Supplementary material

Vertically-aligned Co_3O_4 arrays on Ni foam as monolithic structured catalysts for CO oxidation: Effect of morphological transformation

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Experimental Section

Synthesis of Co_3O_4 NAs-NC on Ni foam: All the purchased chemicals were analytical grade and used without further purification. In a typical synthesis process, the Ni foams (approximately 5 cm x 7 cm, thickness 1.6 mm and pore density 110 ppi) were cleaned by a 3 M HCl aqueous solution, ethanol and deionized (DI) water with assistance of ultrasonicationand for 15 min to remove the surface dirt, grease and NiO layer. Then, the cleaned Ni foam was put against the 50.0 mL Teflon-lined autoclave which contained a homogeneous solution of $Co(NO_3)_2 \cdot 6H_2O$ (4 mmol), urea (8 mmol) and 40 ml DI water. The autoclave was sealed and maintained at 95°C for 8 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 °C. Finally, the Ni foam with the as-grown precursors was put into a quartz tube and then annealed at 400°C for 2 h to obtain monolithic structured Co_3O_4 nanoarrays catalysts. The as-prepared catalyst was denoted as NAs-NC.

Synthesis of Co_3O_4 NAs-CTAB on Ni foam:The cleaned Ni foam was put against the 50.0 mL Teflon-lined autoclave which contained a homogeneous solution of $Co(NO_3)_2 \cdot 6H_2O$ (4 mmol), 0.3g cetyl trimethylammonium bromide (CTAB), urea (8 mmol) and 40 ml DI water. The autoclave was sealed and maintained at 95 °C for 8 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 °C. Finally, the Ni foam with the as-grown precursors was put into a quartz tube and then annealed at 400°C for 2 h to obtain monolithic structured Co_3O_4 nanoarrays catalysts. The as-prepared catalyst was denoted as NAs-CTAB.

Synthesis of Co_3O_4 NAs-8-CTAB on Ni foam:The cleaned Ni foam was put against the 50.0 mL Teflon-lined autoclave which contained a homogeneous solution of $Co(NO_3)_2 \cdot 6H_2O$ (4 mmol), 0.3g cetyl trimethylammonium bromide (CTAB), NH_4F (8 mmol), urea (8 mmol) and 40 ml DI water. The autoclave was sealed and maintained at 95°C for 8 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 °C. Finally, the Ni foam with the as-grown precursors was put into a quartz tube and then annealed at 400°C for 2 h to obtain monolithic structured Co_3O_4 nanoarrays catalysts. The as-prepared catalyst was denoted as NAs-8-CTAB.

Materials 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 $10/\text{min}^{-1}$ within the range of scattering angle 2θ of 5 to 90°, operated at 40kv and 40mA. N_2 adsorption/desorption isotherms were obtained via N_2 adsorption at -196°C on an automatic surface analyzer (SSA-7300, China). The BET specific surface area was obtained according to the Brunauer−Emmett−Teller (BET). 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 microstructures of samples were obtained using transmission electron microscopy (TEM, JEOLJEM-2010F) with an accelerating voltage of 200 kV. 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.

The in-situ Raman experiment (laser wavelength = 532 nm)was designed as shown in **FigureS1**,and the spectra was achieved at every 10 °C from 25 °C to 200 °Cunder N_2, 20% O_2/N_2, and 20% O_2/N_2/CO (1vol.%) respectively. N_2 was used as inert gas to flush the sample after treatmentin active atmosphere. The dry air (O_2/N_2) was aimed to investigate the oxygen replenishment ability of the catalysts, which adsorbed gaseous oxygen and transformed it into active oxygen species. The $O_2/N_2/CO$ mixture was put into the cell to get the surface oxygen vacancies concentration under reaction condition. It would take 45 min to start one temperature point to the next: 20 min for temperature stabilization, followed by 20 min for Raman analysis, and the last 5 min for heating to the next temperature with a ramp rate of 2 °C min^{-1}).

Catalytic activity measurements:the as-prepared Co_3O_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 thefinal 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 Co_3O_4 NAs catalysts were calculated on the basis of the concentrationchange 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.

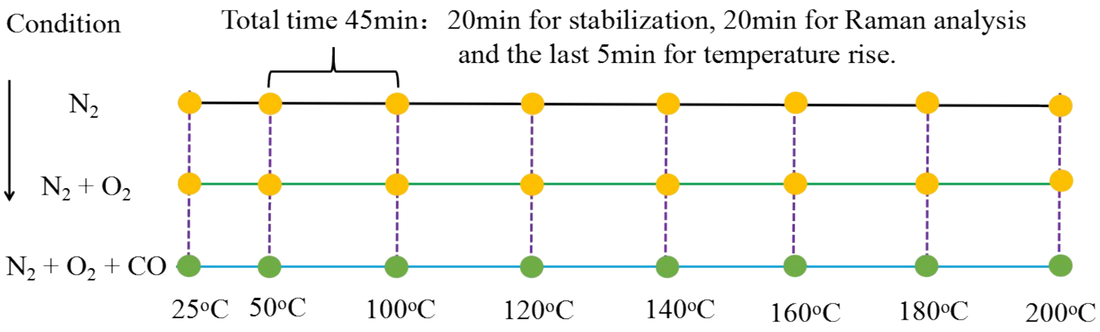

Figure S1. Experimental scheme for *in-situ* Raman experiment.

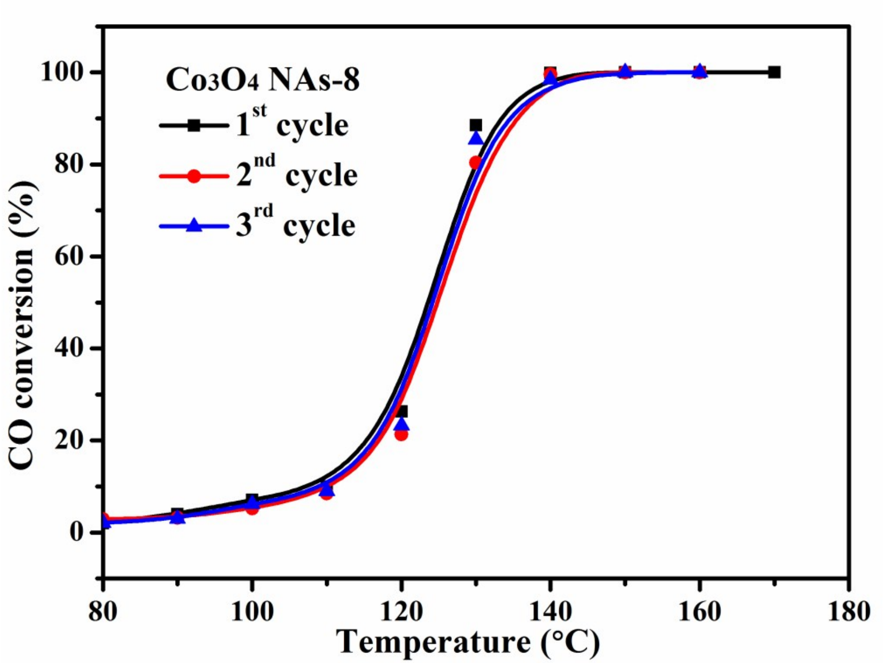

Figure S2. The recycle test of Co_3O_4 NAs-8.

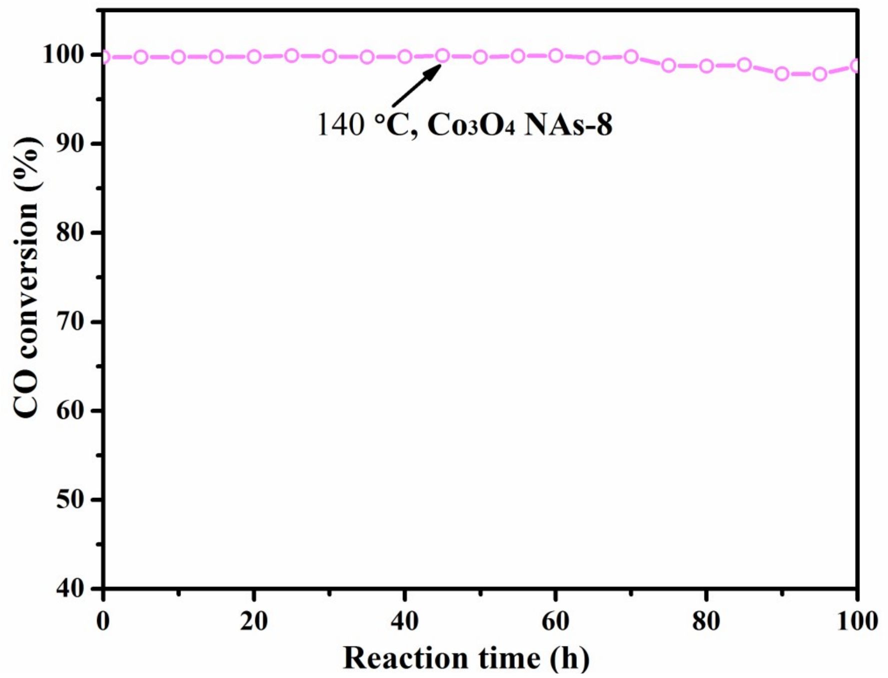

Figure S3. The stability test of Co_3O_4 NAs-8.