

## Supplementary Information

### **Surface Ni-O-Co Sites in Cube-Shaped Ni-Co<sub>3</sub>O<sub>4</sub> Spinel Oxides for Boosting Soot Oxidation**

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## Methods

### Chemicals

Cobalt(II) nitrate hexahydrate  $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , nickel(II) nitrate hexahydrate  $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$  and sodium hydroxide  $[\text{NaOH}]$  purchased from Aladdin Ltd. (Shanghai, China), were used as received without further purification.

### Catalyst preparation

#### Preparation of cube-shaped $\text{Co}_3\text{O}_4$ .

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 10 mL of deionized water to yield a precursor solution with a metal cation concentration of 2 mol/L.  $\text{NaOH}$  was dissolved in 10 mL of deionized water to yield a solution with a metal cation concentration of 2 mol/L. The solution of  $\text{NaOH}$  was slowly added dropwise to the precursor solution and stirred continuously for 40 minutes to form a slurry. The slurry was transformed into a Teflon-lined stainless-steel autoclave and hydrothermally treated at 180 °C for 12 h to obtain black precursor. After being cooled to room temperature, the obtained precipitate was collected by centrifugation and washed with deionized water and ethanol, and then dried overnight at 50 °C. The black precursor was annealed at 500 °C for 4 hours in air to obtain cube-shaped  $\text{Co}_3\text{O}_4$ .

**Preparation of  $\text{Ni}_x\text{-Co}_3\text{O}_4$  catalysts.** Different quantities of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in deionized water to prepare solutions with Ni ion concentrations of 0.5, 1.0, and 2.0 mol  $\text{L}^{-1}$ . The black precursor of 0.1g was annealed at 500 °C in a muffle furnace. After annealing for 3 hours, the precursor is removed from the furnace and immediately quenched by pouring it into 50 mL pre-prepared Ni solutions of 0 (deionized water), 0.5, 1.0, and 2.0 mol  $\text{L}^{-1}$  to obtain water- $\text{Co}_3\text{O}_4$ ,  $\text{Ni}_{0.5}\text{-Co}_3\text{O}_4$ ,  $\text{Ni}_{1.0}\text{-Co}_3\text{O}_4$  and  $\text{Ni}_{2.0}\text{-Co}_3\text{O}_4$  catalysts respectively.

### Characterizations

Powder X-ray diffraction (XRD) patterns were obtained by a diffractometer (Bruker D8

advance) over the  $2\theta$  range from 5 to  $90^\circ$  with a  $5^\circ \text{ min}^{-1}$  scanning rate using Cu-K $\alpha$  radiation to obtain the phase structure of all as-prepared catalysts. The Ni/Co content of catalysts was measured by using inductively coupled plasma optical emission spectrometry (ICP-OES). Scanning electron microscopy (SEM), images were obtained by Quanta 200F. Transmission electron microscope (TEM) and mapping images were obtained by FEI Tecnai G2 F20 transmission electron microscope. Raman spectra of all catalysts were measured on an inVia Reflex-Renishaw spectrometer with an excitation wave-length of 532 nm. The temperature programmed reduction of hydrogen ( $\text{H}_2$ -TPR) was carried out on an Automatic Chemisorption Analyzer. The catalysts were pretreated with  $\text{N}_2$  at  $350^\circ\text{C}$  for 30 min before test. After cooling to room temperature,  $\text{H}_2$ -TPR was conducted with flowed the gaseous contained  $\text{H}_2$  (7 vol%) balanced with  $\text{N}_2$  ( $30 \text{ mL min}^{-1}$ ). And the temperature range of the  $\text{H}_2$ -TPR is 50 to  $900^\circ\text{C}$  with a ramp rate of  $10^\circ\text{C min}^{-1}$ . The temperature-programmed oxidation of NO (NO-TPO) was carried out on a fixed-bed tubular quartz reactor, and the products can be detected by online FT-IR. The catalysts were pretreated with  $\text{N}_2$  at  $100^\circ\text{C}$  for 30 min before test. After cooling to room temperature, NO-TPO was conducted with flowed the gaseous contained  $\text{O}_2$  (5 vol%) and NO (0.1 vol%) balanced with  $\text{N}_2$  ( $50 \text{ mL min}^{-1}$ ). And the temperature range of the NO-TPO reaction is 50 to  $500^\circ\text{C}$  with a ramp rate of  $2^\circ\text{C min}^{-1}$ . Temperature-programmed desorption of  $\text{O}_2$  ( $\text{O}_2$ -TPD) measurements were conducted on a fixed bed and the desorption signal of oxygen was recorded with an online mass spectrometer apparatus (HIDEN DECRA). 0.1 g fresh catalyst was put into a quartz tube reactor and pretreated in an Ar flow with a flow rate of  $50 \text{ mL min}^{-1}$  for 30 min at  $300^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ . After cooling to room temperature, the catalyst was exposed to high-purity  $\text{O}_2$  with  $50 \text{ mL min}^{-1}$  for 30 min. Then, the stream was switched to Ar to purge for 1 h. Finally, the heating rate was set to be  $10^\circ\text{C min}^{-1}$  with a  $50 \text{ mL min}^{-1}$  Ar flow. Temperature programmed surface reaction of CO (CO-TPSR) was performed on a fixed-bed tubular quartz microreactor. 0.1 g catalyst was pretreated with

pure oxygen at 350 °C for 30 min. After being cooled to ambient temperature under pure argon, a 10 vol% CO/Ar gas stream was introduced (50 mL min<sup>-1</sup>). The temperature was increased from room temperature to 900 °C with a heating rate of 10 °C min<sup>-1</sup>. The outlet gases were monitored with an online mass spectrometer apparatus (HIDEN DECRA). The CO<sub>2</sub> signal (*m/z* = 44) and CO signal (*m/z* = 28) were monitored during the surface reaction without gaseous oxygen supply. The surface element valence state was detected by X-ray photoelectron spectra (XPS, XPSPHI-1600 ESCA spectrometer), calibrated using a C 1*s* binding energy of 284.8 eV. *In situ* diffuse reflectance infrared Fourier transforms (*in situ* DRIFT) spectra were carried on a Bruker FT-IR spectrometer (TENSOR II) equipped with a liquid nitrogen-cooling mercury-cadmium-telluride (MCT) detector. The catalyst was added into high-temperature IR cell with ZnSe window, and heated in N<sub>2</sub> flow at 200 °C for 30min to remove adsorbed H<sub>2</sub>O and other materials. After cooling down to 50 °C with N<sub>2</sub> atmosphere, the background spectrum was recorded. Finally, the gas to be measured were fed into cell at a flow rate of 50 mL min<sup>-1</sup>. IR spectra of simultaneous NO and CH<sub>4</sub> oxidation were recorded in a flow of 0.2 vol % NO/5 vol% O<sub>2</sub>/N<sub>2</sub> balance (50 mL min<sup>-1</sup>) under heating from 30 to 450 °C.

### **Catalytic activity tests**

The catalytic activity of all as-prepared catalysts for soot oxidation was evaluated by soot temperature programmed oxidation (soot-TPO) on a continuous flow micro-reactor constituted of a quartz tube of 8 mm of the outside diameter. The reactor was heated from 150 to 650 °C at a heating rate of 2 °C min<sup>-1</sup> in a stream of 0.2 vol% NO and 5 vol% O<sub>2</sub> balanced with N<sub>2</sub> at a total flow rate of 50 mL min<sup>-1</sup>. The catalyst (0.1 g) and soot (0.01 g) were fully mixed using a spatula for 10 min to simulate loose contact. The concentration of CO and CO<sub>2</sub> in the outlet gas was monitored by online gas chromatography (GC 9890B, Shanghai) with a flame ionization detector (FID). The catalytic activity was evaluated and compared in terms of T<sub>10</sub>, T<sub>50</sub>, and T<sub>90</sub>, corresponding to the temperature at which 10%, 50%, and 90% of soot is

converted. The selectivity of CO<sub>2</sub> formation (S<sub>CO2</sub>) was defined as the CO<sub>2</sub> outlet concentration (C<sub>CO2</sub>) divided by the sum of CO<sub>2</sub> and CO outlet concentration. S<sub>CO2</sub><sup>m</sup> was denoted as the S<sub>CO2</sub> at which the C<sub>CO2</sub> value was the maximum. The CO<sub>2</sub> selectivity (S<sub>CO2</sub>) was measured according to the following equation (1):

$$S_{CO_2}(\%) = \frac{[CO_2]_{out}}{[CO]_{out} + [CO_2]_{out}} \times 100\% \quad (1)$$

Here, the [CO<sub>2</sub>]<sub>out</sub> and [CO]<sub>out</sub> represent the outlet CO<sub>2</sub> and CO concentration, respectively.

he apparent activation energy of soot oxidation was measured by the single heating rate method (Coats-Redfern integral method) according to the equation (2):

$$\beta \frac{d\alpha}{dT} = k(T)f(\alpha) \rightarrow \beta \frac{d\alpha}{dT} = A \times \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (2)$$

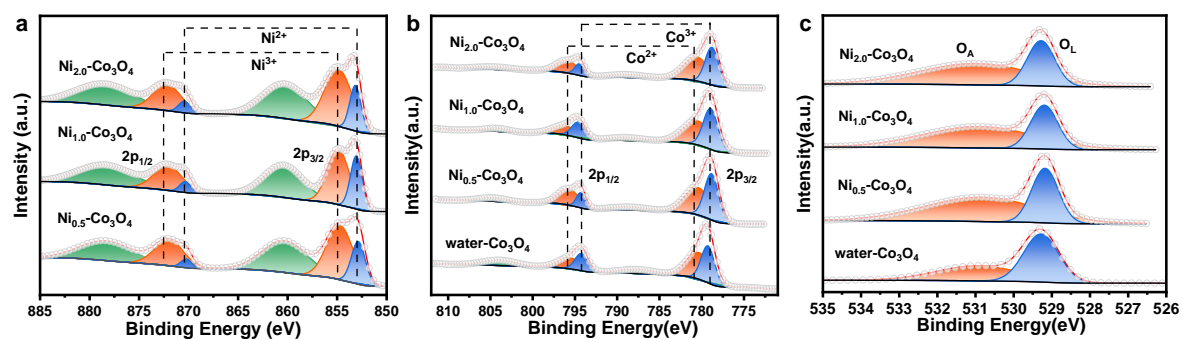
Where  $\beta$  is the heating rate (K min<sup>-1</sup>),  $\alpha$  is the soot conversion rate ( $\alpha < 15\%$ ),  $T$  is the reaction temperature (K),  $k$  is the reaction rate constant,  $f(\alpha)$  is the kinetic expression for the reaction model,  $f(\alpha) = (1-\alpha)^n$ , where  $n$  is the number of reaction stages.  $A$  is the pre-factor (s<sup>-1</sup>),  $E_a$  is the apparent activation energy (kJ mol<sup>-1</sup>),  $R$  is the ideal gas constant. Previous studies have shown that the reaction of soot with NO<sub>2</sub> is a one-stage reaction, i.e.,  $n=1$ . The equation (5) can be obtained:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \quad (3)$$

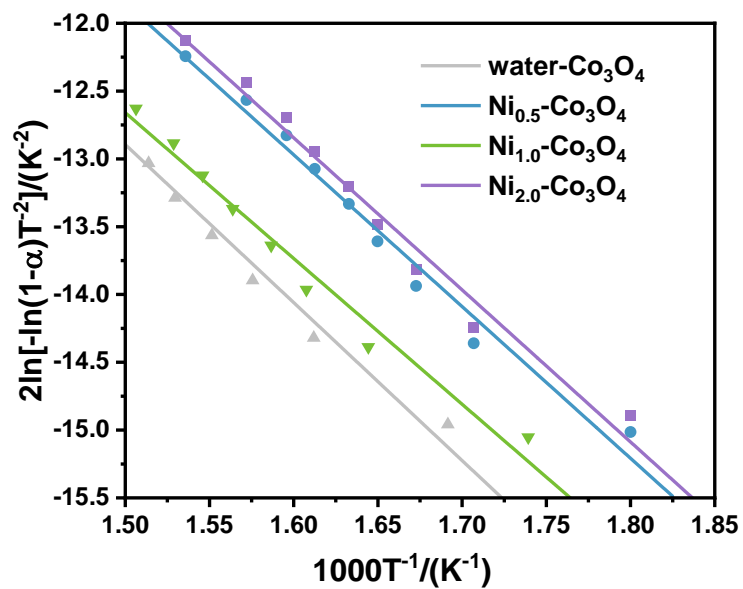
In most cases,  $\frac{2RT}{E_a}$  much smaller than 1, and  $\ln\left[\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right]$  can be regarded as a

constant. Then, the apparent activation energy is estimated by plotting  $\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]$  vs  $1/RT$ .

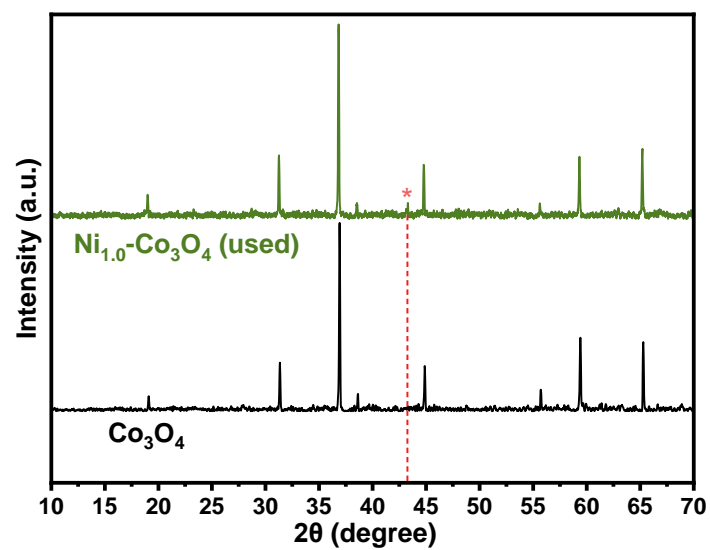
## Supplementary Figures



**Figure S1.** XPS spectra of Ni 2p (b), Co 2p (a), and O 1s (c) over water- $\text{Co}_3\text{O}_4$  and  $\text{Ni}_x\text{-Co}_3\text{O}_4$  catalysts.

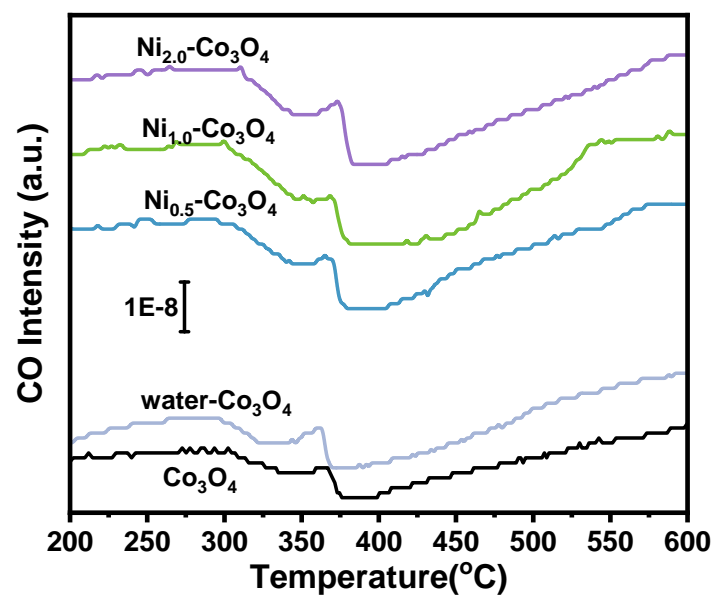


**Figure S2.** The apparent activation energy of water- $\text{Co}_3\text{O}_4$  and  $\text{Ni}_x\text{-Co}_3\text{O}_4$  catalysts for soot oxidation.

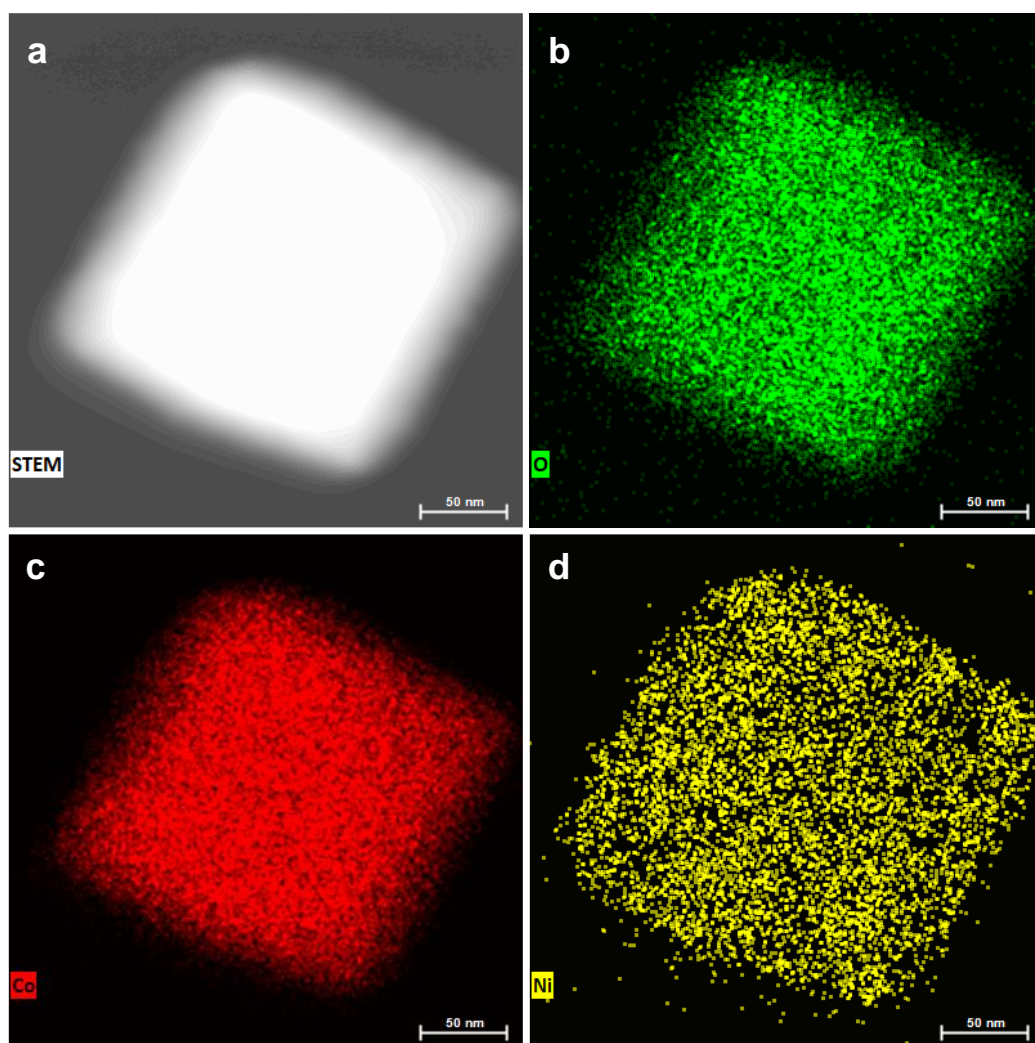


**Figure S3.** XRD patterns of  $\text{Ni}_{1.0}\text{-Co}_3\text{O}_4$  after five cycles tests and fresh  $\text{Co}_3\text{O}_4$  catalysts.

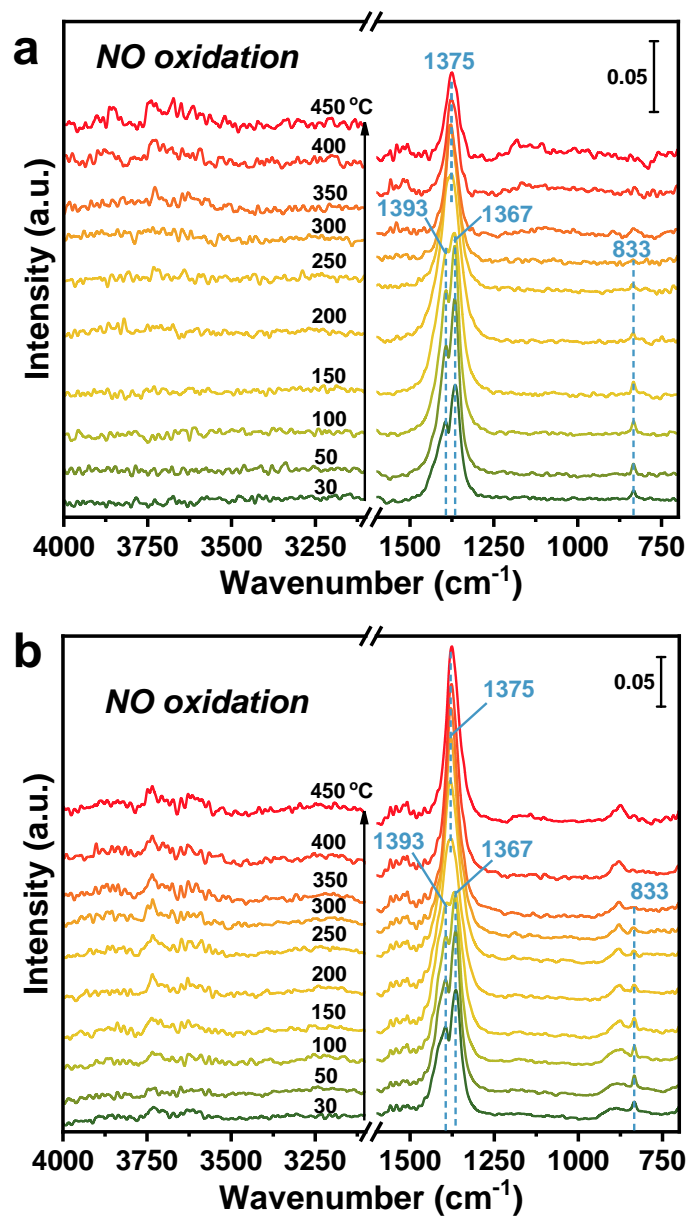




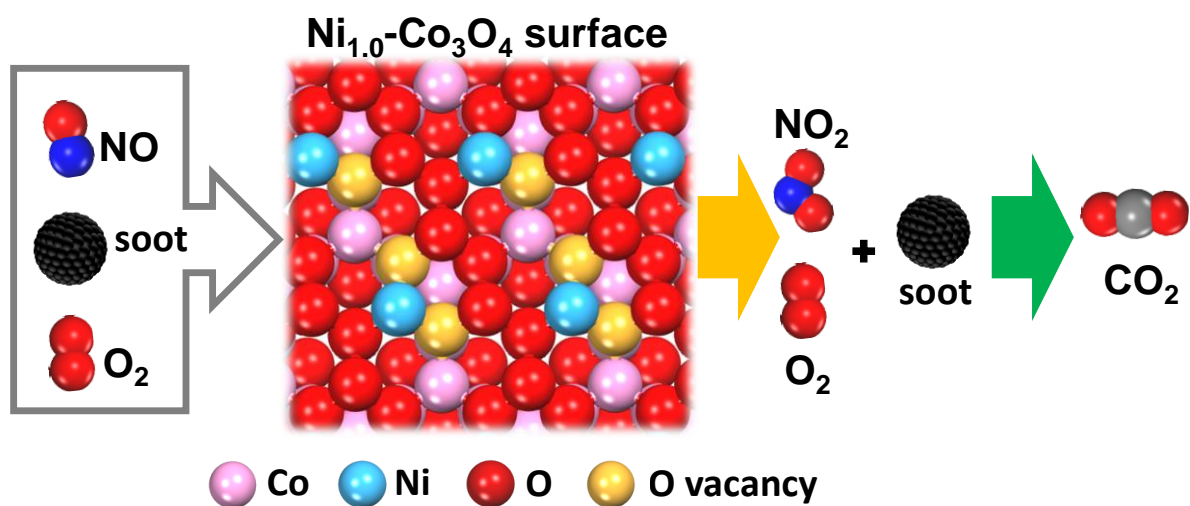
**Figure S4.** CO signal intensity in CO-TPSR testing of catalysts



**Figure S5.** STEM and corresponding element mapping images of cube-shaped  $\text{Ni}_{1.0}\text{-Co}_3\text{O}_4$  catalyst.



**Figure S6.** Temperature-dependent *in situ* DRIFT spectra of NO oxidation over (a) water-Co<sub>3</sub>O<sub>4</sub> and (b) Ni<sub>1.0</sub>-Co<sub>3</sub>O<sub>4</sub> catalysts.



**Figure S7.** Schematic diagram of  $\text{NO}_x$ -assisted soot oxidation mechanism on  $\text{Ni}_{1.0}\text{-Co}_3\text{O}_4$  catalyst surface.

## Supplementary Tables

**Table S1.** The practical Ni/Co molar ratios in the prepared catalysts determined by ICP-OES

Catalyst	Ni/Co
Ni <sub>0.5</sub> -Co <sub>3</sub> O <sub>4</sub>	0.124
Ni <sub>1.0</sub> -Co <sub>3</sub> O <sub>4</sub>	0.222
Ni <sub>2.0</sub> -Co <sub>3</sub> O <sub>4</sub>	0.386

**Table S2.** Curve-fitting results of Ni (*2p*), Co (*2p*) and O (*1s*) for catalysts.

Catalysts	Ni <i>2p</i>			Co <i>2p</i>			O <i>1s</i>		
	Ni <sup>3+</sup>	Ni <sup>2+</sup>	Ni <sup>3+</sup> /Ni <sup>2+</sup>	Co <sup>3+</sup>	Co <sup>2+</sup>	Co <sup>3+</sup> /Co <sup>2+</sup>	O <sub>A</sub>	O <sub>L</sub>	O <sub>A</sub> /O <sub>L</sub>
water-Co <sub>3</sub> O <sub>4</sub>	-	-	-	0.43	0.57	0.75	0.57	0.43	1.33
Ni <sub>0.5</sub> -Co <sub>3</sub> O <sub>4</sub>	0.76	0.24	3.12	0.42	0.58	0.72	0.65	0.35	1.85
Ni <sub>1.0</sub> -Co <sub>3</sub> O <sub>4</sub>	0.71	0.29	2.45	0.46	0.54	0.85	0.67	33.2	2.01
Ni <sub>2.0</sub> -Co <sub>3</sub> O <sub>4</sub>	0.78	0.22	3.55	0.41	0.59	0.69	0.66	0.34	1.93

**Table S3.** Catalytic activities of catalysts for soot oxidation.

Catalysts	T <sub>10</sub> (°C)	T <sub>50</sub> (°C)	T <sub>90</sub> (°C)	S <sub>co2</sub> <sup>m</sup> (%)	E <sub>a</sub> (kJ mol <sup>-1</sup> )
Without catalyst	461	584	648	65.2	-
Co <sub>3</sub> O <sub>4</sub>	380	447	502	82.2	-
water-Co <sub>3</sub> O <sub>4</sub>	330	393	443	89.6	96.7
Ni <sub>0.5</sub> -Co <sub>3</sub> O <sub>4</sub>	302	366	408	99.1	93.0
Ni <sub>1.0</sub> -Co <sub>3</sub> O <sub>4</sub>	282	339	378	99.3	89.4
Ni <sub>2.0</sub> -Co <sub>3</sub> O <sub>4</sub>	318	381	418	98.9	93.3

**Table S4.** Comparison of Co-based oxides system for soot oxidation: synthesis method, reaction condition, catalytic activity ( $T_{50}$ ) and corresponding reference.

Catalysts	Synthesis method	Reaction condition	$T_{50}$ (°C)	Ref.
Ni <sub>1.0</sub> -Co <sub>3</sub> O <sub>4</sub>	Quenching method	2000 ppm NO/5% O <sub>2</sub> /N <sub>2</sub> , 50 mL min <sup>-1</sup>	339.3	This work
3DOM-NiCo <sub>2</sub> O <sub>4</sub>	Carboxy-modified colloidal crystal templating method	1000 ppm NO/5% O <sub>2</sub> /N <sub>2</sub> , 300 mL min <sup>-1</sup>	379	1
3DOMM PdCo <sub>2</sub> O <sub>4</sub> /CZO	Evaporation-induced self-assembly and colloidal crystal templates methods	2000 ppm NO/5% O <sub>2</sub> /Ar, 50 mL min <sup>-1</sup>	367	2
Ag/Co <sub>3</sub> O <sub>4</sub> @CeO <sub>2</sub>	Hydrothermal, chemical precipitation and impregnating methods	500 ppm NO/5% O <sub>2</sub> /N <sub>2</sub> , 500 mL min <sup>-1</sup>	395	3
K-Co <sub>3</sub> O <sub>4</sub> nanowire	Hydrothermal and facile wet impregnation methods	600 ppm NO/5% O <sub>2</sub> /N <sub>2</sub> , 100 mL min <sup>-1</sup>	324	4
3DOM La <sub>0.9</sub> K <sub>0.1</sub> CoO <sub>3</sub>	Carboxy-modified colloidal crystal templates method	2000 ppm NO/5% O <sub>2</sub> /Ar, 50 mL min <sup>-1</sup>	398	5
3DOM Pt@CoO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	colloidal crystal template and GBMR/P methods	2000 ppm NO/5% O <sub>2</sub> /Ar, 50 mL min <sup>-1</sup>	357	6
0.5%Pd-1%Co/Beta	Impregnation method	1000 ppm NO/10% O <sub>2</sub> /N <sub>2</sub> , 500 mL min <sup>-1</sup>	398	7
5%Cs/1%Co/MnO <sub>x</sub>	Hydrothermal, wetness impregnation method	1000 ppm NO/10% O <sub>2</sub> /N <sub>2</sub> , 300000 mL g <sup>-1</sup> h <sup>-1</sup>	371	8



CoO <sub>x</sub> /TiO <sub>2</sub>	Sequential deposition–precipitation with urea method	250 ppm NO <sub>x</sub> /50% Air/N <sub>2</sub> , 100 mL min <sup>−1</sup>	358	9
Co/Ce-YSZ	Impregnated and redox-aging cycle methods	500 ppm NO/5% O <sub>2</sub> /N <sub>2</sub> , 500 mL min <sup>−1</sup>	509	10

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