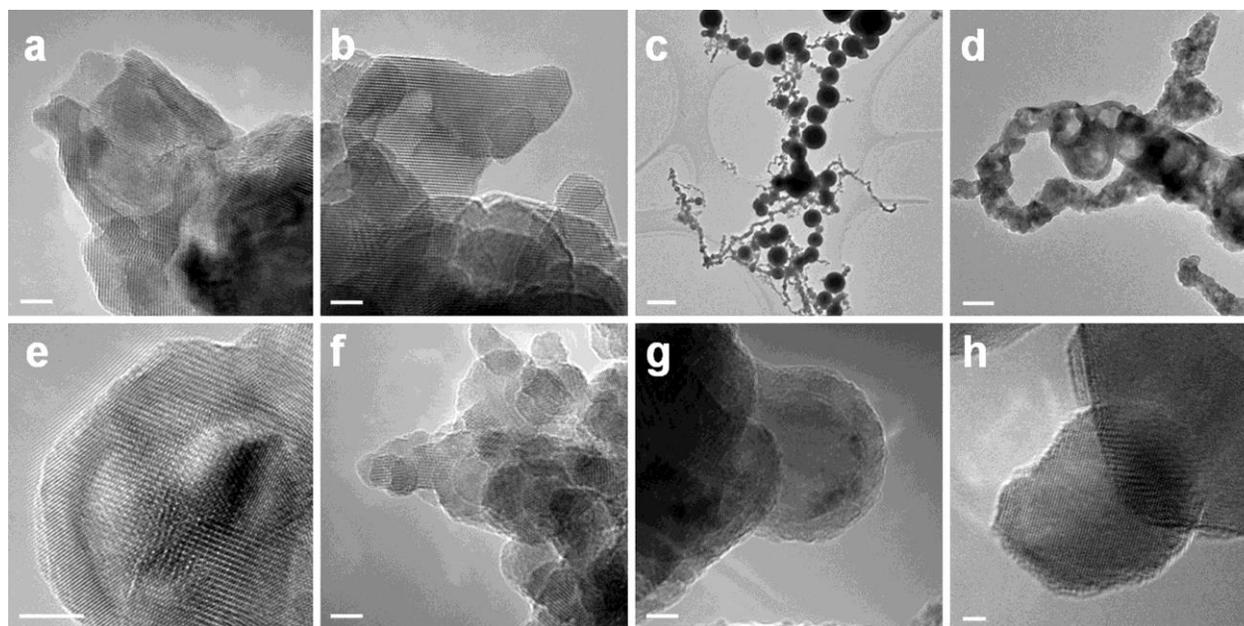
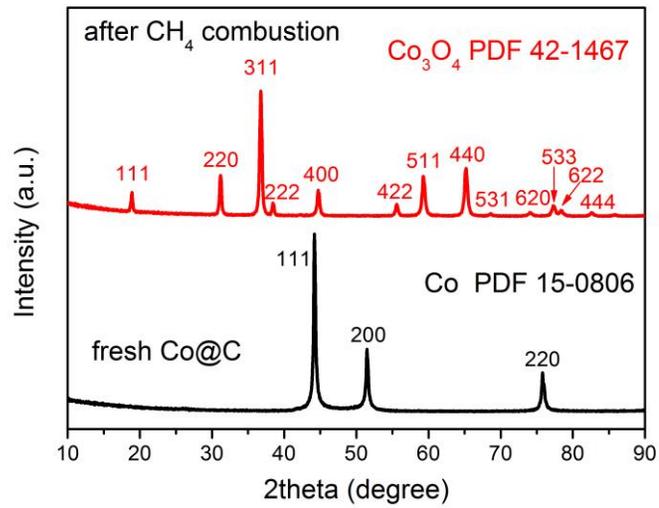


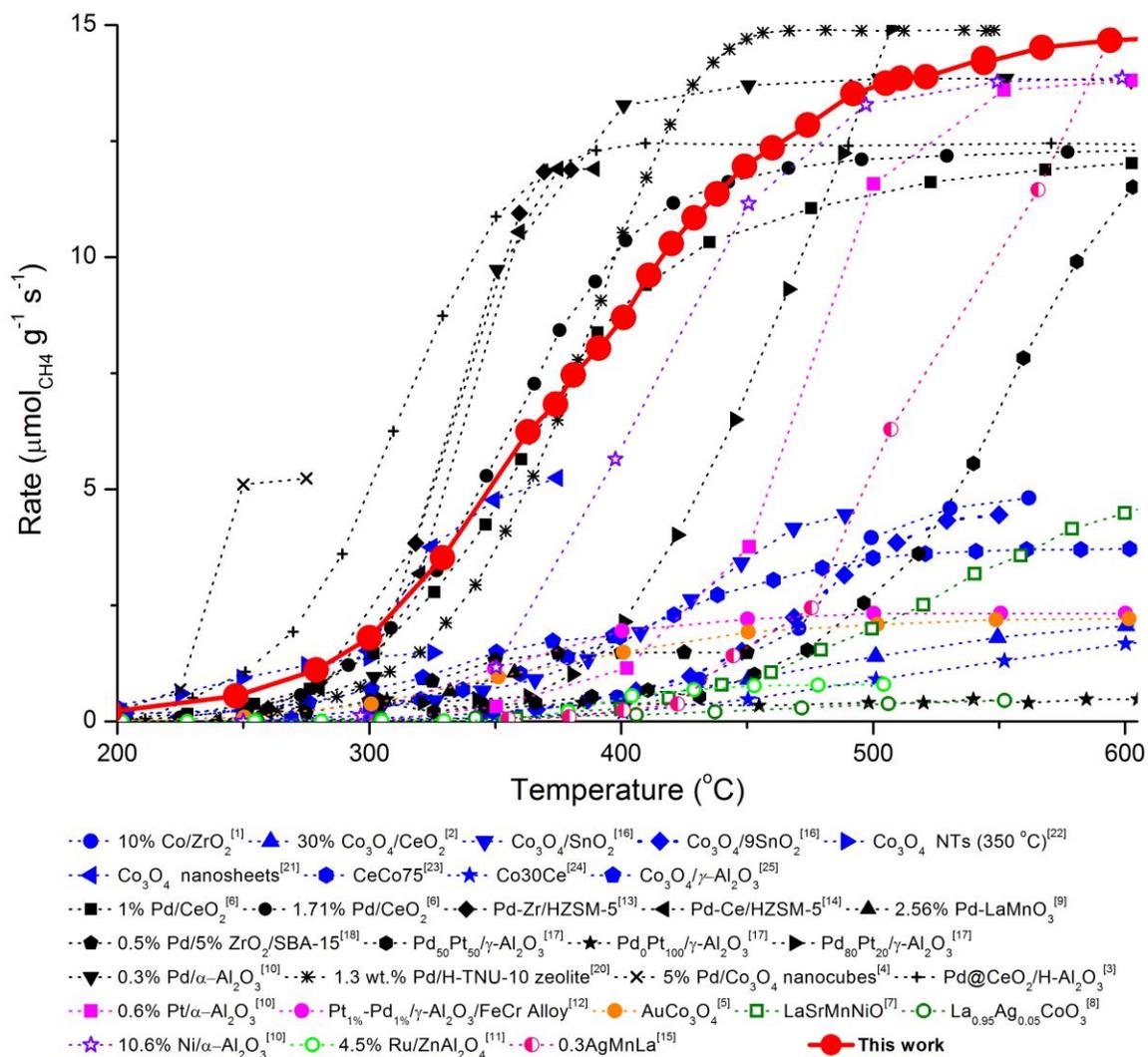
## Supplementary Information:



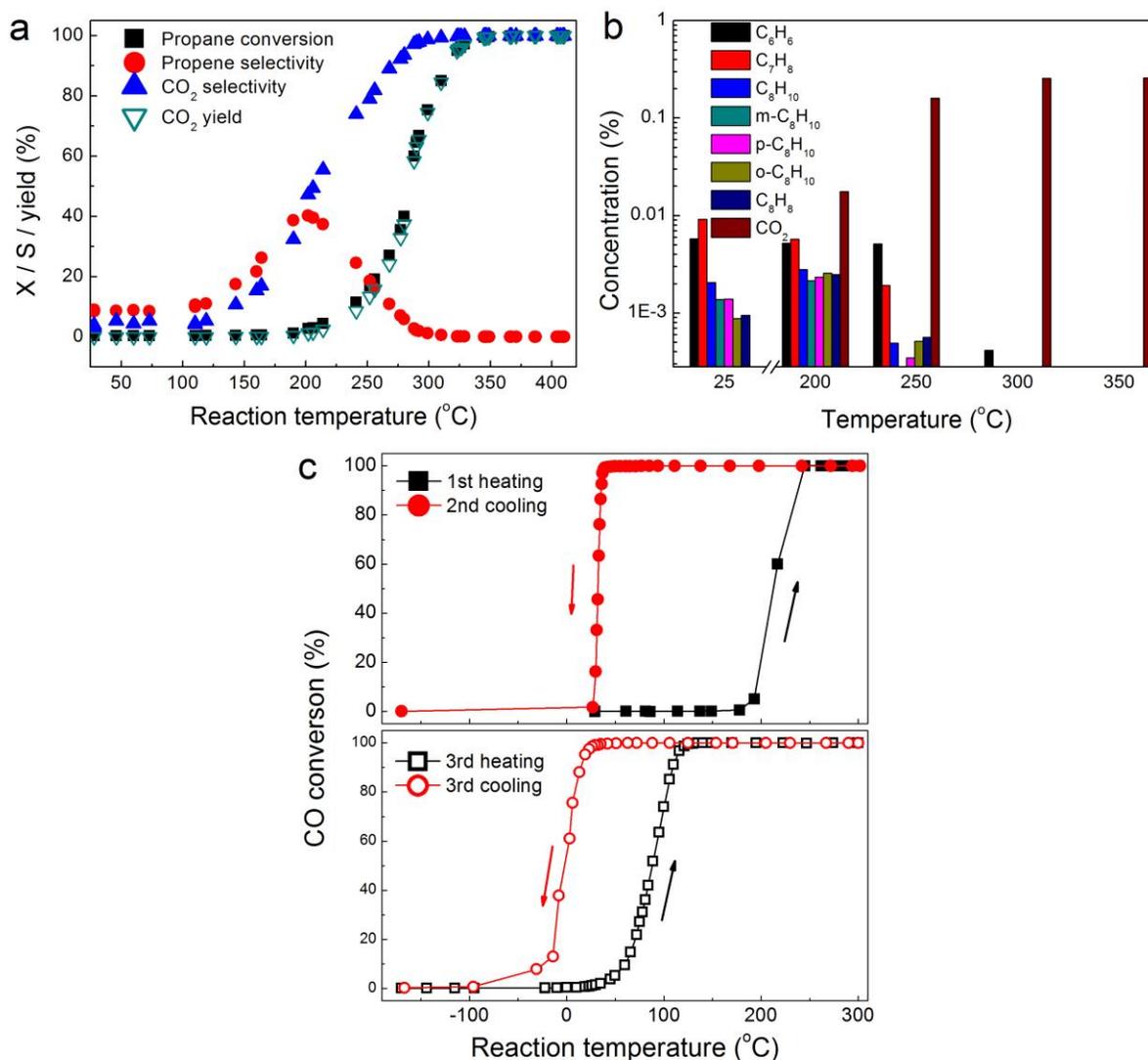
**Supplementary Figure 1. TEM images.** Co@C nanocapsules oxidized at (a, e) 300 °C and (b, f) 400 °C. Carbon-free Co nanoparticles oxidized at (c, g) 20 °C and (d, h) 450 °C. The carbon-free Co nanoparticles were synthesized by the same process without using ethanol. Scale bars, 5 nm (in a, b, e-g), 500 nm (in c), 50 nm (in d) and 2 nm (in h).



**Supplementary Figure 2. Powder XRD patterns of the fresh and reacted Co@C samples.** The curves of fresh and reacted samples were matched well with that of metallic cobalt (PDF 15-0806) and cobalt oxide (PDF 42-1467), respectively.



**Supplementary Figure 3. Catalytic performance comparison with references<sup>1-25</sup>.** The CH<sub>4</sub> reaction rates were calculated based on the total mass of these catalysts.



**Supplementary Figure 4. Catalytic performances in combustion of propane, aromatics and carbon monoxide.**

(a) Propane conversion (X), propene selectivity (S), CO<sub>2</sub> selectivity (S) and yield as a function of reaction temperature obtained from room temperature to 420 °C over 100 mg Co@C catalyst, 2.6% C<sub>3</sub>H<sub>8</sub> with excess oxygen.

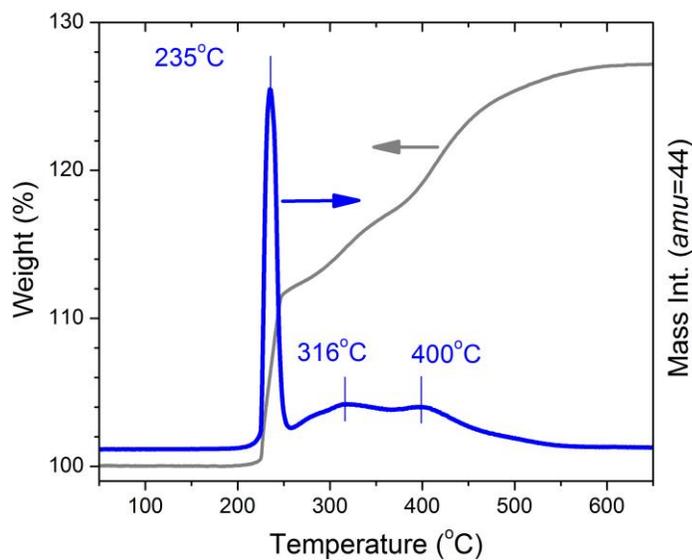
(b) Concentration of aromatic mixture and yielded CO<sub>2</sub> against the reaction temperature over 100 mg Co@C

catalyst with excess oxygen. (c) Heating and cooling light-off curves of CO oxidation against the reaction

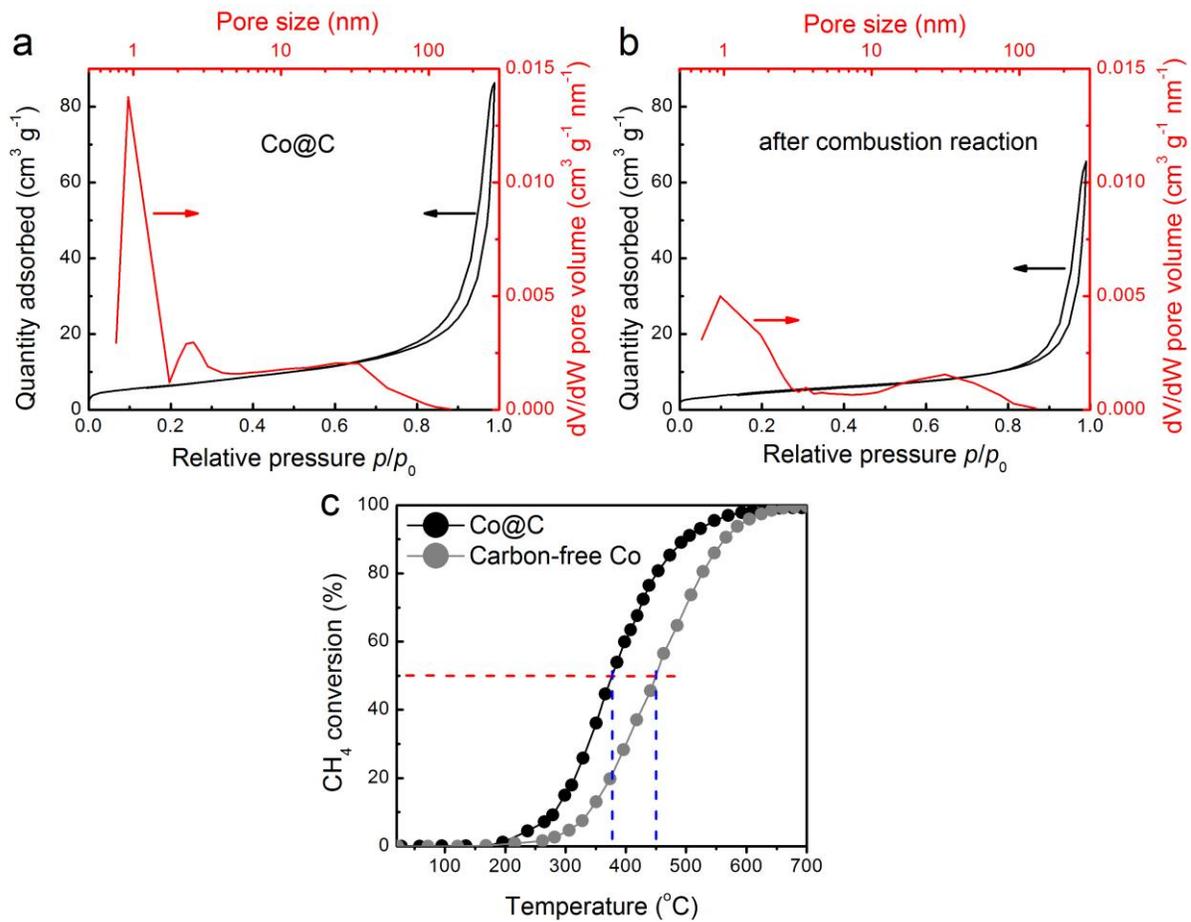
temperature over 100 mg Co@C with 1.24% CO and 3.10% O<sub>2</sub> in helium at the total GHSV of 12.2 L g<sup>-1</sup> h<sup>-1</sup>. We

note that the residual carbon shells may block the diffusion of reactant onto the active sites, resulting in an

underestimation of the catalytic activity.



**Supplementary Figure 5. Temperature-programmed oxidation of pristine Co@C sample in a flow of diluted oxygen.** The pristine nanocapsules showed the chemical and thermal stability at the low temperature below 200 °C. When the temperature elevated from 220 °C to 600 °C, a total weight gain of about 27 wt% on the TG curve arises with synchronous changes in escaping CO<sub>2</sub> MS signals.



**Supplementary Figure 6. Textural structure and catalytic performance of Co@C and carbon-free Co**

**nanoparticles.** N<sub>2</sub> physisorption results of Co@C samples (a) before and (b) after reaction. (c) Light-off curves of Co@C and carbon-free Co. We noted that the BET surface area and pore volume were 23.3 m<sup>2</sup> g<sup>-1</sup>, 0.134 mL g<sup>-1</sup> for the pristine Co@C and 17.5 m<sup>2</sup> g<sup>-1</sup>, 0.102 mL g<sup>-1</sup> for the used sample, respectively. The  $T_{50}$  values of catalytic combustion reaction were 376 °C and 450 °C, while the CH<sub>4</sub> conversion were 50% and 20.2% at 376 °C on Co@C and carbon-free Co catalysts, respectively.

**Supplementary Table 1. Comparison of TOF and kinetic parameters with references.**

Catalyst	TOF (s <sup>-1</sup> )	CH <sub>4</sub> reaction order	O <sub>2</sub> reaction order	Activation energy kJ mol <sup>-1</sup>	Reference
Co <sub>3</sub> O <sub>4</sub>	0.016 <sup>a</sup> (533K)	0.652	0.003	68±1	This work
Co(1.9)/ZrO <sub>2</sub>	—	—	—	108.68	26
Co(0.9)La/ZrO <sub>2</sub>	—	—	—	121.22	
Co–Mg/Al ternary hydrotalcites	—	—	—	86~134	27
aCoO <sub>3</sub> (a=La, Pr, Nd, and Gd)	—	—	—	98.6~110	28
ZrLaMn <sub>x</sub> (x=2,4,6,12,16)	—	0.79~0.82	—	85.2~100.9	29
LaMnO <sub>3</sub>	—	0.83	—	97.5	
Pt/γ-Al <sub>2</sub> O <sub>3</sub>	0.0015	—	—	67~138	30
Pd wire	5.4 (673K)	0.8	0.1	71.0	31
Pt wire	0.13 (773K)	1.0	-0.6	87.8	
Rh wire	0.52 (773K)	0.6	0	100	
0.038~1.0wt% Pd/Al <sub>2</sub> O <sub>3</sub>	0.024~0.31 (673K)	0.6~0.8	0~0.1	71~84	
0.22wt% Pt/Al <sub>2</sub> O <sub>3</sub>	0.048~0.14 (773K)	1.1~1.2	-0.6 ~ -0.5	100	
0.03~1.153wt% Rh/Al <sub>2</sub> O <sub>3</sub>	0.048~0.14 (773K)	0.4~0.5	0~0.1	92~96	
Pd(111)	2.8-2.9 (598K)	0.8	-0.1	140 ± 20	
Pd(100)	5.0-5.3 (598K)	0.8	0.1	125 ± 15	
Pd(110)	1.2-1.4 (598K)	0.7	0.2	160 ± 20	
2.7wt% Pd/γ-Al <sub>2</sub> O <sub>3</sub>	2.28 (623K)	1.0	0	84 ± 3 (<680 K); 23 ± 2 (>680 K)	33
3.3wt% Pd/γ-Al <sub>2</sub> O <sub>3</sub>	0.03-0.29 (473K)	0.95	0.86	78.6 ± 5.0	34
1.0~10.0wt% Pd/γ-Al <sub>2</sub> O <sub>3</sub>	—	1.0	0	76 (473-673K)	35
Pd/H-TNU-10	0.171 (673K)	0.6	0.0	78	20
Pd/H-ZSM-5(II)	0.109 (673K)	0.5	-0.2	84	
Pd/H-mordenite	0.075 (673K)	0.7	-0.1	77	
Pd/H-beta	0.068 (673K)	0.5	0.2	72	
Pd(1%)/CeO <sub>2</sub> (9%)/H-Al <sub>2</sub> O <sub>3</sub>	0.047	—	—	103 (493~543K)	
Pd(1%)/CeO <sub>2</sub> IWI	0.0013	—	—	90(493~543K)	
Pd(1%)/CeO <sub>2</sub> (9%)/Al <sub>2</sub> O <sub>3</sub> IMP	0.0015	—	—	120(523~563K)	
0.5~4.5wt% Ru/ZnAl <sub>2</sub> O <sub>4</sub>	0.006~0.010 (648K)	—	—	124~129	11

<sup>a</sup> The surface area of cobalt was measured by the CO chemisorption test according to Ref. 36. The density of active sites is 51.9 μmol<sub>Co</sub> g<sup>-1</sup>.

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