

Supporting Information

Hetero-epitaxially Anchoring Au Nanoparticles onto ZnO Nanowires for CO Oxidation

Jiaxin Liu,^{a,b} Botao Qiao,^{a,c} Yian Song,^a Yudong Huang^b and Jingyue (Jimmy) Liu^{a*}

^a Department of Physics, Arizona State University, Tempe, Arizona 85287, USA

^b College of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China

^c State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Experimental

Catalysts Preparation

ZnO nanowires were fabricated by a thermal evaporation-condensation method in a high temperature tube furnace. ZnO powders were purchased from US Research Nanomaterials, Inc. Gold was deposited onto the two supports via a modified deposition-precipitation method. For a typical synthesis process, ZnO nanowires (powders) were dispersed into deionized water and the suspension was under constant stirring. Then HAuCl₄ aqueous solution was added stepwise to the suspension, during which the pH value of the mixture was maintained at a fixed value by adding appropriate amounts of Na₂CO₃ solution. The suspension was heated to 60°C and stirred for 2 h. After filtration and being washed with deionized water, the resultant solid was dried at 60°C overnight. Finally, the catalyst was calcined in a muffle furnace at various temperatures (200°C, 400°C and 600°C) for 4h. The obtained Au catalysts were named as Au/ZnO-NW200/400/600, where 200,400,600 represents the calcination temperature, respectively. The Au content in these catalysts was calculated to be 2.0wt. %. The 5.0wt%Au/ZnO nanocatalysts calcined at 600°C were synthesized for XRD analysis.

Measurement of Catalytic Activity

The catalytic performances of the prepared samples for CO oxidation were evaluated in a fixed-bed reactor. For a typical run, 50 mg of the catalyst was loaded in a quartz reactor. Then, the feed gas containing 1 vol% CO, 1 vol% O₂ and balance He was allowed to pass through the reactor at a flow rate of 33.6 ml/min (corresponding to a space velocity of $\sim 40,400 \text{ ml g}^{-1}_{\text{cat}} \text{ h}^{-1}$). The effluent gas compositions were on line analyzed by a gas chromatograph (HP 7890) equipped with a TDX-01 column and a thermal conductivity detector using He as carrier gas. The CO conversion was calculated based on the difference between inlet and outlet concentrations.

For measuring the specific reaction rate, the catalytic CO oxidation reaction was conducted at a differential mode where the CO conversion was controlled below 20%. For this purpose, certain amounts of the sample (5~50mg) was diluted with Al₂O₃ (50~200 mg). For each run at a specified reaction temperature (100°C), the CO conversions at 20, 40, and 60 min were averaged and used for calculation of the specific rate.

Characterization Techniques

The actual Au loadings were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The Brunauer-Emmett-Teller (BET) specific surface areas were measured by nitrogen adsorption at -196°C on a Micromeritics ASAP 2010 apparatus.

Powder X-ray diffraction (XRD) pattern was taken on a PANalytical X'pert PRO MRD X-ray diffractometer using Cu K α radiation ($\lambda=0.154 \text{ nm}$) operated at 45 kV and 40 mA, diffraction pattern

from 10 to 80 degree (2θ) was collected with a step size of 0.013 degree under continuous scan mode.

High angle annular dark field (HAADF) and bright field electron microscopy images of the ZnO nanowires and the Au/ZnO catalysts were obtained on a JEOL ARM-200F aberration-corrected scanning transmission electron microscope (AC-STEM) operated at 200 kV with a nominal spatial resolution of 0.08nm in the STEM mode. Samples were prepared by collecting a drop of the ethanol/catalyst solution onto a TEM copper grid coated with a thin holey carbon film.

Table S1 Physicochemical properties of different catalysts and supports

	BET surface area m^2g^{-1}	Au loading wt%
Au/ZnO-NW	17.61 ^a	1.94
Au/ZnO-P	22.61 ^a	1.88

^a surface area of the support without loading of Au

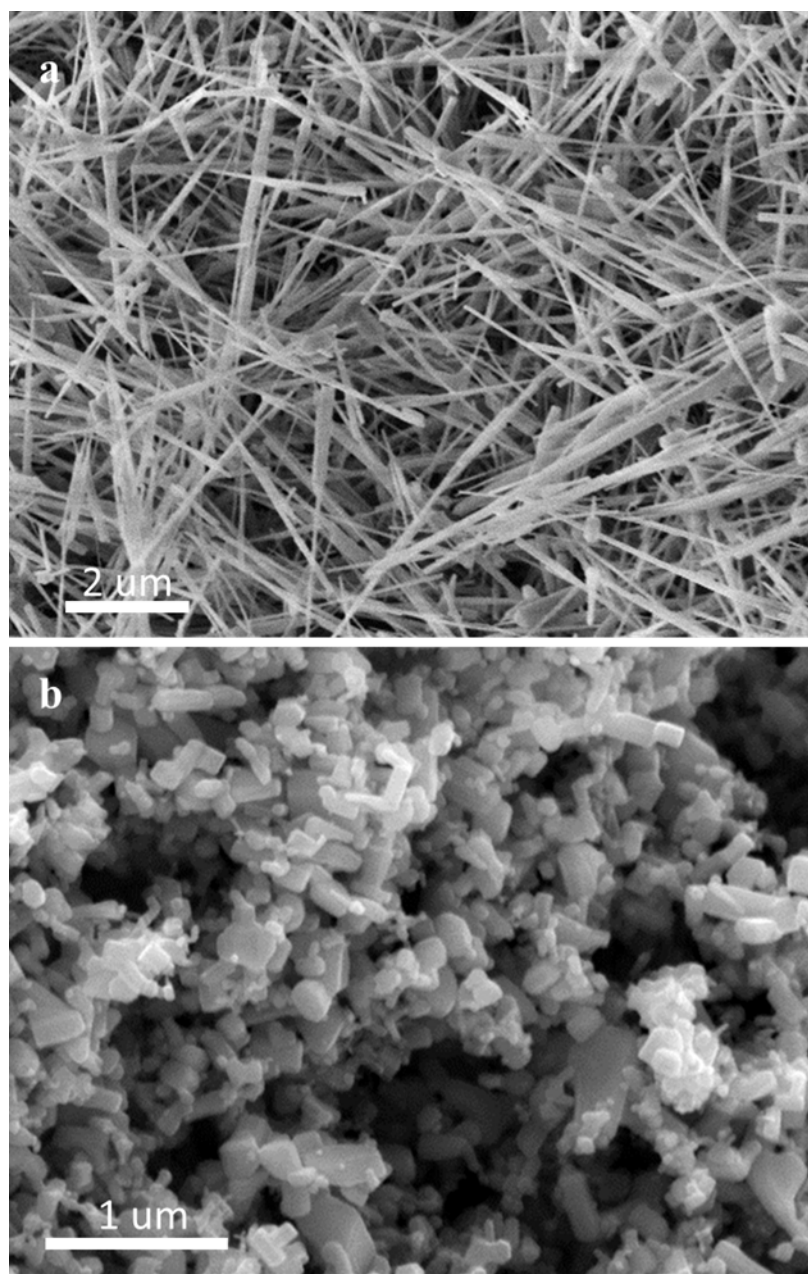


Figure S1. SEM images of (a) ZnO nanowires and (b) ZnO powders.

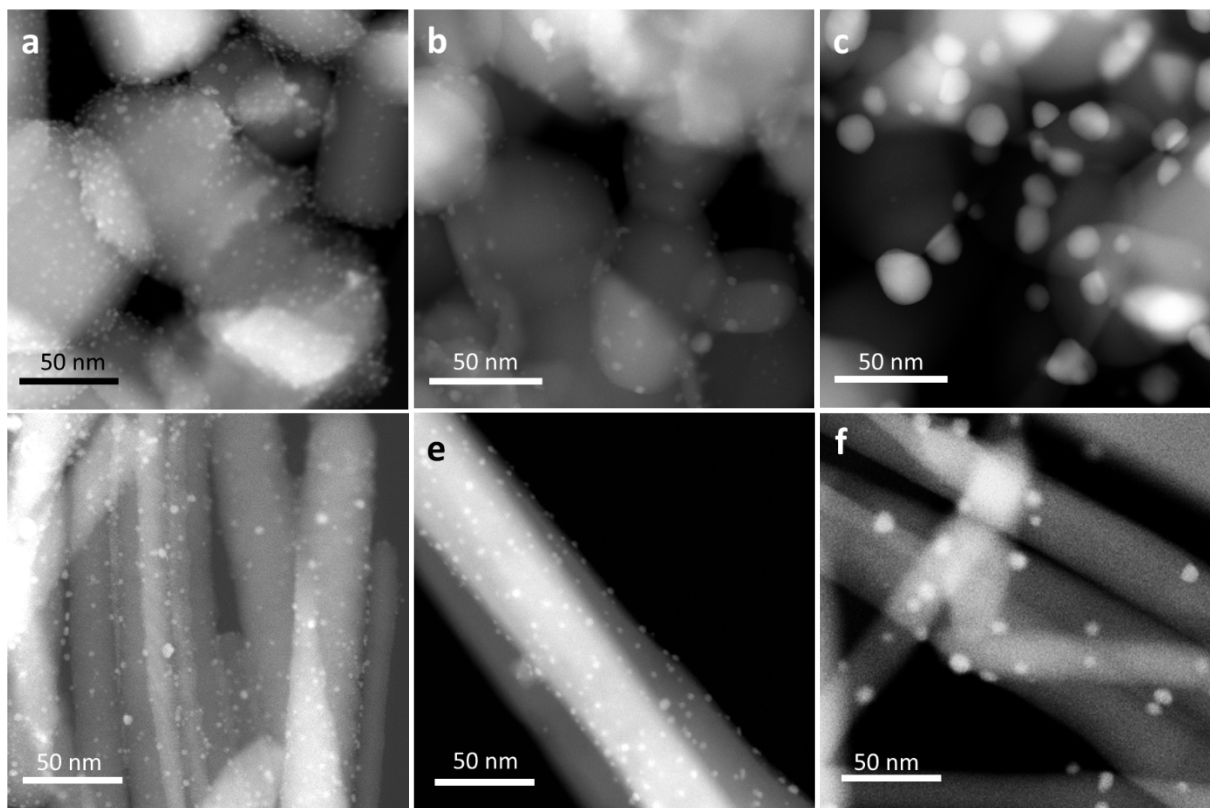


Figure S2. HAADF-STEM images of Au/ZnO-P200 (a), Au/ZnO-P400 (b), Au/ZnO-P600 (c), Au/ZnO-NW200 (d), Au/ZnO-NW400 (e) and Au/ZnO-NW600 (f), clearly revealing the sinter-resistance of the Au/ZnO-NW catalysts at high calcination temperatures.

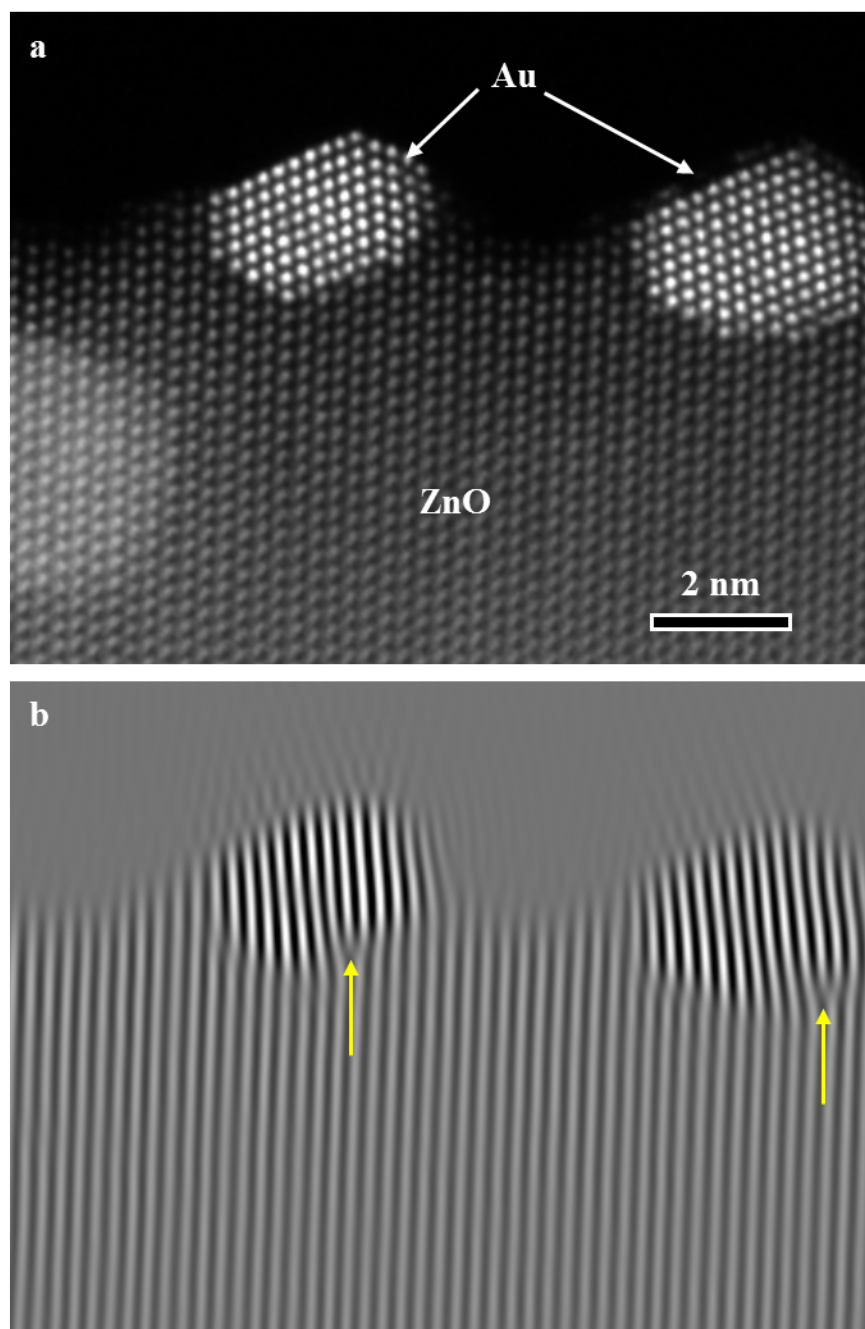


Figure S3. Atomic resolution HAADF-STEM image (a) of two Au NPs epitaxially anchored into a ZnO NW and the corresponding Fourier filtered image to reveal the interfacial misfit dislocations (indicated by the yellow arrows).

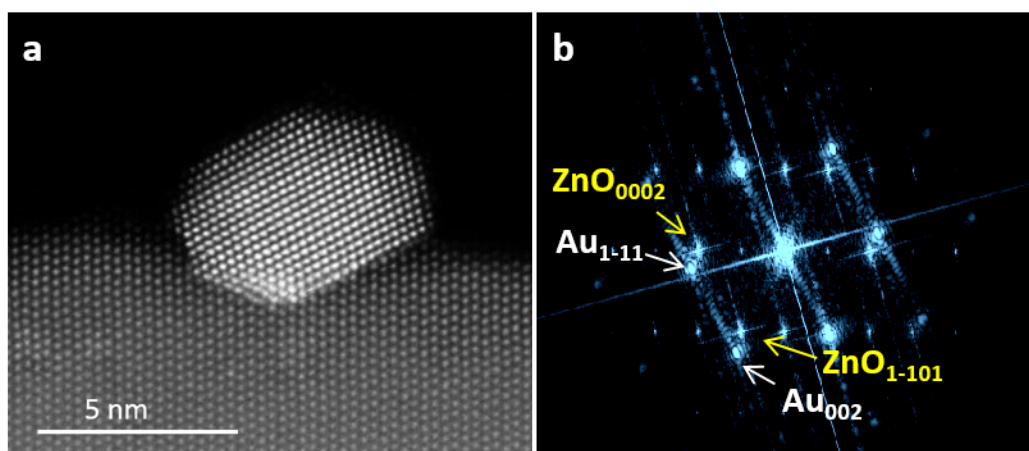


Figure S4. (a) HAADF-STEM image of Au/ZnO-NW600 and (b) the corresponding digital diffractogram confirming the epitaxial relationships between Au and ZnO.

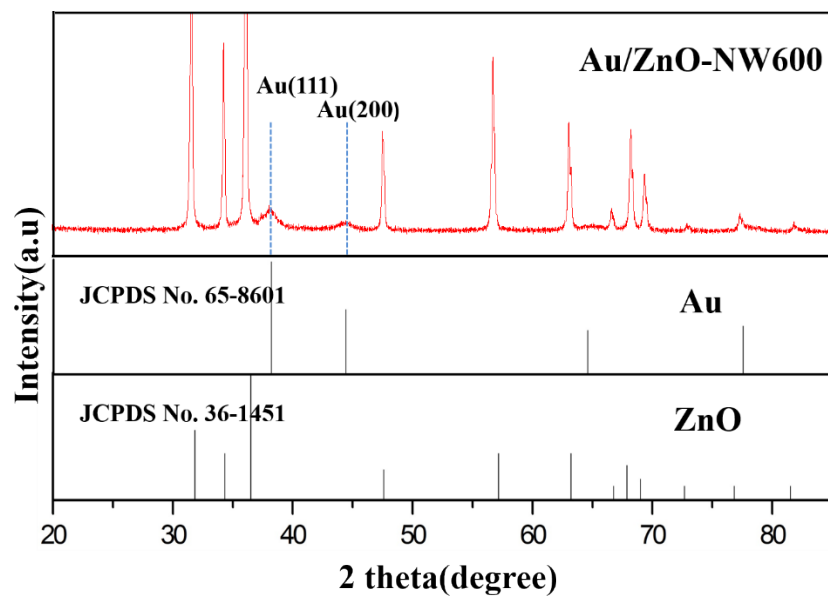


Figure S5. XRD pattern of 5.0% Au/ZnO NW after calcination at 600°C for 4h.