Supplementary Information

Trace doping of cobalt oxide using lanthanum for effective catalytic oxidation of carbon monoxide

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Material characterization

The morphology of materials was determined using a Quanta 250 FEG field-emission scanning electron microscope (FEI Co., USA). The XRD patterns of the samples were obtained on an D/max-RA powder diffraction meter (Rigaku Co., Japan), operating with Cu Kα radiation (40 kV, 40 mA). Surface areas of the catalysts were obtained using N_2 adsorption–desorption isotherms at −196 °C on a Micromeritics ASAP 2020 instrument (Micromeritics Instrument Corp., Norcross, USA). The contents of La in catalysts were determined by were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, J-A1100, Jarrell-Ash, Franklin, MA). The XPS of the catalysts was conducted on a ESCALAB 250 X-ray Photoelectron Spectroscopy (Thermo, Co., USA) equipped with a monochromatized Al $K\alpha$ excitation source (hv = 1486.6 eV). H_2 temperature-programmed reduction (H_2-TPR) were performed with an AutochemII 2920 Chemisorption Apparatus (Micrometric Co., USA). The samples were pretreated under N_2 flow at 110 °C for 1h and cooled down to room temperature. The temperature was elevated to 700 °C from room temperature at a heating rate of 10 °C/min under 10 vol.% H_2/Ar flow.

CO oxidation activity experiment

Prior to the oxidation experiment, 20 mg catalyst was tableted and screened by a 40-mesh sieve. Then, the catalyst was immobilized in a quartz tube with quartz wool. The reaction temperature was measured by a thermocouple. The catalyst was pretreated under N_2 flow (20 mL/min) at 100°C for 1 h with a heating rate of 5°C/min. After cooling down to room temperature, the background value was collected. The CO oxidation experiment under dry conditions was conducted at a flow rate of 100 mL/min, with a feed gas consisting of 1 vol.% CO, 10 vol.% O_2, and N_2 balance. For the CO oxidation experiment under wet conditions, the feed gas was changed by the addition of 3 vol.% water vapor. The quartz tube was maintained at each preset temperature to obtain a steady state, and the CO concentration was determined by an IR spectrometer (Thermo Scientific Nicolet iS10, USA).

In situ CO catalytic oxidation experiment

To further clarify the catalytic performance of the catalysts, we conducted in situ CO catalytic oxidation experiments using DRIFT. The catalyst was pretreated under N_2 flow at 100°C with a heating rate of 5°C/min for 1 h. Under dry conditions, the catalyst was exposed to a feed gas consisting of 1 vol.% CO and 10 vol.% O_2 balanced with N_2 at different temperatures for 10 min, and the IR spectrum was obtained. Under wet condition, the feed gas composition was varied by the addition of 3 vol.% water vapor.

Catalyst stability experiment

The stability and activity of different catalysts under dry and wet conditions were investigated at 150°C for 15 h.
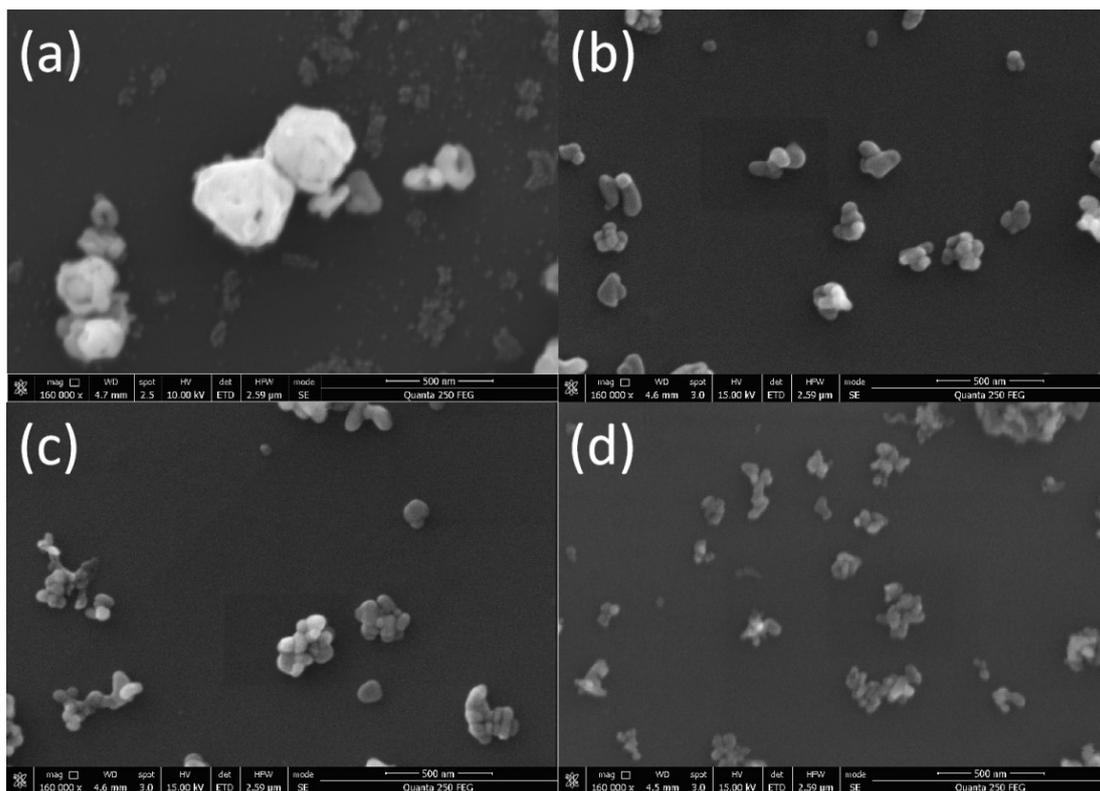
Fig. S1 SEM images of Co$_3$O$_4$ (a), La-Co$_3$O$_4$(IM) (b), La-Co$_3$O$_4$(CP) (c) and 2%La-Co$_3$O$_4$ (d) catalysts
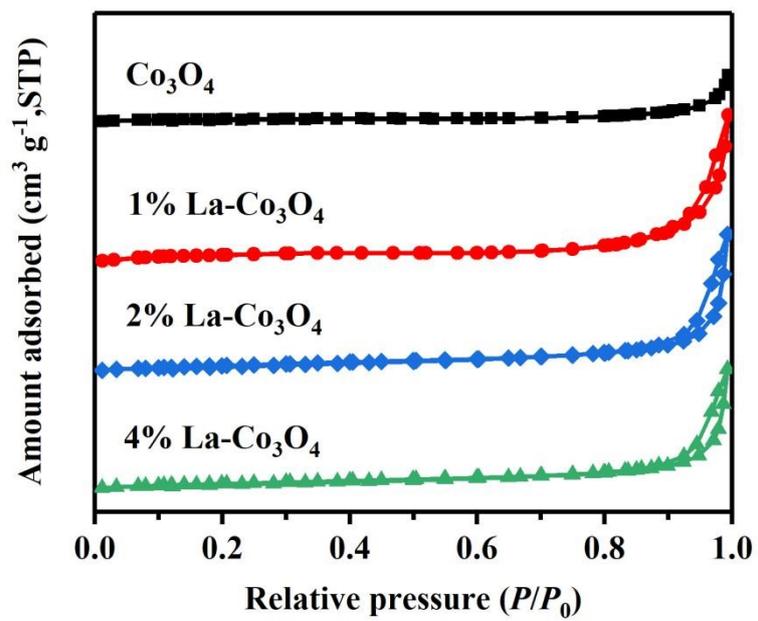
Fig. S2 N$_2$ adsorption-desorption curve of Co$_3$O$_4$ and x%La-Co$_3$O$_4$ catalysts

Table S1 The amounts of H_2 consumption of samples from H_2-TPR experiments

Samples	Total H_2 consumption (mmol/g)
Co_3O_4	1.59
1%La-Co_3O_4	2.90
2%La-Co_3O_4	3.03
4%La-Co_3O_4	2.89
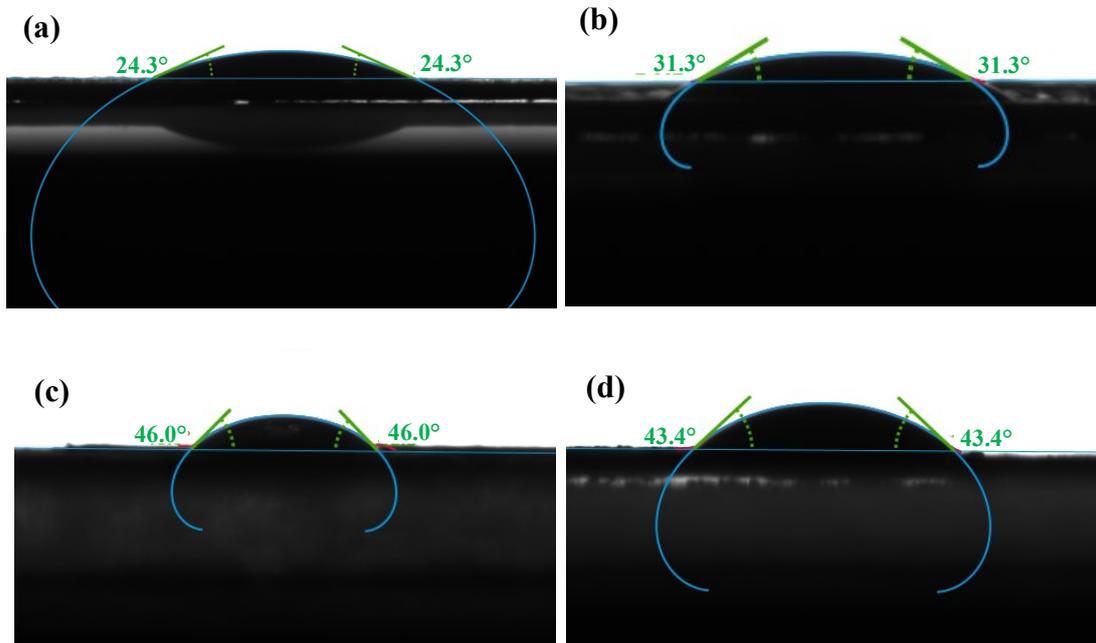
Fig. S3 Water contact angle of Co_3O_4 (a), 1%La-Co_3O_4 (b), 2%La-Co_3O_4 (c) and 4%La-Co_3O_4 (d)
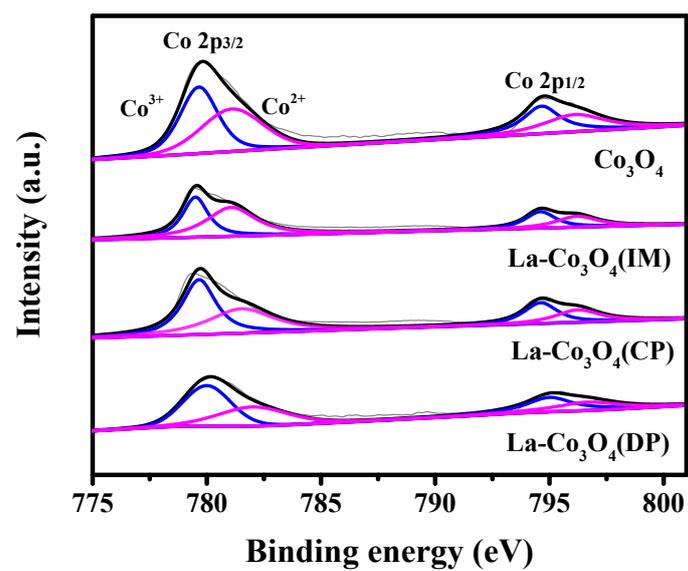
Fig. S4 Co 2p XPS spectra of Co_3O_4 Co_3O_4 and La-doped Co_3O_4 prepared by different synthesis methods

Table S2 Co^{3+}/Co^{2+} ratios in Co_3O_4 and La-doped Co_3O_4 prepared by different synthesis methods

Samples	Co^{3+}/Co^{2+}
Co_3O_4	1.06
La-Co_3O_4(IM)	0.82
La-Co_3O_4(CP)	1.19
La-Co_3O_4(DP)	1.33

Table S3 Comparison of catalytic performance of various catalysts

Catalysts	GHSV (mL g^{-1} h^{-1})	Dry condition		Wet condition		Ref.
		T_{50}	T_{100}	T_{50}	T_{100}	
2%La-Co$_3$O$_4$	120 000	105	130	145	165	This work
Mn-doped Co$_3$O$_4$ spheres	150 000	143	182			1
Co$_{0.50}$Sn$_{0.50}$	18 000	125	150			2
N-Co$_3$O$_4$	30 000	83	125		130	3
A-N-Co$_3$O$_4$	30 000	127	160		180	3
CuO$_x$/Co$_3$O$_4$	60 000	80	110			4
AtCo	60 000	100	120	123	150	5
Co$_3$O$_4$/C-400	40 000	182	195			6
Co$_3$O$_4$-MOF	40 000	142	155			6
Co$_3$O$_4$-CeO$_2$	15 000	128	170			7
20% La-Co$_3$O$_4$	120 000	98	150	117	165	8

The Arrhenius equation presented as follows:

$$\ln r_{CO} = \frac{-E_a}{RT} + n\ln[CO]_{in} + \ln A \tag{1}$$

where r_{CO} is the CO oxidation rate constant, A is the pre-exponential factor, R and T are the universal gas constant and the absolute temperature (K), n is the apparent reaction constant of CO oxidation, respectively. To make a general comparison of E_a values for different catalysts, the reaction temperature was varied to keep the conversion of CO at a relatively low level (less than 20%).

The rate constant was obtained as follows:

$$r_{CO} = \frac{[CO]_{in} \cdot Q \cdot \alpha}{m_{cat}} \tag{2}$$

Where Q is flow velocity (m³/s), m_{cat} is the catalyst mass (g).

$$\alpha = \frac{([CO]_{in} - [CO]_{out}]}{[CO]_{in}} \times 100\% \tag{3}$$
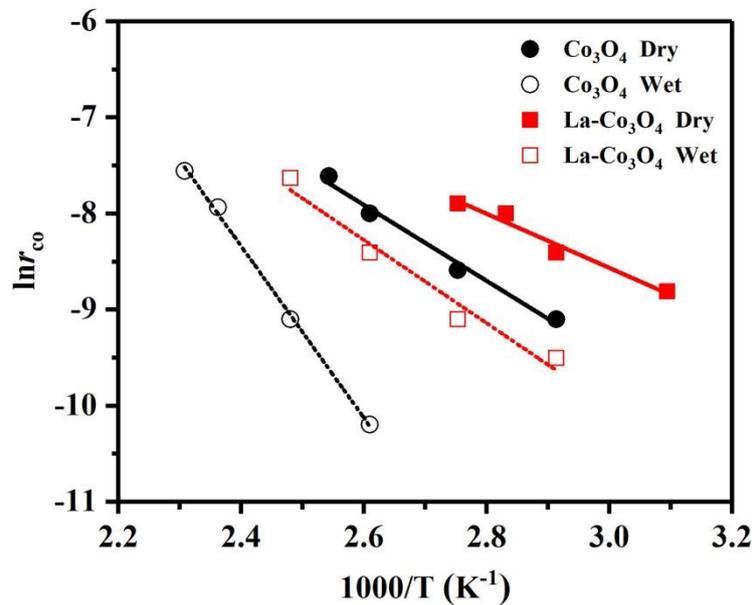
Fig. S5 Arrhenius plots for CO oxidation on Co₃O₄ and 2%La-Co₃O₄ catalysts
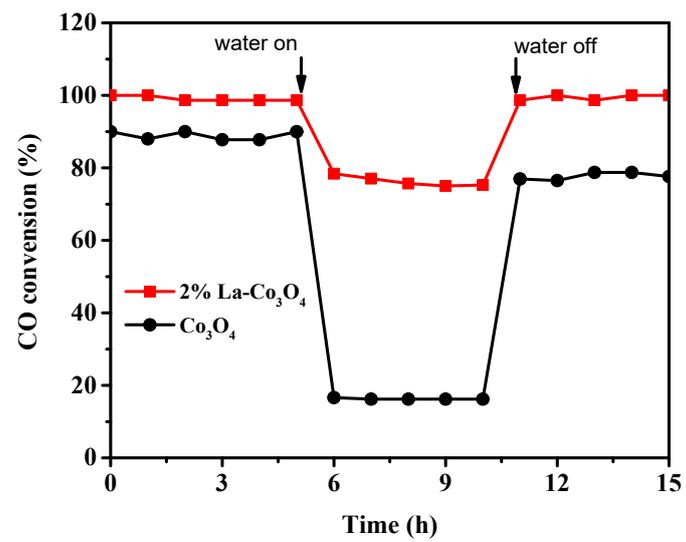
Fig. S6 Long-term catalytic stability test on 2%La-Co_3O_4 and Co_3O_4 at 150 °C.

References

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