SUPPORTING INFORMATION

Catalytic activity of gold supported on ZnO tetrapods for the preferential oxidation of carbon monoxide under hydrogen rich conditions

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SI.1 Experimental details

Preparation of ZnO and Au/ZnO catalysts

Briefly, the synthesis involved the gas phase oxidation of zinc in the presence of air at 1073 K, where the temperature of zinc sublimation and the temperature of oxidation are tuned to achieve shape and size control. This method allowed the production of high puity tetrapods of ZnO formed by the gas phase self assembly of nanorods with aspect ratios > 100. Commercial ZnO (VP ADNANO 20 DW) from Evonik-Degussa, named ZnO_D, with a similar surface area was used for comparison. Catalysts were prepared by the deposition-precipitation method. The source of gold in all cases was chloroauric acid ($HAuCl_4$) supplied by Acros Organics. The deposition precipitation method was used to deposit the gold nanoparticles. Two procedures were followed: in the first one, the gold precursor (calculated for a 5% w/w catalyst) was dissolved in water and methanol (15:1), mixed with ZnO_T under stirring and brought to the desired pH of 11 with a solution of NaOH (0.2 M). The sample prepared by this way was named $Au1/ZnO_T$. The second synthesis used Na_2CO_3 (0.2 M) for pH adjustment to pH 11. Both solutions were stirred for 1h. They were added dropwise to a weighed amount of ZnO_T under stirring and the corresponding catalyst was denoted as $Au2/ZnO_T$. The latter procedure was repeated with the commercially available ZnO powder and this sample is denoted as Au/ZnO_D. For all the samples, the supports were stirred for 4 h with alternate stirring and sonication (ultrasonic bath, 298 K) the precipitate was washed several times with deionized water (until no Cl^- was detected with silver nitrate solution), and finally dried overnight at 373 K in air.

Characterization techniques

TEM images of the Au/ZnO catalysts before and after the reaction were taken on a JEOL 1011 transmission electron microscope. High resolution images were obtained on a JEOL JEM 2100F transmission electron microscope with a field emission gun (TEM-FEG). Average gold nanoparticle diameters were calculated from statistical distributions of measurements made on 400-500 particles per sample. A scanning Seifert XRD 3000 powder diffractometer was used to measure the X-ray powder diffractograms. BET surface areas of the support materials were measured from N_2 adsorption isotherms measured at liquid nitrogen temperature (Belsorp-mini). Raman spectra were taken on powder samples on a Perkin Elmer 400 Raman spectrometer with 830 nm red laser irradiation. The gold content in the catalyst was determined by acid digestion of the catalyst followed by ICP-OES analysis. The surface dispersion of the gold particles was calculated using equation (1):

$$DM = (6n_s M)/(r N d_p) \qquad (1)$$

Where n_s is the number of atoms at the surface per unit area ($1.15 \times 10^{19}/m^2$ for Au), M is the molar mass of gold (196.97 g/mol), r is the density of gold (19.5 g/cm^3), N is the Avogadro number (6.023×10^{23} at/mol) and d_p is the average particle size (determined by HRTEM, assuming that particles are spherical). These values are reported as percentage of the total gold content that is determined analytically.

PROX reaction

The catalytic performances of ZnO catalysts for carbon monoxide oxidation were evaluated in a continuous flow fixed-bed reactor. The gas mixture consisted of 1% CO, 1% O_2 and 40 % H_2 mixed with He at $1x10^{-2}$ cm^3/min and the products were analyzed by gas chromatography using a carboxen 1000 column. The selectivity and conversion values were calculated according to equations 2 and 3, where X and S are percentages of conversion and selectivity, respectively, and F is the inlet and outlet molar flow of the indicated gas.

$X_{CO} = (F_{inCO}-F_{outCO}/g_{Au}h)$ (2)

$S_{CO2} = ((F_{inCO}-F_{outCO}) / 2(F_{inO2}-F_{outO2}))\bullet 100$ (3)

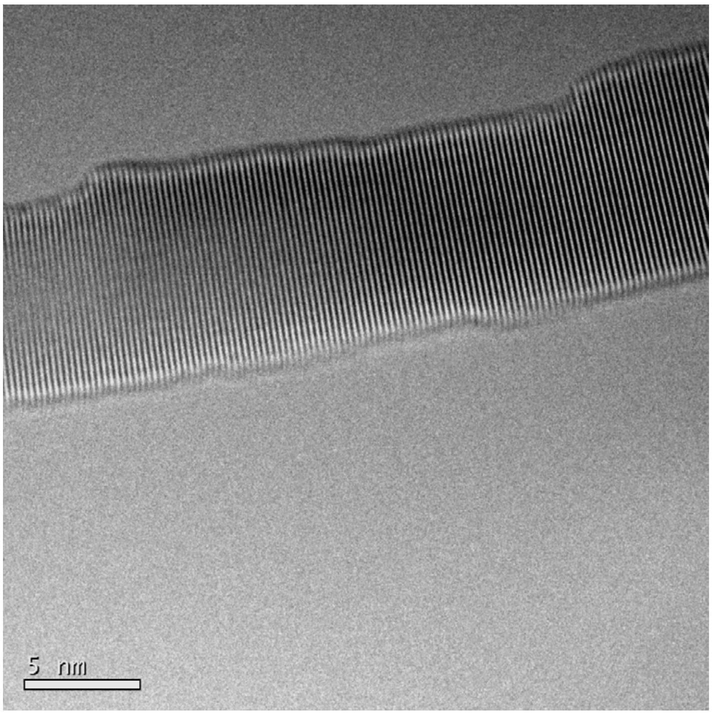

Figure SI.2 HRTEM of a single ZnO nanorod.

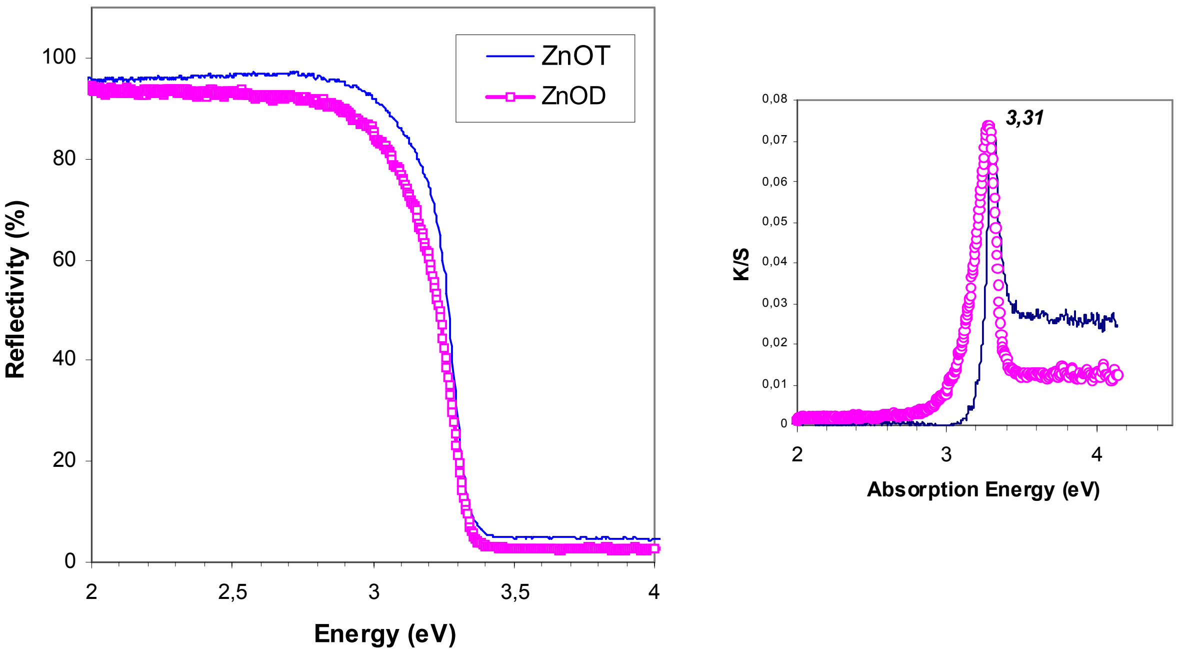

Figure SI.3 Diffuse reflectance spectra of ZnO$_T$ and ZnO$_D$ powders at 298 K. The plot of the Kubelka Munk function for the two spectra is shown on the right.

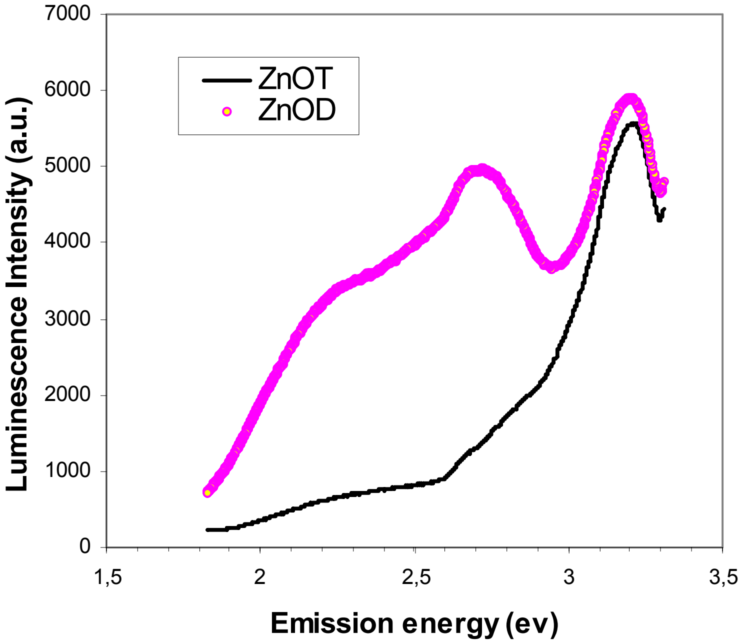

Figure SI.4 Luminescence spectra of ZnO_T and ZnO_D powders at 298 K.

Excitation energy = 3.65 eV.

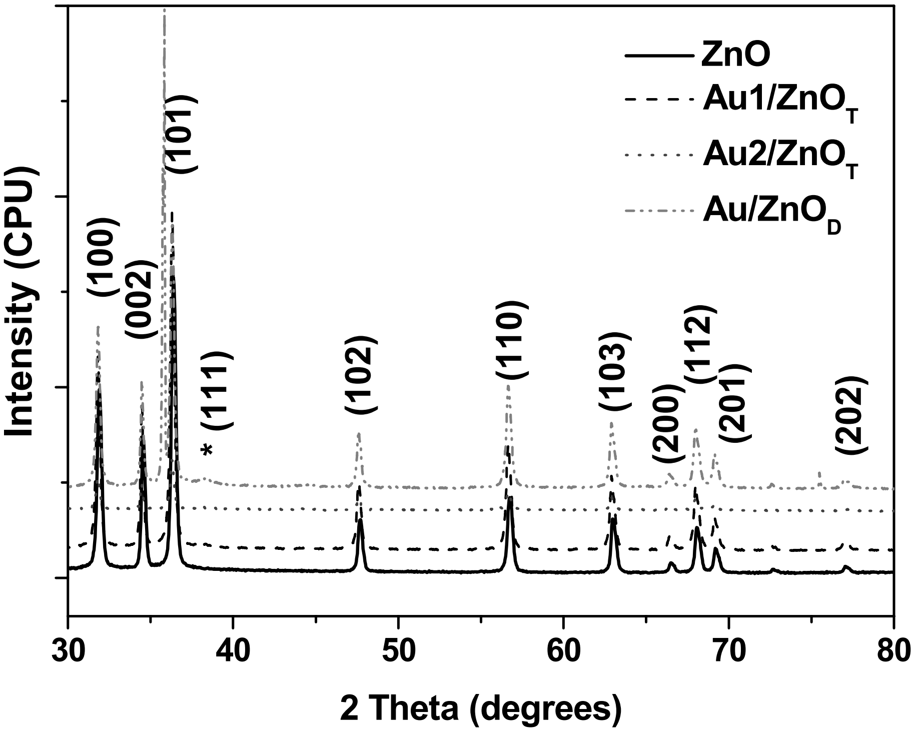

Figure SI.5 Powder X-ray diffractograms of the pure ZnO$_T$ support and Au/ZnO catalysts.

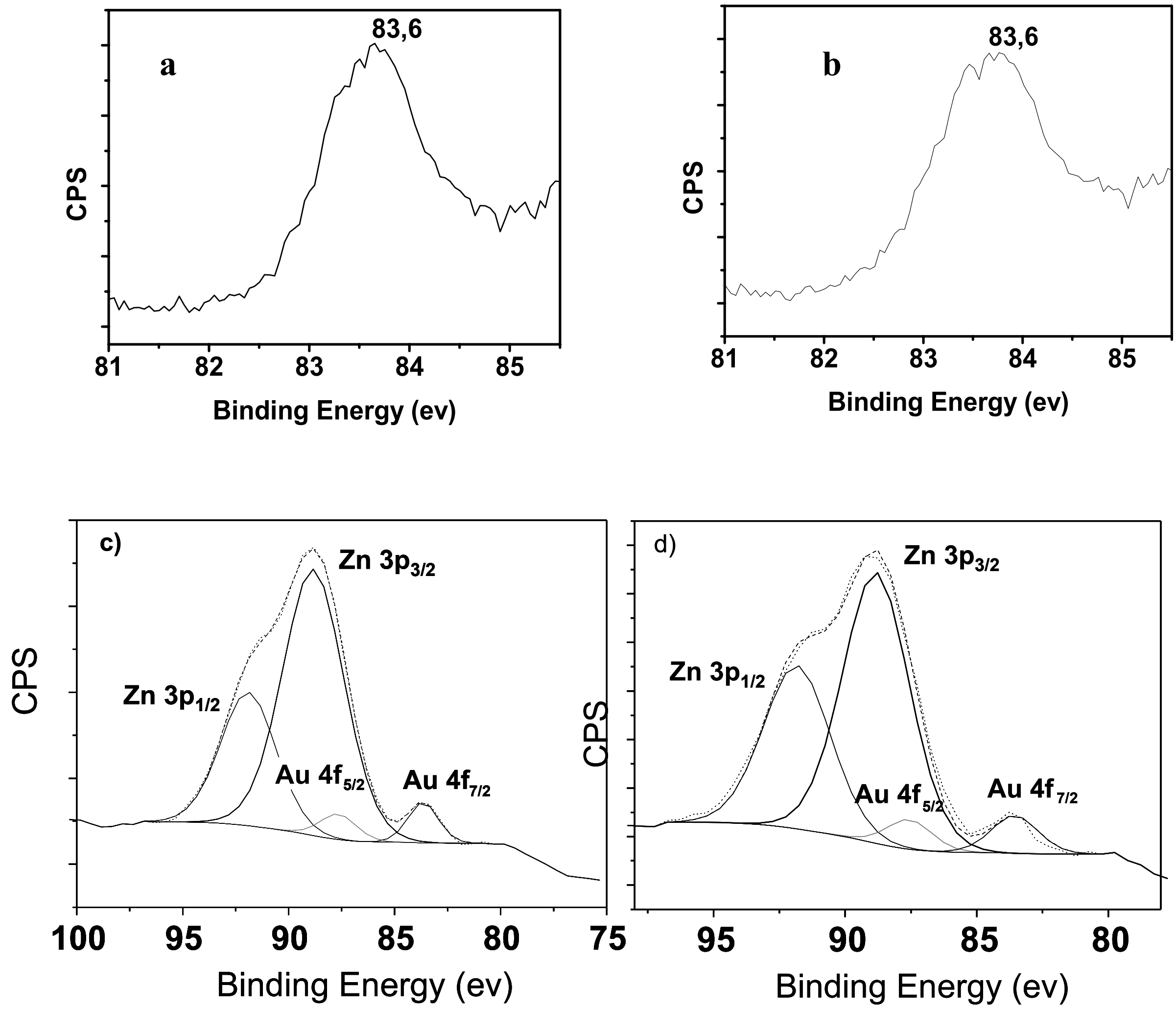

Figure SI6 XPS spectra of Au/ZnO$_D$ a) before and b) after reaction, c) the complete spectrum before reaction, and d) the complete spectrum after reaction.

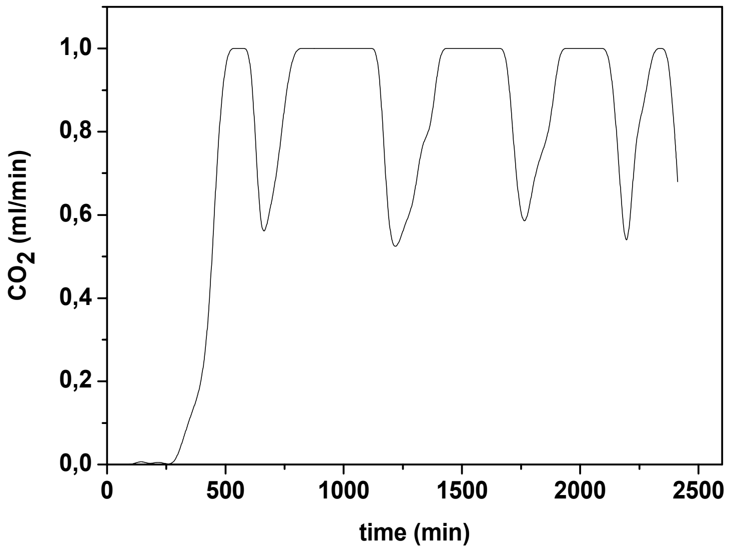

Figure SI.7 Produced CO_2 versus time for AU2/ZnO.