Supplementary material

Low-temperature CO oxidation over integrated Penthorum chinense-like $MnCo_2O_4$ arrays anchored on three-dimensional Ni foam with enhanced moisture resistance

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Experimental section

Synthesis of $MnCo_2O_4$-X nanoarrays on Ni foam *:* The cleaned Ni foam was put against the 50.0 mL Teflon-lined autoclave which contained a homogeneous solution of $Mn(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$ (Co^{2+} + Mn^{2+} = 3 mmol, Co^{2+}/Mn^{2+}=2), NH_4F (6 mmol), urea (12 mmol) and a 40 ml mixed solvent of water/ethanol (v/v = 40/0, 30/10, 20/20 and 10/30). The autoclave was sealed and maintained at 95 ^oC for 12 h to synthesize the Co_3O_4 nanoarrays (NAs) precursors in an electric oven. After the autoclave was cooled down to room temperature, the samples were rinsed several times with the assistance of ultrasonication and dried in air at 80 ^oC. Finally, the Ni foam with the as-grown precursors was put into a quartz tube and then annealed at 400 ^oC for 2 h to obtain monolithic structured nanoarrays catalysts. The as-prepared catalyst was denoted as MCo_2O_4-X (X represents the volume of water).

Synthesis of $Co_{3-x}Mn_xO_4$ nanoarrays on Ni foam *:* The cleaned Ni foam was put against the 50.0 mL Teflon-lined autoclave which contained a homogeneous solution of $Mn(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$ (Co^{2+} + Mn^{2+} = 3 mmol, Co^{2+}/Mn^{2+}=2.5/0.5, 2/1, 1.5/1.5 and 1/2), NH_4F (6 mmol), urea (12 mmol) and a 40 ml water. The autoclave was sealed and maintained at 95 ^oC for 12 h to synthesize the Co_3O_4 nanoarrays (NAs) precursors in an electric oven. After the autoclave was cooled down to room temperature, the samples were rinsed several times with the assistance of ultrasonication and dried in air at 80 ^oC. Finally, the Ni foam with the as-grown precursors was put into a quartz tube and then annealed at 400 ^oC for 2 h to obtain monolithic structured nanoarrays catalysts. The as-prepared catalyst was denoted as $Co_{3-x}Mn_xO_4$.

Synthesis of $Co_{3-x}Cu_xO_4$ nanoarrays on Ni foam *:* The cleaned Ni foam was put against the 50.0 mL Teflon-lined autoclave which contained a homogeneous solution of $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ (Co^{2+} + Cu^{2+} = 3 mmol, Co^{2+}/Cu^{2+}=2.5/0.5, 2/1, 1.5/1.5 and 1/2), NH_4F (6 mmol), urea (12 mmol) and a 40 ml water. The autoclave was sealed and maintained at 95 ^oC for 12 h to synthesize the Co_3O_4 nanoarrays (NAs) precursors in an electric oven. After the autoclave was cooled down to room temperature, the samples were rinsed several times with the assistance of ultrasonication and dried in air at 80 ^oC. Finally, the Ni foam with the as-grown precursors was put into a quartz tube and then annealed at 400 ^oC for 2 h to obtain monolithic structured nanoarrays catalysts. The as-prepared catalyst was denoted as $Co_{3-x}Cu_xO_4$.

Material characterizations X-ray powder diffraction (XRD) patterns of the monolithic structured samples were recorded on a Panalytical X'Pert PRO system with Cu-Kα (λ=1.5406Å) radiation at a scan rate of 10/min^{-1} within the range of scattering angle 2θ of 5 to 90°, operated at 40kV and 40mA. The size and morphology of samples were characterized using field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F) with an acceleration voltage of 15 kV, 10mM. The reduction behavior of the samples was studied by the temperature–programmed reduction of hydrogen (H_2–TPR) with Automated Catalyst Characterization System (Autochem 2920, MICROMERITICS) equipped with thermal conductivity detector (TCD). The monolithic structured Co_3O_4 NAs sample (1 cm × 2cm ×1.6 mm) was placed in a quartz reactor under a gas flow (10% H_2/Ar, 25 ml min^{-1}) with a constant rate of 10 °C min^{-1} up to 800 °C. The Raman spectra of the monolithic samples were conducted on a Renishaw RM2000 Raman Spectrometer (laser wavelength = 532 nm). Surface species of the catalysts were characterized by X–ray photoelectron spectroscopy (XPS) using an XLESCALAB 250Xi electron spectrometer from VG Scientific with monochromatic Al Ka radiation, and the binding energies of elements were calibrated based on the C 1s peaks at 284.6 eV.

Catalytic activity measurements The as-prepared MCo_2O_4 catalysts (1 cm × 2cm ×1.6 mm) buckling into a cylinder were evaluated in a fixed-bed quartz tubular micro-reactor (φ= 6 mm) with quartz wool packed at both ends of the catalyst bed (gas hourly space velocity = 20,000 h^{-1}). The reactant gas composed of 1 vol.% gaseous CO balanced with air (20 vol.% O_2 + balance N_2) was purged into the reactor at a flow rate of 100 mL min^{-1}. After reacted at the final temperature for 1 h, the concentrations of effluent gases were analyzed on-line by a gas chromatograph (Shimadzu GC-2014) equipped with a thermal conductivity detector (TCD). The catalytic activities over the monolithic structured catalysts were calculated on the basis of the concentration change of CO.

$$\eta_{CO} = \frac{C_{CO,in} - C_{CO,out}}{C_{CO,in}} \times 100\%$$

Where η_{CO}, $C_{CO,\,in}$ (ppm) and $C_{CO,\,out}$ (ppm) are the CO conversion, CO in the inlet and outlet gas, respectively.

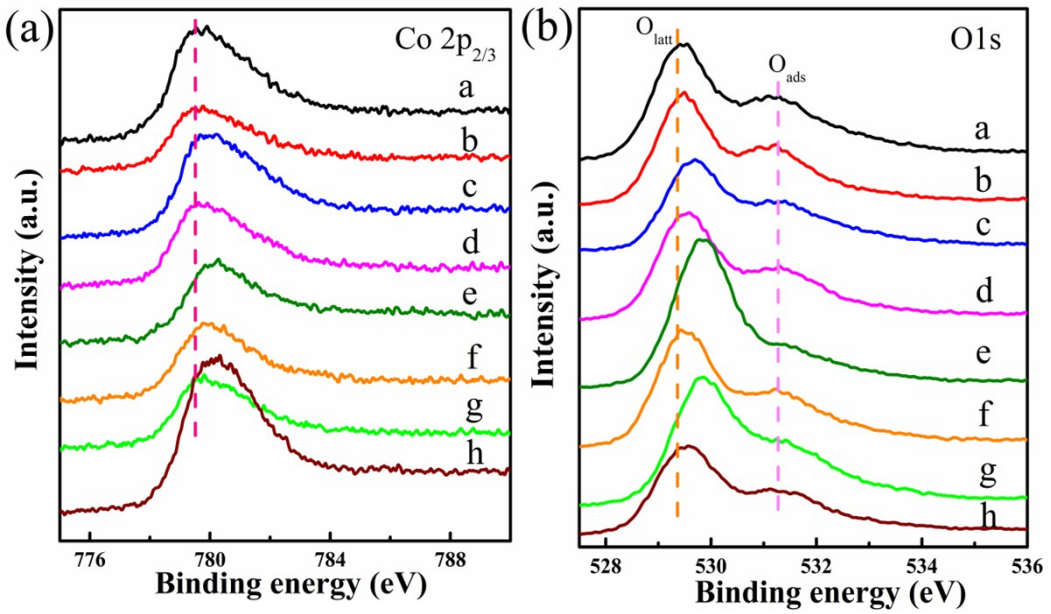

Fig. S1 XPS spectra of the MCo_2O_4 NAs samples supported on Ni foam: (a) Co $2p_{3/2}$, (b) O 1s; insert a-h correspond to $CuCo_2O_4$, $MnCo_2O_4$, Co_3O_4, $NiCo_2O_4$, $FeCo_2O_4$(2), $FeCo_2O_4$(3), $ZnCo_2O_4$ and Co_2AlO_4, respectively.

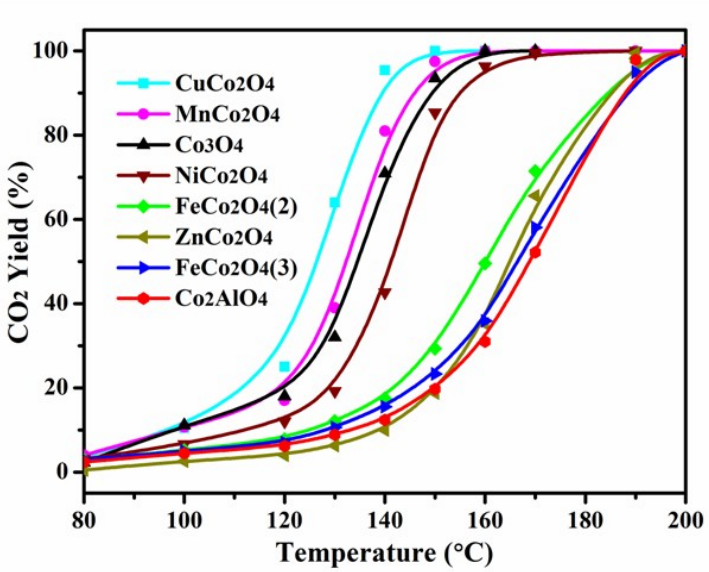

Fig. S2 the CO_2 yield curves over all the MCo_2O_4 NAs samples as a function of temperature.

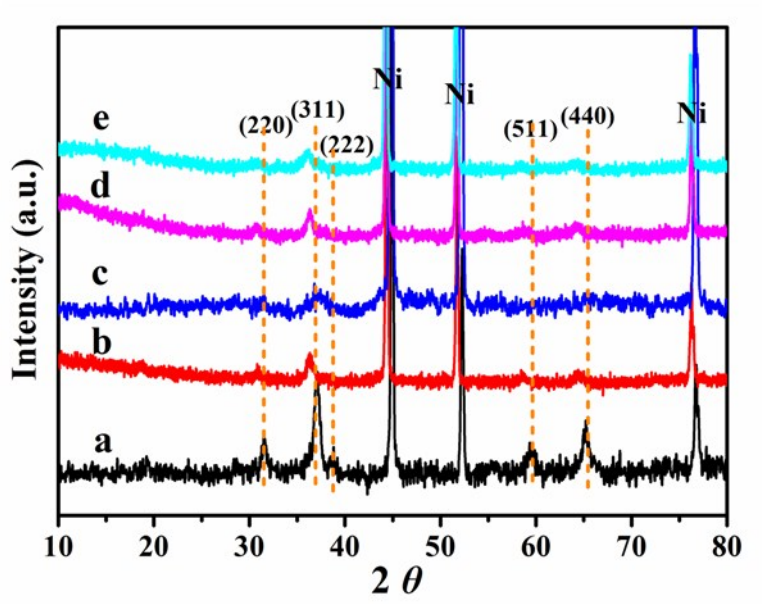

Fig. S3 the XRD patterns of $Co_{3-x}Mn_xO_4$ NAs: inserted a-e correspond to Co_3O_4, $Co_{2.5}Mn_{0.5}O_4$, $MnCo_2O_4$, $Co_{1.5}Mn1.5O_4$, and Mn_2CoO_4, respectively.

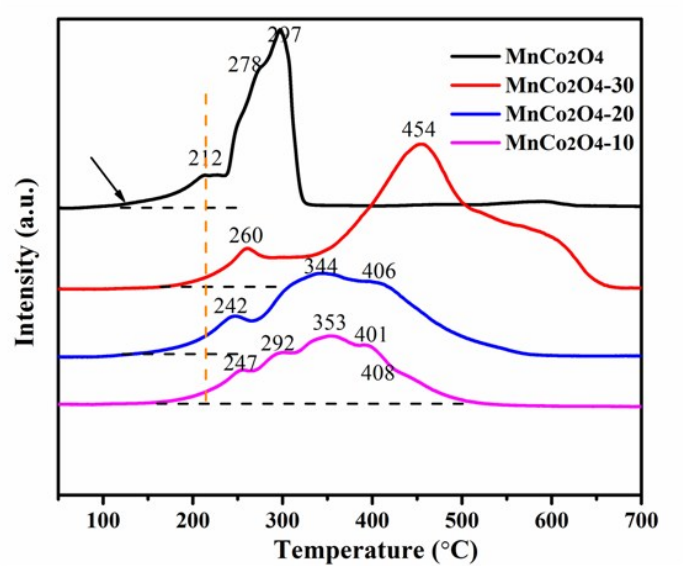

Fig. S4 H_2-TPR profiles of the $MnCo_2O_4$-X NAs samples.

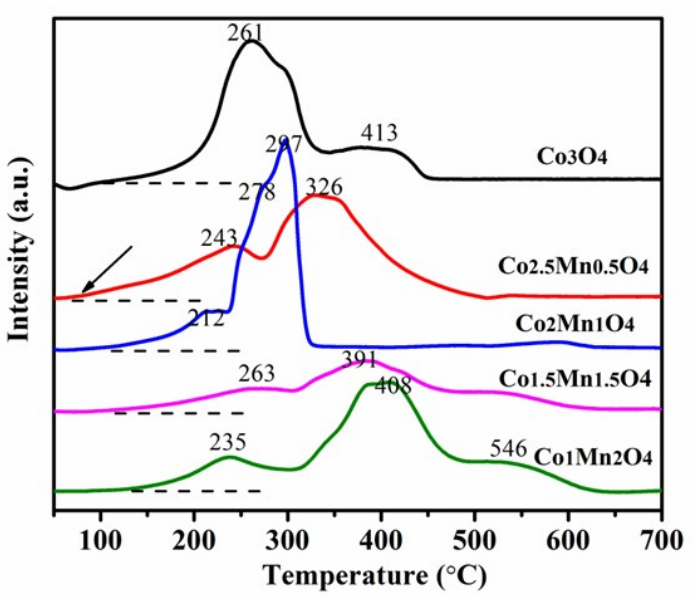

Fig. S5 H_2-TPR profiles of the $Co_{3-x}Mn_xO_4$ NAs samples.

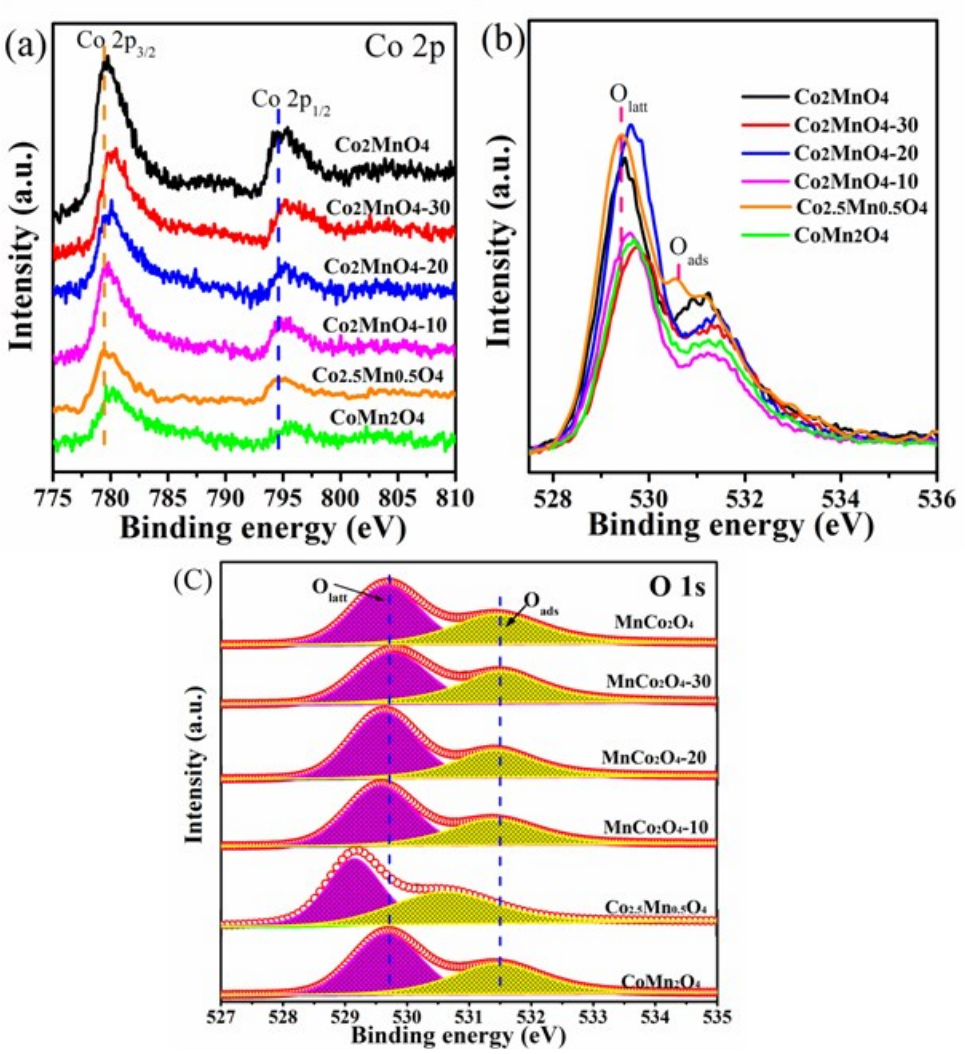

Fig. S6 (a) Co 2p XPS spectra, (b) O 1s XPS spectra and (c) Core level O 1s XPS spectra of the $MnCo_2O_4$, $MnCo_2O_4$-30, $MnCo_2O_4$-20, $MnCo_2O_4$-10 and $CoMn_2O_4$ NAs samples.

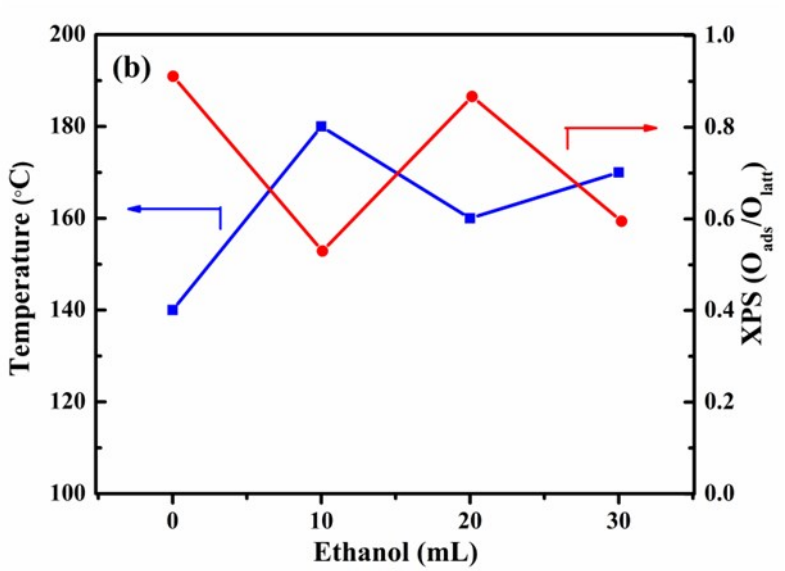

Fig. S7 (a) CO conversion percentages curves over all the $MnCo_2O_4$, $MnCo_2O_4$-30, $MnCo_2O_4$-20, $MnCo_2O_4$-10 and $CoMn_2O_4$ catalysts as a function of temperature.

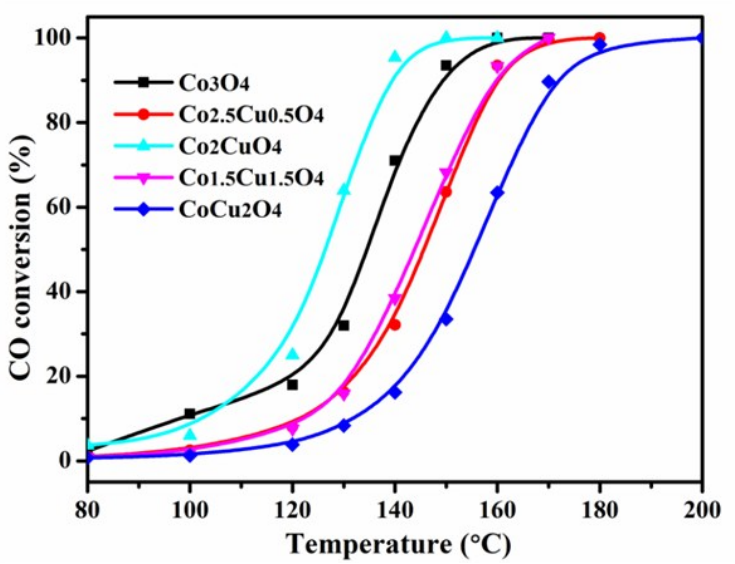

Fig. S8 the catalytic activities of the as-prepared integrated $Co_{3-x}Cu_xO_4$ NAs catalysts for CO oxidation.

Table S1. Catalytic activities and surface elemental compositions of the MCo_2O_4-X, $Co_{2.5}Mn_{0.5}O_4$ and $CoMn_2O_4$ NAs catalysts.

Samples	T_{10}/°C	T_{50}/°C	T_{100}/°C	Co $2p_{3/2}$/eV	O 1s/eV	O_{ads}/O_{latt}
$MnCo_2O_4$-30	126	158	200	780.2	529.8	0.530
$MnCo_2O_4$-20	110	142	170	779.95	529.6	0.869
$MnCo_2O_4$-10	120	148	175	779.85	529.65	0.595
$Co_{2.5}Mn_{0.5}O_4$	100	125	151	779.4	529.4	0.878
$CoMn_2O_4$	122	163	190	779.6	529.8	0.55