

Supplementary information

Gaseous CO and toluene co-oxidation over monolithic core-shell Co_3O_4 -based hetero-structured catalysts

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Experimental section

Material characterizations

X-ray powder diffraction (XRD) patterns of the monolithic samples were performed by using a Panalytical X'Pert PRO system with Cu-K α ($\lambda=1.5406\text{\AA}$) radiation operated at 40kV and 40mA. The data were collected with a scan rate of $10^\circ \text{ min}^{-1}$ within the range of scattering angle 2θ of 5 to 90° .

The size and morphology of samples were characterized by using field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F) with an acceleration voltage of 15 kV, 10 mM. The microstructures of the samples were characterized on a transmission electron microscope (TEM, JEOL JEM-2010F) at a voltage of 200 kV.

A Micromeritics ASAP2020 was used to measure the surface areas and pore size distribution of the samples at -196°C . Before the tests, the corresponding samples were degassed at 150°C for 6 h to remove physically adsorbed impurities.

The hydrogen temperature programmed reduction (H_2 -TPR) and oxygen temperature programmed desorption (O_2 -TPD) measurement was measured on an Automated Catalyst Characterization System (Autochem 2920, MICROMERITICS) equipped with a thermal conductivity detector (TCD). The corresponding samples ($1\text{ cm} \times 3\text{ cm} \times 1.6\text{ mm}$) was placed in a quartz reactor under a gas flow ($5\% \text{ H}_2/\text{Ar}$, 30 ml min^{-1}) with a constant rate of $10^\circ\text{C min}^{-1}$ up to 700°C . The temperature programmed desorption of O_2 (O_2 -TPD) with $1\text{ cm} \times 3\text{ cm} \times 1.6\text{ mm}$ catalysts was pre-heated in $5\% \text{ O}_2/\text{He}$ flow from room temperature to 300°C and held for 1h (30 mL min^{-1}), and then cooling to room temperature. The catalysts were heated from room temperature to 800°C at $10^\circ\text{C min}^{-1}$ in pure He (30 mL min^{-1}).

The Raman spectrum of the monolithic samples was performed on a Renishaw RM2000 Raman Spectrometer (laser wavelength = 532 nm) with a scan number of 10 from 100 to 900 cm^{-1} and a resolution of 1 cm^{-1} .

X-ray photoelectron spectroscopy (XPS) measurement was performed by using an XLESCALAB 250Xi electron spectrometer from VG Scientific with monochromatic Al K α (1486.6 eV) radiation, and the binding energy was calibrated based on the C 1s peaks at 284.8 eV .

The collected exhaust gas was detected by mass spectrometry (HPR-20 QIC, Benchtop Gas

Analysis System).

All of the operando diffuse reflectance infrared FT spectroscopy (DRIFTS) results were collected on an FTIR spectrometer (Nicolet IS50R FT-IR) equipped with a Harrick DRIFT cell and an MCT/A detector in the range of 650–8000 cm^{-1} with 32 scans at a resolution of 4 cm^{-1} using a KBr window. In a typical experiment, the powder samples were pre-treated in pure N_2 (100 mL min^{-1}) at 300 °C for 1 h to remove the residuals. After cooled down to 35 °C, and a background spectrum was collected at 4 cm^{-1} resolution for 32 scans in N_2 atmosphere. Then, the reactant gas (1 vol. % CO or 500 ppm toluene) was continuously introduced into the in-situ reaction chamber. The DRIFTS spectra (4000–650 cm^{-1}) were collected and continuously recorded for 1 h to realize the adsorption equilibrium.

Catalytic activity measurements

Catalytic activities over each monolithic sample for 1.0 vol.% CO or 1000 ppm toluene combustion reaction were carried out using a fixed-bed quartz tubular micro-reactor ($\phi = 6$ mm) with quartz wool packed at both ends of the catalyst bed, and gas hour space velocity (GHSV = 10,000 h^{-1}) was controlled by adjusting the gas volume ratio. The CO/toluene balanced with air (20 vol.% O_2 + balance N_2) was purged into the reactor at a certain flow rate (100 mL min^{-1}). After reacted at the final temperature for 1 h, the concentrations of reactants and products were analyzed on-line by a gas chromatograph (Shimadzu GC-2014) equipped with thermal conductivity detector (FID).

To investigate the effect of water vapor on the catalytic activity, the on-stream CO or toluene oxidation experiment was carried out in the presence and absence of 1.0 or 5.0 vol% water vapor.

Typically, an air flow containing gaseous CO/toluene was used for bubbling through water in a 250 mL conical flask at 50 °C to give a water vapor amount of 1.0 or 5.0 vol.%, and CO/toluene was used for catalytic testing.

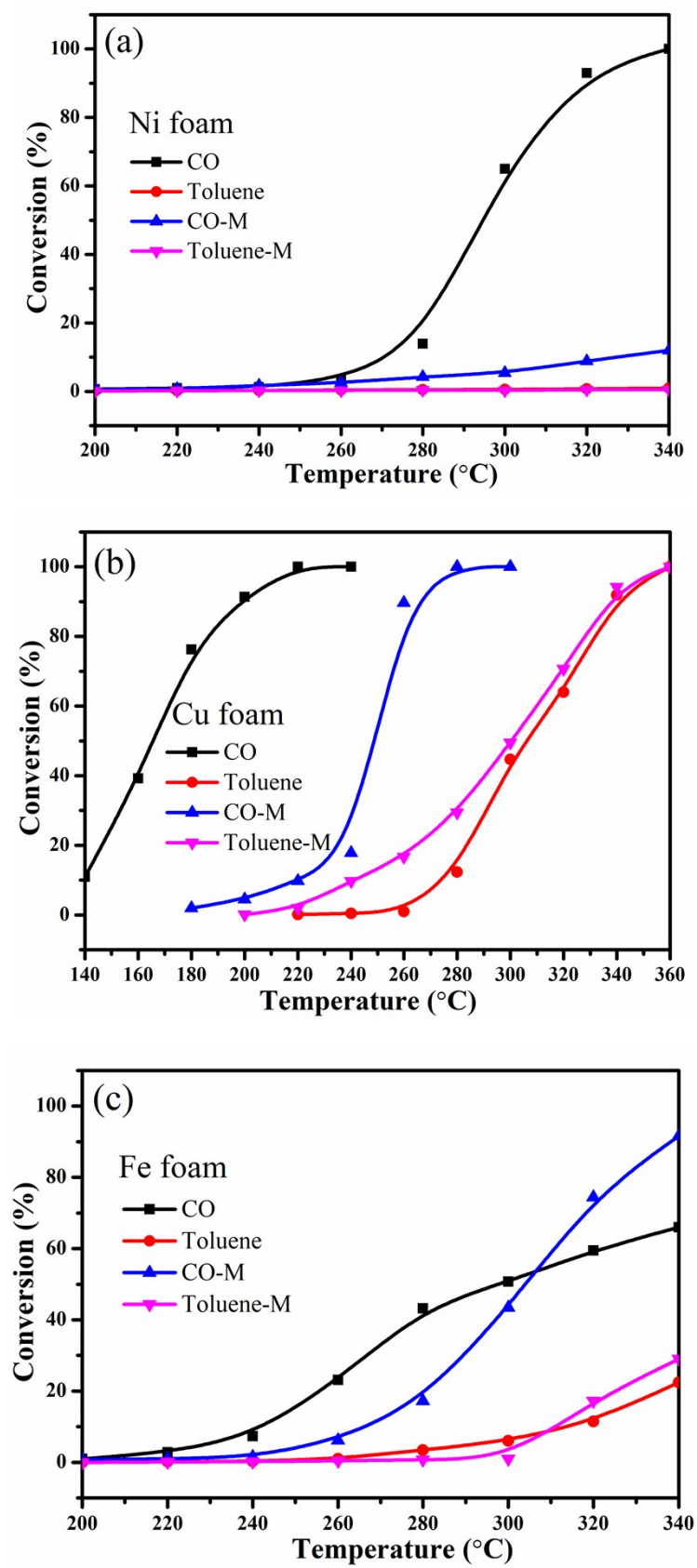


Fig. S1 The catalytic behaviors for CO/toluene oxidation over metal substrates (Ni foam, Fe foam and Cu foam). Simple conditions: 1.0% CO or 1000 ppm toluene balanced with air; Mixture conditions: 1.0 vol.% CO and 1000 ppm toluene balanced with air. All the reactions were kept at

GHSV= 10,000 h⁻¹.

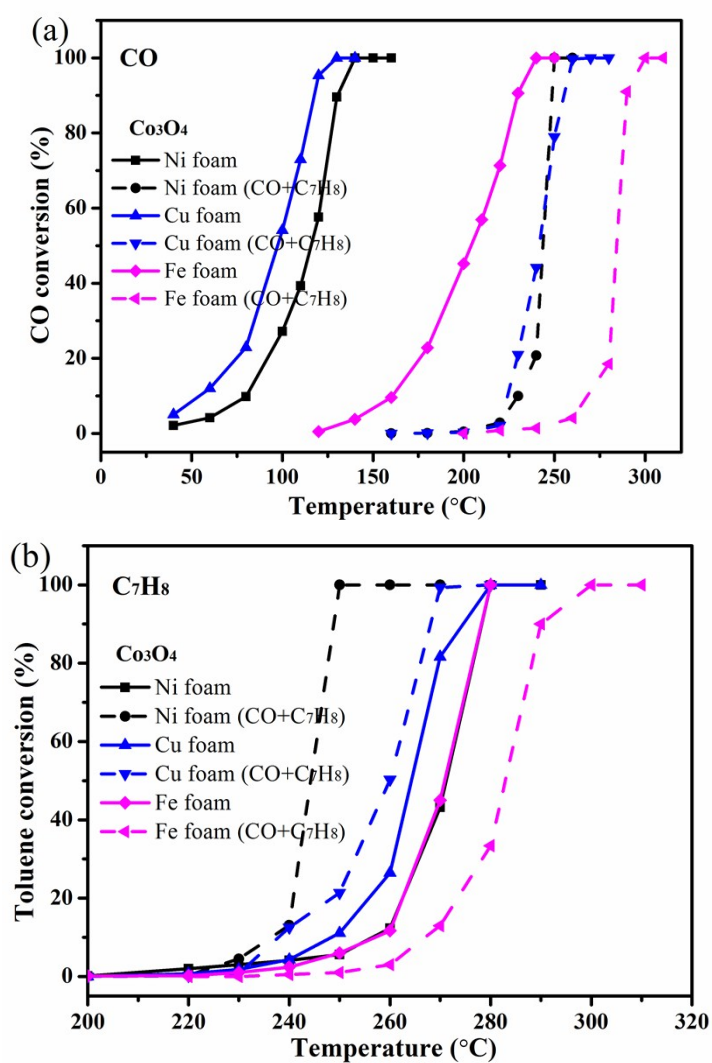


Fig. S2 (a) CO conversion and (b) toluene conversion curves in different atmospheres over the Co₃O₄ samples in-situ grown on different metal substrates as a function of temperature. Simple conditions: 1.0 vol.% CO or 1000 ppm toluene balanced with air; Mixture conditions: 1.0 vol.% CO and 1000 ppm toluene balanced with air. All the reactions were kept at GHSV= 10,000 h⁻¹.

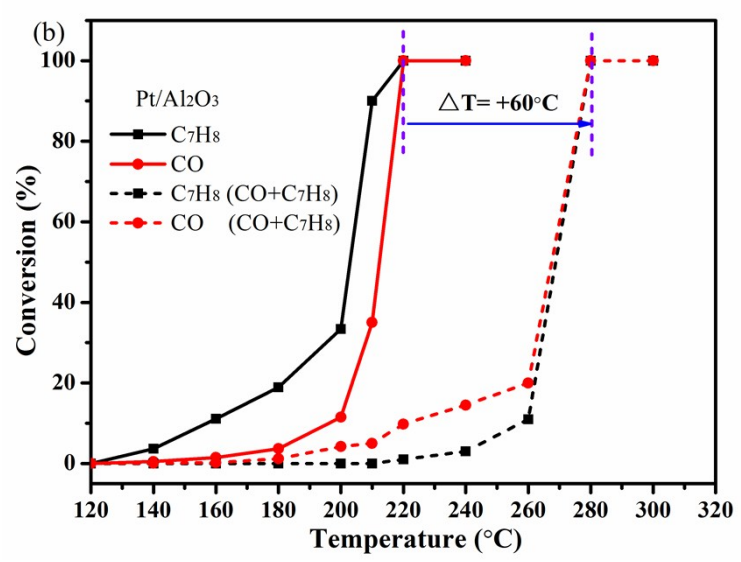
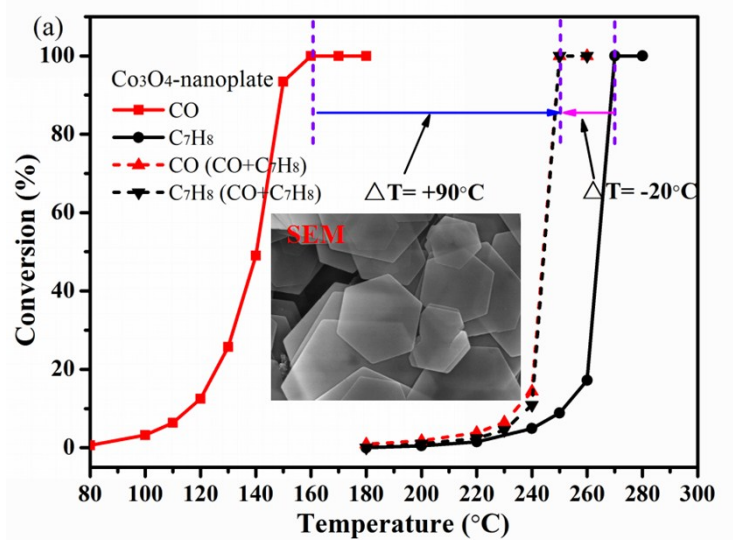


Fig. S3 Different pollutants conversion in different atmospheres over the powder (a) Co_3O_4 -nanoplate and (b) $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts as a function of temperature. Simple conditions: 1.0 vol.% CO or 1000 ppm toluene balanced with air; Mixture conditions: 1.0 vol.% CO and 1000 ppm toluene balanced with air. All the reactions were kept at $\text{WHSV} = 60,000 \text{ mL g}^{-1} \text{ h}^{-1}$.

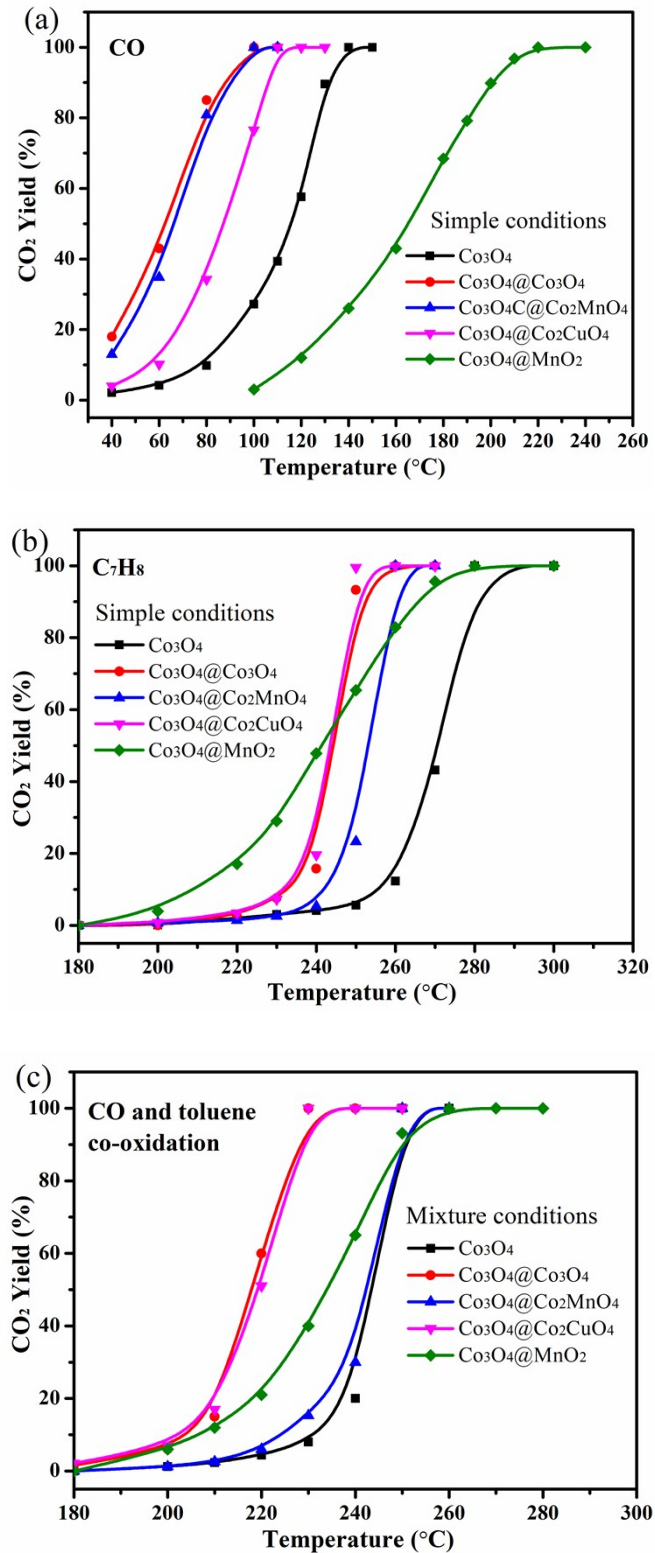


Fig. S4 The CO₂ yield curves of (a) CO oxidation, (b) toluene oxidation, and (c) CO-toluene co-oxidation over the monolithic Co₃O₄-based NA catalysts, respectively. Simple conditions: 1.0 vol.% CO or 1000 ppm toluene balanced with air; Mixture conditions: 1.0 vol.% CO and 1000 ppm toluene balanced with air. All the reactions were kept at GHSV= 10,000 h⁻¹.

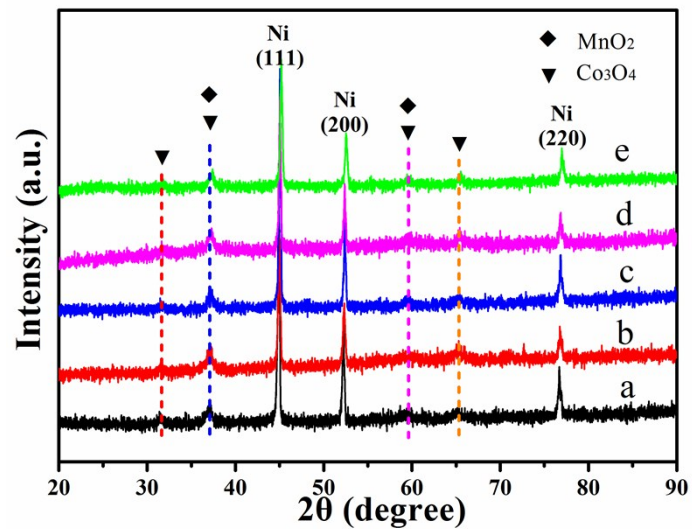


Fig. S5 XRD patterns of the hetero-structured NA samples in-situ grown on Ni foam, labels a–e corresponded to Co_3O_4 , $\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4$, $\text{Co}_3\text{O}_4@\text{Co}_2\text{MnO}_4$, $\text{Co}_3\text{O}_4@\text{Co}_2\text{CuO}_4$, and $\text{Co}_3\text{O}_4@\text{MnO}_2$, respectively.

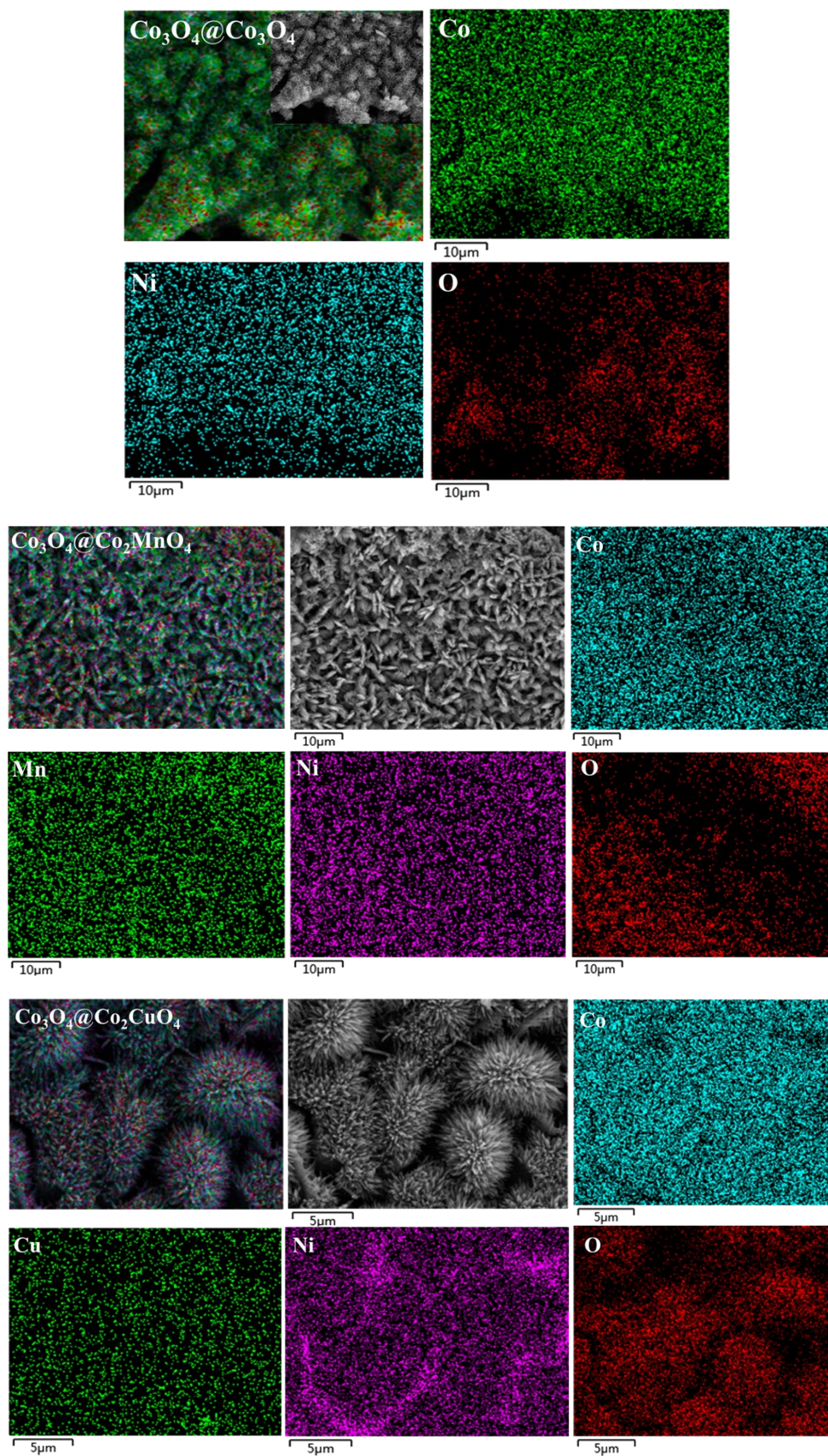


Fig. S6 EDS analysis and elemental mapping of $\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4$, $\text{Co}_3\text{O}_4@\text{Co}_2\text{MnO}_4$ and $\text{Co}_3\text{O}_4@\text{Co}_2\text{CuO}_4$ samples.

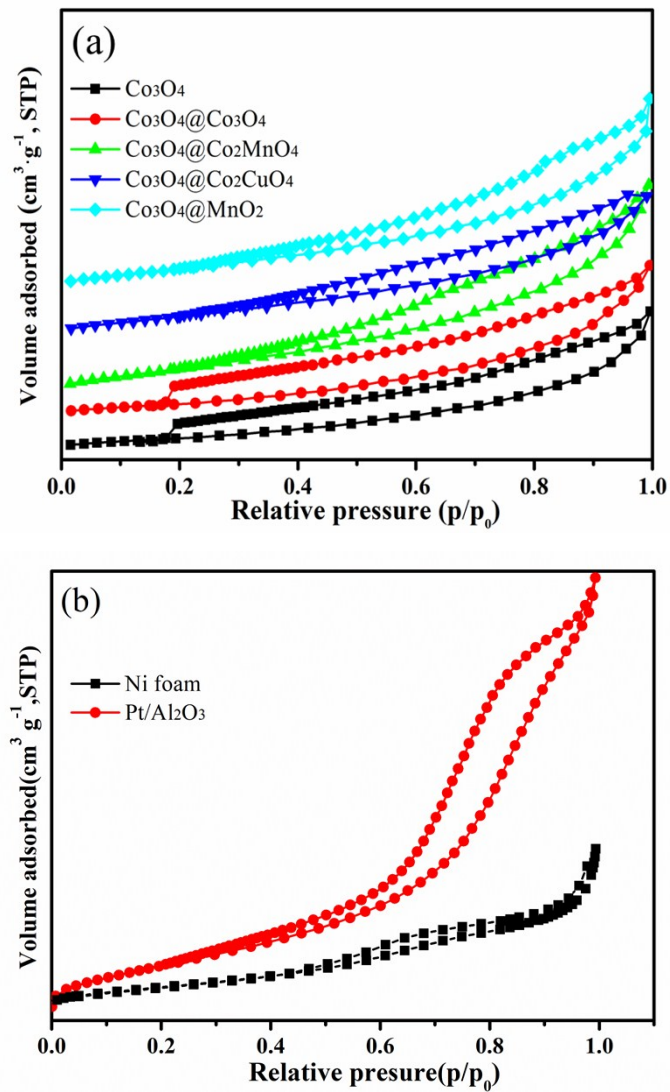


Fig. S7 N_2 adsorption/desorption isotherms of all the samples.

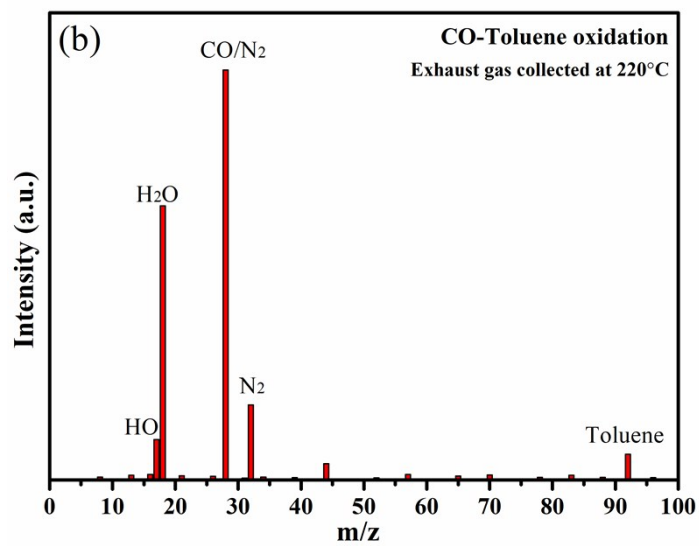
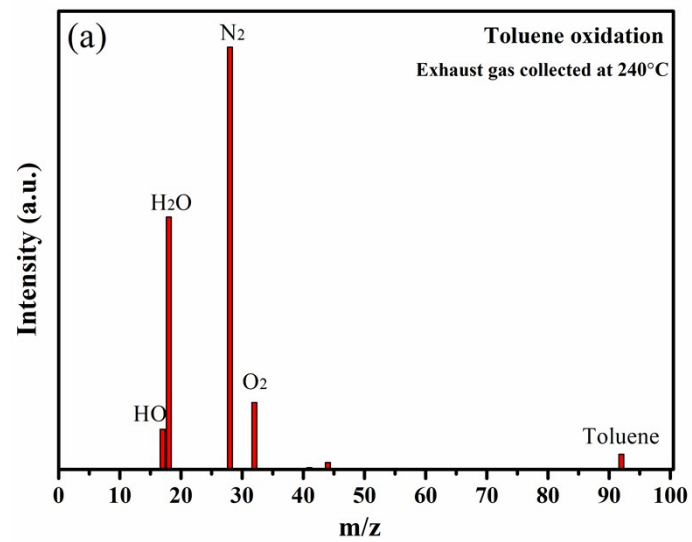


Fig. S8 Mass spectra of exhaust gas collected at different conditions over $\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4$ catalyst.

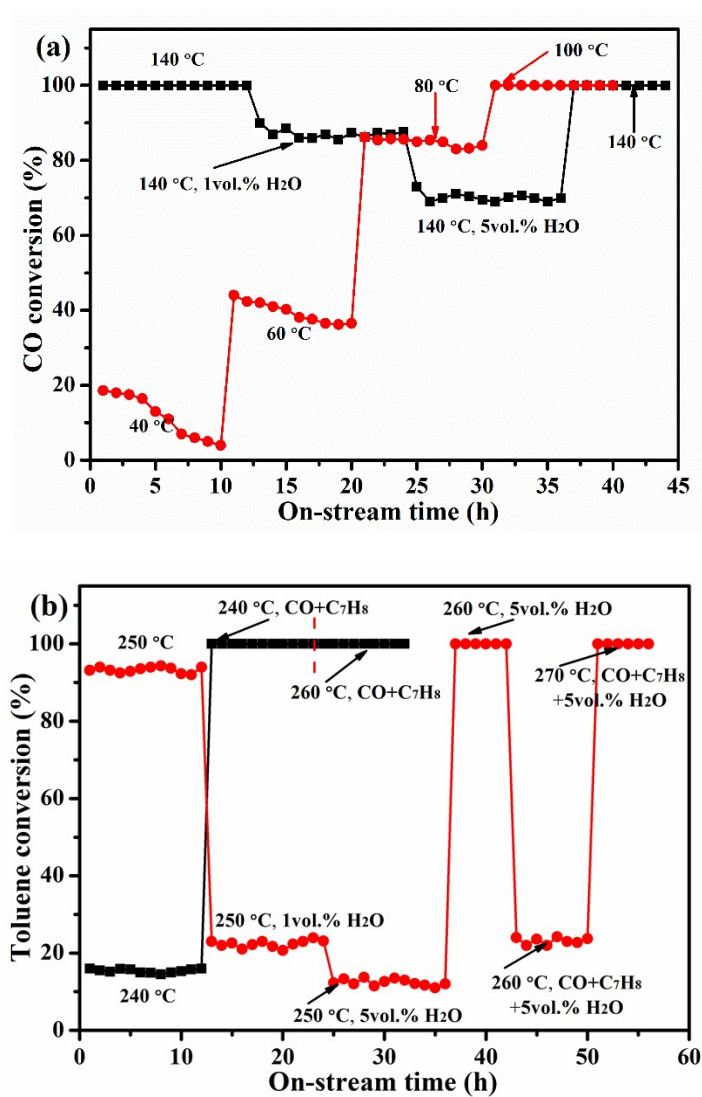


Fig. S9 (a) CO conversion and (b) toluene conversion curves at different reaction conditions over the $\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4$ catalyst as a function of time. All the reactions were kept at $\text{GHSV} = 10,000 \text{ h}^{-1}$.

Table S1 Catalytic performances of as-synthesized catalysts for CO and/or toluene oxidation in

different atmospheres.

Samples	Simple conditions				Mixture conditions			
	CO		toluene		CO		toluene	
	T ₅₀ /°C	T ₉₉ /°C	T ₅₀ /°C	T ₉₉ /°C	T ₅₀ /°C	T ₉₉ /°C	T ₅₀ /°C	T ₉₉ /°C
Co ₃ O ₄	115	140	273	280	245	250	246	250
Co ₃ O ₄ @Co ₃ O ₄	64	100	243	260	216	230	217	230
Co ₃ O ₄ @Co ₂ MnO ₄	70	100	254	260	245	250	246	250
Co ₃ O ₄ @Co ₂ CuO ₄	90	110	244	250	218	230	223	240
Co ₃ O ₄ @MnO ₂	170	230	242	280	225	260	240	280
Pt/Al ₂ O ₃	213	220	206	220	270	280	272	280

Table S2 Physical and Chemical parameters of all the samples.

Samples	Mass loadings of per unit area (mg cm ⁻²)	S _{BET} (m ² g ⁻¹)	V _{pore} (cm ³ g ⁻¹)	Co ³⁺ /Co ²⁺	O _α	O _β	O _γ
					%	%	%
Co ₃ O ₄	2.586	27.49	0.131	1.85	54.21	21.65	22.28
Co ₃ O ₄ @Co ₃ O ₄	3.356	60.92	0.204	2.36	46.02	29.76	23.5
Co ₃ O ₄ @Co ₂ MnO ₄	3.394	48.88	0.144	2.19	50.47	29.15	20.37
Co ₃ O ₄ @Co ₂ CuO ₄	3.271	31.38	0.151	2.32	48.16	29.56	22.28
Co ₃ O ₄ @MnO ₂	3.374	51.82	0.137	1.86	71.35	12.18	16.47
Pt/Al ₂ O ₃	—	259.91	0.934	—	—	—	—
Ni foam	—	21.65	0.059	—	—	—	—

Table S3 Catalytic performances of CO and/or toluene oxidation over $\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4$ and $\text{Co}_3\text{O}_4@\text{Co}_2\text{MnO}_4$ catalysts at different atmospheres.

Samples	moisture	Simple conditions			
		CO		toluene	
		$T_{50}/^\circ\text{C}$	$T_{99}/^\circ\text{C}$	$T_{50}/^\circ\text{C}$	$T_{99}/^\circ\text{C}$
$\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4$	Dry	64	100	243	260
	1 vol.%	113	140	255	260
	5 vol.%	118	150	265	270
$\text{Co}_3\text{O}_4@\text{Co}_2\text{MnO}_4$	Dry	70	100	254	260
	1 vol.%	130	170	257	270
	5 vol.%	137	180	260	270

Table S4 Catalytic performances of as-synthesized Co_3O_4 -based catalysts for CO and toluene co-oxidation in different moisture.

Samples	1.0 vol.% H_2O				5.0 vol.% H_2O			
	CO		toluene		CO		toluene	
	$T_{50}/^\circ\text{C}$	$T_{99}/^\circ\text{C}$	$T_{50}/^\circ\text{C}$	$T_{99}/^\circ\text{C}$	$T_{50}/^\circ\text{C}$	$T_{99}/^\circ\text{C}$	$T_{50}/^\circ\text{C}$	$T_{99}/^\circ\text{C}$
Co_3O_4	272	280	273	280	275	280	274	280
$\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4$	253	260	253	260	256	270	263	270
$\text{Co}_3\text{O}_4@\text{Co}_2\text{MnO}_4$	264	270	258	270	265	270	263	270
$\text{Co}_3\text{O}_4@\text{Co}_2\text{CuO}_4$	262	270	263	280	263	280	263	280
$\text{Co}_3\text{O}_4@\text{MnO}_2$	234	280	250	290	240	280	255	290