

Supplementary Information

SnO₂ nano-rod with superior CO oxidation performance

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1. Catalyst Preparation

Reagents: SnCl₄·5H₂O, SnCl₂·2H₂O, hydrochloric acid (37.5%), ammonia solution (25%), PVP (K-30), KCl, and NH₄F were purchased from Sinopharm Chemical Reagent (Shanghai, China). Two type of 4-Nonylphenol branched ethoxylated NP-5 and NP-9 were purchased from Tianjin Yongda Chemical Reagent Development Center. All reagents were used as received without further purification.

1.1 Synthesis of SnO₂ nanorods (SnO₂-Rod)

The SnO₂ nanorods were prepared according to the molten salt synthesis method. Firstly, 3.5 g of SnCl₂·2H₂O, 2 g of NaCl and 2.6 g of KCl were mixed with 6 ml of NP9/ NP5(1/1 v/v) in a mortar, ground for 30 min and named as mixture A. At the same time, 1.6 g of KBH₄, 2 g of NaCl and 2.6 g of KCl were mixed with 5 ml of NP9/ NP5(1:1, v/v) in a mortar, ground for 30min and named as mixture B. Secondly, mixture A and B were blended and ground for 60 min. The prepared powder were washed several times with acetone then dried in an oven at 80 °C for 2 h before calcination at 800°C for 2h. The calcined samples were washed with distilled water several times and then dried at 110°C overnight.

1.2 Synthesis of SnO₂ nanoparticles (SnO₂-NPh) by hydrothermal method

In a typical synthesis, 1.0 g of SnCl₄·5H₂O, 1.8 mL of HCl, and 1.0 g of PVP were added in sequence into ethanol/distilled water mixture (30.00 mL, 1:1, v/v) under intense ultrasonic treatment. The resulting solution was transferred to a Teflon-lined stainless steel autoclave and kept at 200°C for 12 h. The products were collected by centrifugation at 4000 rpm, and washed several times with

deionized water and ethanol, then dried at 110 °C overnight and calcined at 500 °C in air atmosphere for 4 h.

1.3 Synthesis of SnO₂ nanoparticles (SnO₂-NPP) by precipitation method

For comparison study, the precipitation method was used to prepare SnO₂ samples. In detail, aqueous ammonia solution (7.5 M) was dripped slowly into SnCl₄·5H₂O solution (1.0 M) under constant stirring until the pH value reached 7. Then the mixture was filtered under vacuum and washed thoroughly with deionized water. The achieved solid were dried at 110 °C for 12 h, and then calcined at 500 °C in air atmosphere for 4 h to get the final SnO₂ catalysts.

1.4 Synthesis of SnO₂ microspheres (SnO₂-Sphere)

The SnO₂ solid microspheres were prepared via hydrothermal method, using NH₄F as morphology controlling agents. In a typical experiment, 2.0 g of SnCl₄·5H₂O and 1.0 g of NH₄F were added into 60 mL of H₂O with magnetic stirring. After the solution turn transparent and clear, then it was transferred to a 100 mL Teflon-lined stainless steel autoclave and kept in an oven at 180 °C for 24h. The other steps are same to what described in part 1.2.

1.5 Preparation of Pd/SnO₂

Supported Pd catalysts were prepared by the impregnation method. SnO₂-NPP was selected as the support. PdCl₂ (8 mg ml⁻¹) aqueous solution was used as the Pd source. SnO₂-Precip was impregnated with the Pd solution and equal volumes of alcohol. Under constant stirring at 70 °C for several hours, the mixture was dried. Subsequently, the resulting powder was dried at 110°C overnight, and then calcined at 500 °C for 4 h in air atmosphere. The Pd loading is 0.5 wt%, which was also measured and confirmed by ICP.

2. Catalyst Characterization

The specific surface area and pore size distributions of the calcined samples were determined by nitrogen adsorption-desorption analysis, which was measured at 77 K on the Micromeritics ASAP 2020 using the Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. Samples were degassed in vacuum (~10⁻⁴ Torr) at 250 °C for at least 4 h prior to measurements.

Powder X ray diffraction (XRD) patterns were recorded on a Bruker AXS D8Focus diffractometer instrument operating at 40 kV and 40 mA with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). Scans were taken with a 2θ range from 10-90° and with a step of 0.02 °/s. The mean crystallite size of the samples was

calculated with Scherrer equation based on the three strongest peaks of SnO₂ with hkl of (110), (101) and (211), for which the 2θ are 26.6, 33.8 and 51.7 degree, respectively.

H₂-TPR experiments were carried out on a FINESORB 3010C instrument in a 10% H₂/Ar gas mixture flow, with the temperature being increased from room temperature to 900 °C at a rate of 10 °C·min⁻¹. Generally, 10 mg of catalysts were used for the test. A thermal conductivity detector (TCD) was employed to monitor the H₂ consumption. For H₂ consumption quantification, a calibration experiment were carried out by using a high-purity CuO (99.99%) sample.

The microstructure and morphology of the synthesized product were characterized by scanning electron microscopy (SEM). Small amounts of the dried powders were dispersing in ethanol then dropping a few drops onto silicon slice. The samples were viewed in an FEI Quanta 200 scanning electron microscope at 20 kV.

Transmission electron microscopy (TEM), high resolution TEM (HR-TEM) and electron diffraction investigations were carried out using a JEOL 3000F TEM working at 300 kV. Samples for TEM investigation were prepared by dispersing some products in ethanol and immersing them in an ultrasonic bath for 30 min, and then dropping a few drops of the resulting suspensions onto a copper grid coated with a layer of amorphous carbon.

The X-ray photoelectron spectroscopy (XPS) were measured with a Perkin-Elmer RBD upgraded PHI-5000C ESCA system. XPS spectra with PHI-5000C ESCA system using a single Mg-Kα X-ray source operating at 250 W and 14 kV of voltage. The spectra were obtained at ambient temperature with an ultrahigh vacuum. The binding energies were calibrated using the C 1s peak of graphite at 284.6 eV as a reference.

3. Catalytic Activity Evaluation

The catalysts were evaluated for CO oxidation in a continuous flow reactor with a gas composition of 1%CO, 21%O₂ and balanced by high purity N₂. 30 mg of catalyst was used for each measurement with a flow rate of 15 ml/min, which corresponds to a gas hourly space velocity (GHSV) of 30,000 ml·h⁻¹·g⁻¹. The reactants and products were analyzed on-line on a GC9310 gas chromatograph equipped with a TDX-01 column and a TCD.

Table S1 XPS quantitative analysis of SnO₂ with various morphologies.

Catalysts	Sn _{3d} Binding Energy (eV)		ΔE (eV)	O _{1s} Binding Energy (eV)		O _{ads} /O _{lat}
	3d _{3/2}	3d _{5/2}		O _{ads}	O _{lat}	
SnO ₂ -Rod	495.4	487.0	8.4	532.5	531.5	0.41
SnO ₂ -NPh	495.2	486.8	8.4	532.2	530.9	0.97
SnO ₂ -NPP	495.0	486.6	8.4	532.0	530.8	0.87
SnO ₂ -Sphere	494.8	486.4	8.4	533.1	531.1	0.41

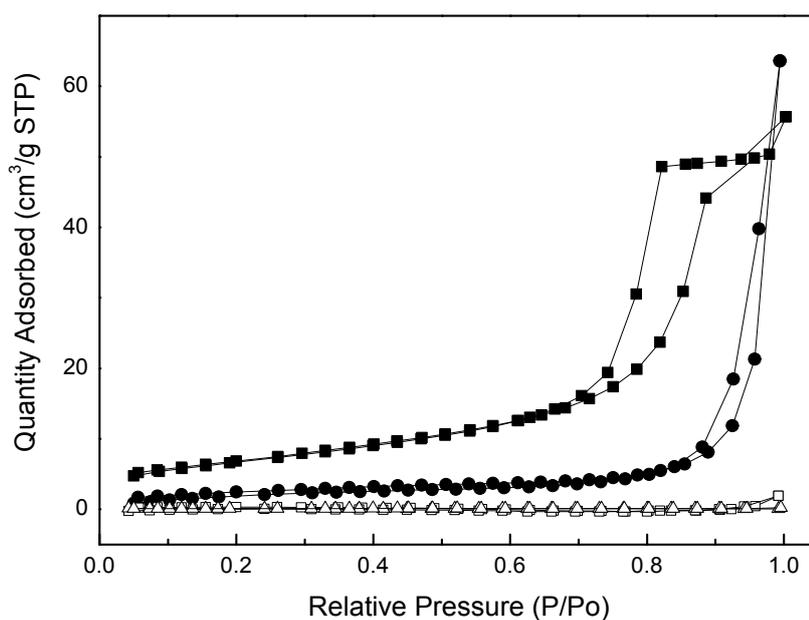


Figure. S1 N₂ adsorption-desorption isotherms of SnO₂ with various morphologies. The symbols:

■ SnO₂-NPP, ● SnO₂-NPh, □ SnO₂-Sphere, ○ SnO₂-Rod

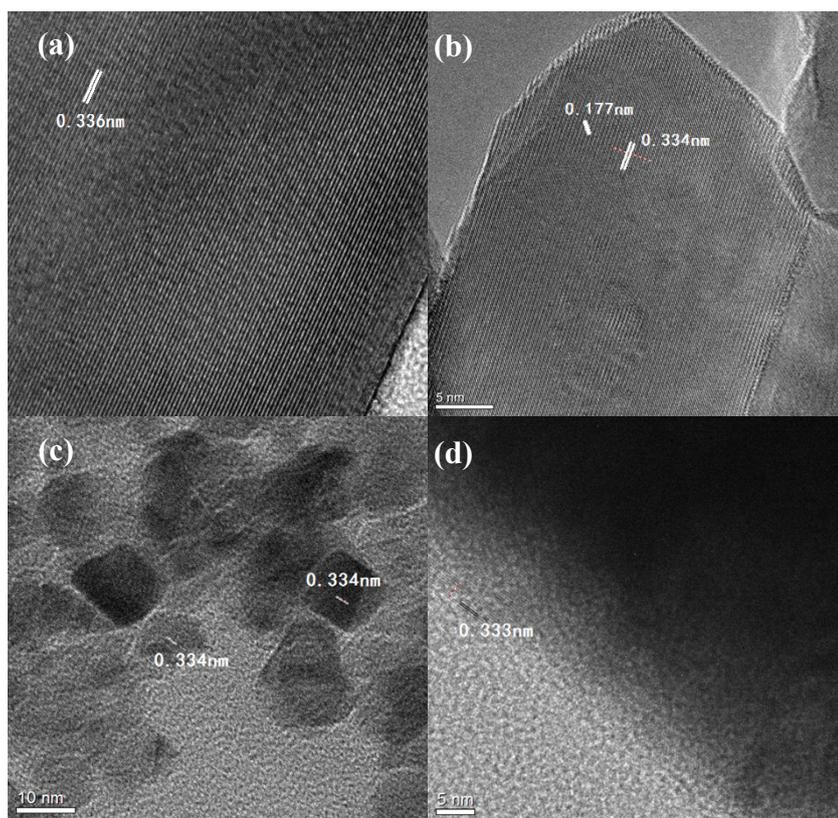


Figure S2. HRTEM images of SnO₂-Rod (a), SnO₂-NPh (b), SnO₂-NpP(c), and SnO₂-Sphere (d).

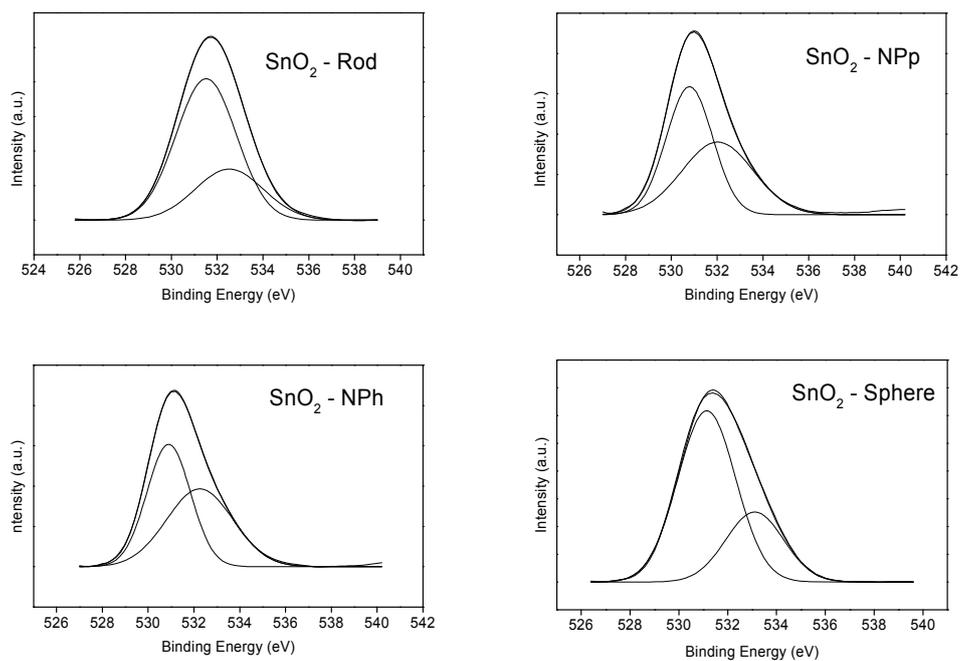


Figure S3. XPS spectra of O1s of SnO₂ with various morphologies.

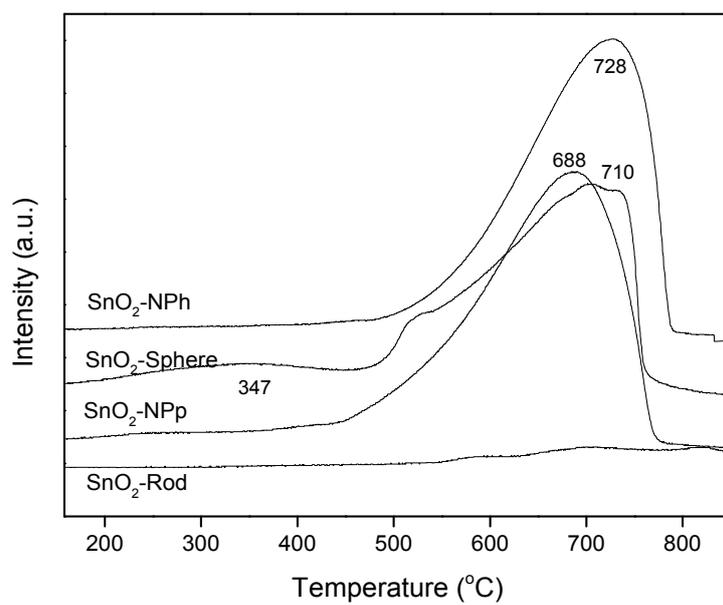


Figure S4. H₂-TPR profile of SnO₂ with various morphologies.

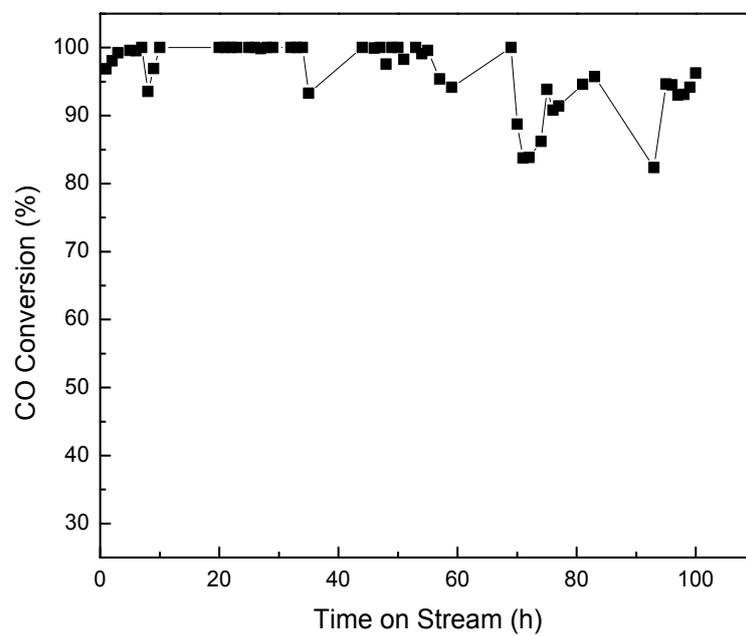


Figure S5. The long term stability of CO oxidation over SnO₂ nano-rod. Reaction conditions: Temp. 260 °C; GHSV 30,000 ml·h⁻¹·g⁻¹.

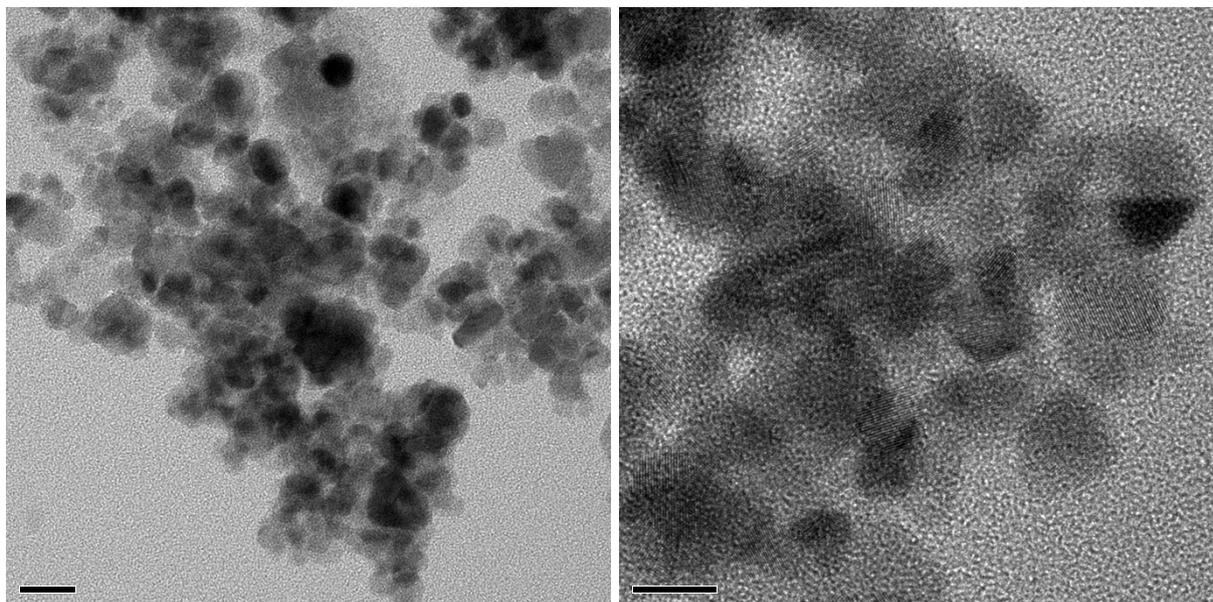


Figure S6. HRTEM images of Pd/SnO₂ after reduced in 10% H₂/Ar at 200 °C for 3 h