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Supporting Information

ZnO/Au Nanohybrids by Rapid Microwave-Assisted Synthesis for CO Oxidation

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Experimental Methods

ZnO/Au Hybrid Synthesis: The ZnO nanorods were first synthesized by the procedure reported earlier with slight modification in the duration of steps to control the length of rods[1]. For the synthesis of ZA-1, 100 mg of dry ZnO nanorods were dispersed in 30 ml distilled water by sonication. 5 mg $HAuCl_4$ (purchased from Sigma-Aldrich, USA) was dissolved in the reaction mixture taken in a standard 250 ml conical flask and subjected to microwave radiation (2.45 GHz, 800 W) for 180 s. The temperature measured at the end of reaction was ~ 100 ^oC. For ZA-2 and ZA-3, 50 mg and 20 mg of ZnO were taken, respectively, and all the other conditions were held to be same. Finally, the mixture was cooled to room temperature and the solid washed with water several times until there is no further reduction on addition of $NaBH_4$ indicating the absence of unreduced Au-salt and subsequently dried at 120 ^oC for 1 h. To understand the role of microwave (MW), control experiment (CE) was conducted where the synthesis of ZnO/Au was carried out at room temperature and 100^oC without microwave. All the steps were same as in ZA-2, however, in absence of MW. Samples were collected and characterized after 3 mins and 6 days.

Catalytic CO-oxidation Study: CO oxidation was carried out in continuous flow quartz reactors of 8 mm internal diameter. 35 mg of the catalyst in powder form was mixed with 965 mg of silica beads and was placed between ceramic wool plugs for a bed length of 11 mm to ensure a total bed volume of 553 mm^3. An inlet CO and O_2 flow rates of 2.4 ml/min each was maintained by control valves and the flow was diluted with N_2 for a total flow rate of 80 ml/min. The gas hourly space velocity calculated based on the catalyst bed volume (~15 mm^3) was 300,000 h^{-1}. All experiments were conducted in the isothermal mode. In order to carry out reactions under isothermal conditions, a PID temperature controller was used to maintain the temperature of the bed within ± 0.5 ^{o}C. A thermocouple was placed in the catalyst bed to continuously monitor the temperature. The temperature of the reactor was set at a predetermined temperature and the gases were allowed to flow continuously through the reactor. The gas chromatogram readings were taken after ensuring that the gases passed through the catalyst bed at constant temperature for at least 15 min. Three readings at the set temperature were taken and the temperature was then increased to the next set temperature. The reported conversions are the average of the three readings and the sample standard deviation of the reported conversions was less than ± 1%.

The gas mixture from the outlet of the reactor consisted of a mixture of CO, CO_2, O_2 and N_2. Three distinct peaks in the gas chromatogram were observed corresponding to CO, CO_2 and a combined N_2-O_2 peak. CO and CO_2 were detected using a flame ionization detector (FID) while N_2 and O_2 were detected using a thermal conductivity detector. The gas chromatographic system was equipped with a methanator, which used Ru catalyst at 350 ^{o}C, to convert CO to methane. Separation and quantification of N_2-O_2 was not possible. However, CO and CO_2 were quantified using a calibration gas mixture having a predetermined concentration of the gases. The conversions reported for CO oxidation is based on the formation of CO_2.

Experiments were also conducted in order to ensure the stability of the catalyst. The oxidation of CO was carried out continuously for 6 h over the samples at 210 ^{o}C and no decrease in conversion was observed. Experiments were also conducted by using the spent catalyst. The system was cooled and the temperature of the system was raised again in steps of 5 ^{o}C up to 250 ^{o}C. The conversions were monitored and the conversions obtained in the first cycle were similar (within ± 1%) to that obtained in the following few cycles indicating the stability of the catalyst. The XPS spectra of the catalyst before the reaction and after the first cycle were recorded.

Characterization Techniques: Transmission electron microscopy studies were carried out in Tecnai F30 microscope using 300 kV accelerating voltage. Samples were prepared on C-coated Cu grids and dried without heating. HAADF micrographs and EDS spectra were recorded at an α-tilt = 15^o using a spot size 6. A quantitative estimation of Au loading was done based on EDS data collected from 10-15 different regions on each sample and at% of Au was plotted as histogram.

X-ray photoelectron spectroscopy (XPS) were carried out in ThermoScientific Multilab 2000 instrument using Mg Kα source with a constant pass energy of 30 eV with the **chamber pressure** being maintained at 667 Pa. Charging effects were compensated by an **electron flood gun** and all BE shift correction due to charging were made with respect to C1s (graphitic carbon) peak at 284.5 eV. The deconvolution of spectra were done in Avantage Data System (a part of Thermo Fischer Scientific) software using the appropriate FWHM and the peak intensity ratio for the respective elements.

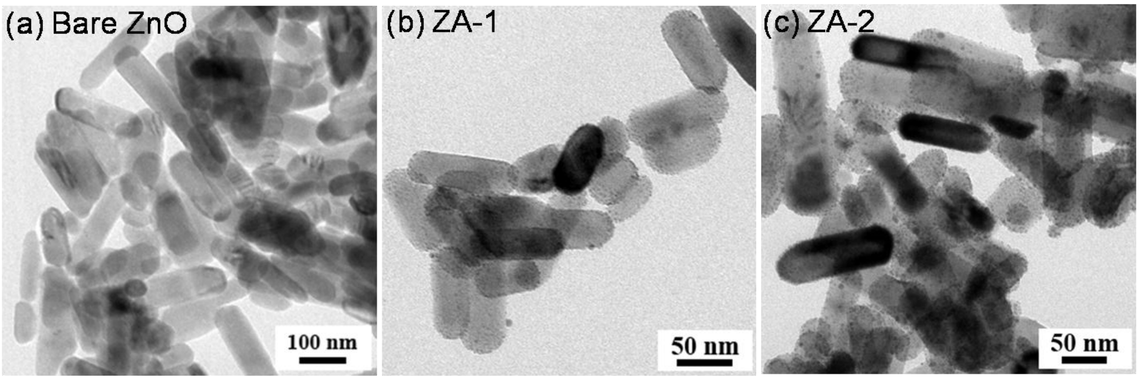

Figure S1. TEM bright field images of the bare ZnO nanorods (a), ZA-1(b) and ZA-2(c) for comparison of the site specific nucleation of the Au on reduction with water.

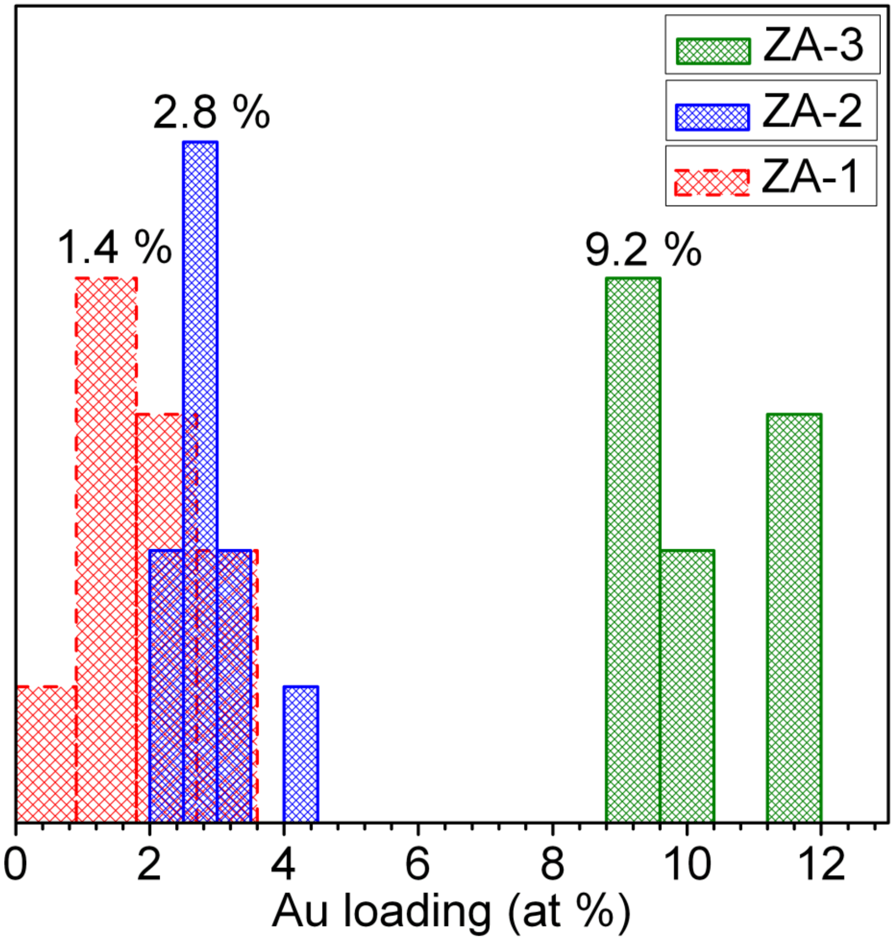

Figure S2. EDS Analysis of ZA-1, ZA-2 and ZA-3 hybrids with different loadings of Au

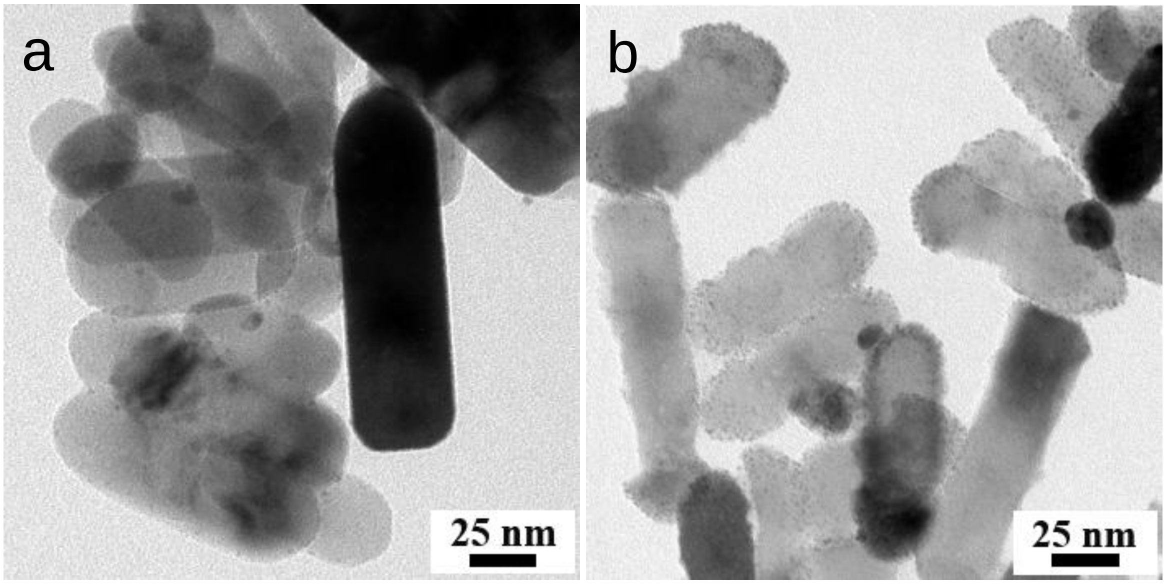

Figure S3. Bright field TEM images of ZnO-Au obtained by keeping the reaction mixture at room temperature for (a) 3 mins and (b) 6 days using the same concentration of ZnO and Au precursor as in ZA-2. It indicates that the nucleation of Au on ZnO is a slow process when microwave is not applied as in (a) and the particles nucleated after long time are often non-uniform in size as well as distribution as in (b). However, at several places preferential nucleation at the basal plane of the rods is observed but the morphology of the rods is deformed as in (b).

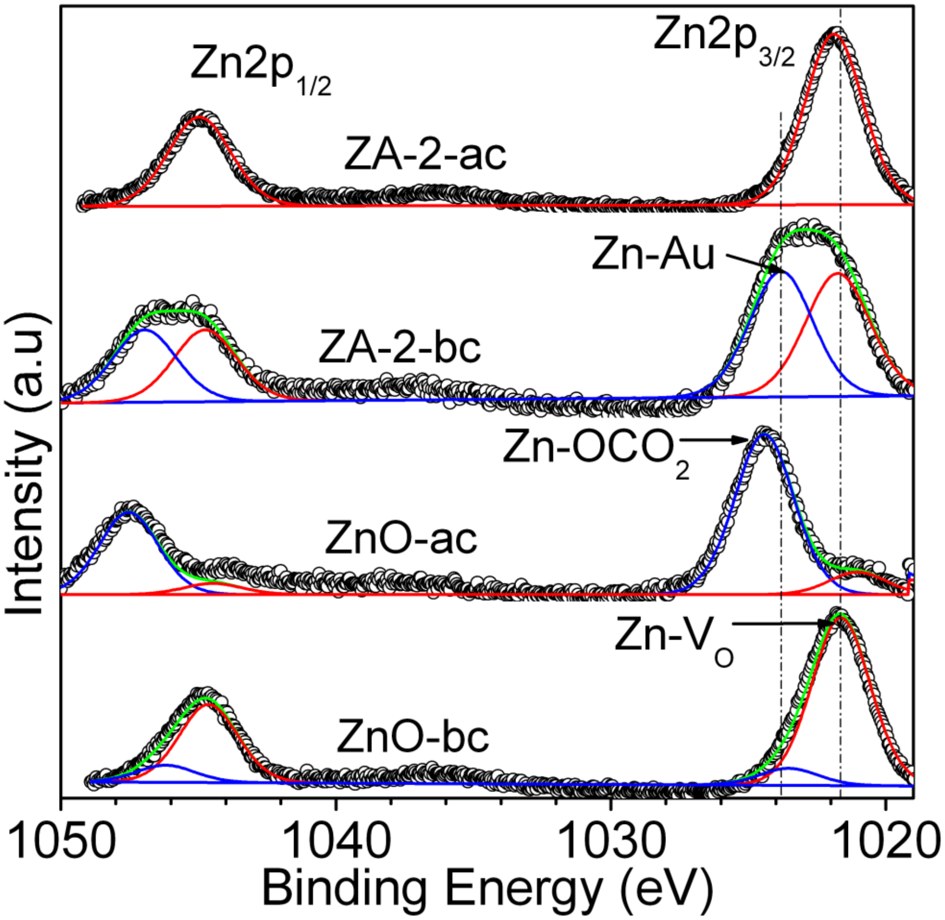

Figure S4. Core level Zn2p XPS for ZnO and ZA-2, before (-bc) and after catalysis (-ac) showing the BE shift to higher value (1024.4 eV) for ZnO (1021.6 eV) after catalysis due to the retension of the undecomposed carbonate, where it is linked to the Zn-site via a oxygen, and when modified with Au (1023.8 eV). The peak shifts back to lower value for ZA-2 after catalysis due to the reduction of the metal-support interaction.

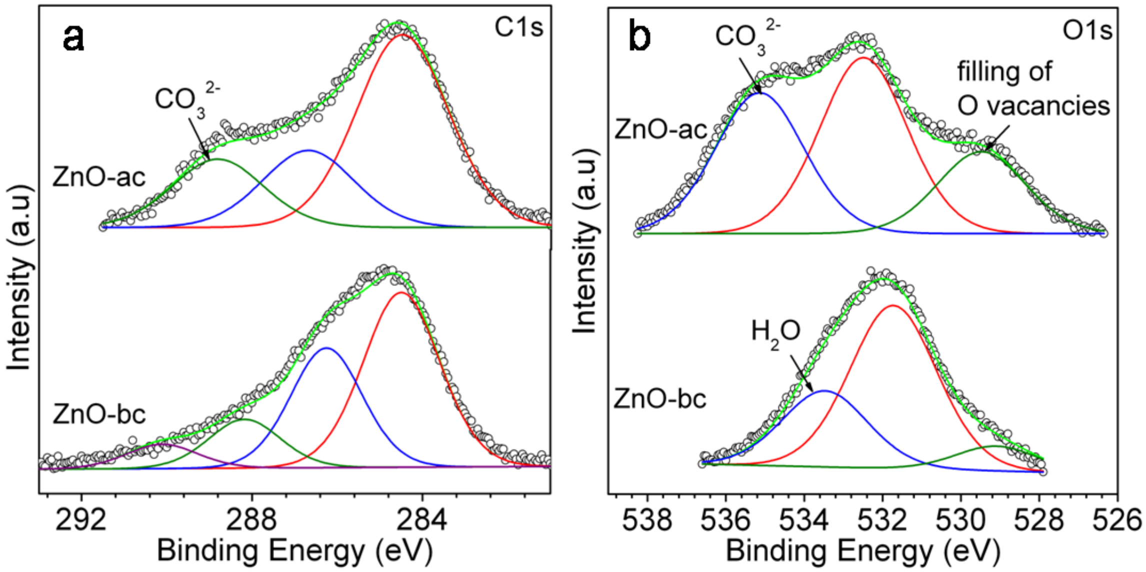

Figure S5. (a) C1s and (b) O1s core level XPS recorded for bare ZnO before (bc) and after (ac) catalysis which indicates formation of CO_3^{2-} species on the ZnO surface after CO oxidation. This is evident from the higher BE peak for C and O obtained in ZnO-ac. The relative increase in intensity of the lower BE peak of O1s indicates formation of Zn-O bonds leading to the occupancy of the O-vacancies after catalysis.

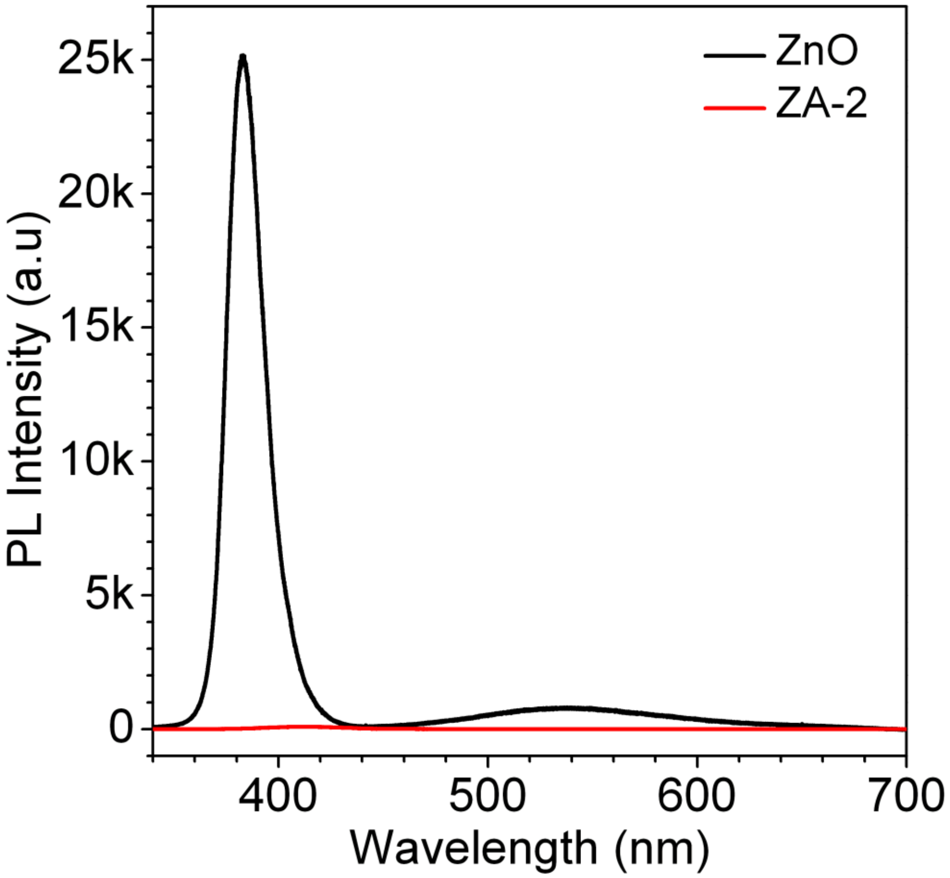

Figure S6. PL spectra of the ZA-2 compared to ZnO(bare) shows a complete quenching of the band edge emission and the green emission related to the O-vacant sites indicating a strong interaction between Au and ZnO where Au acts as a sink for the excitons at the vicinity of the O-vacancies. The PL study was carried out with same amount of samples (20 mg).

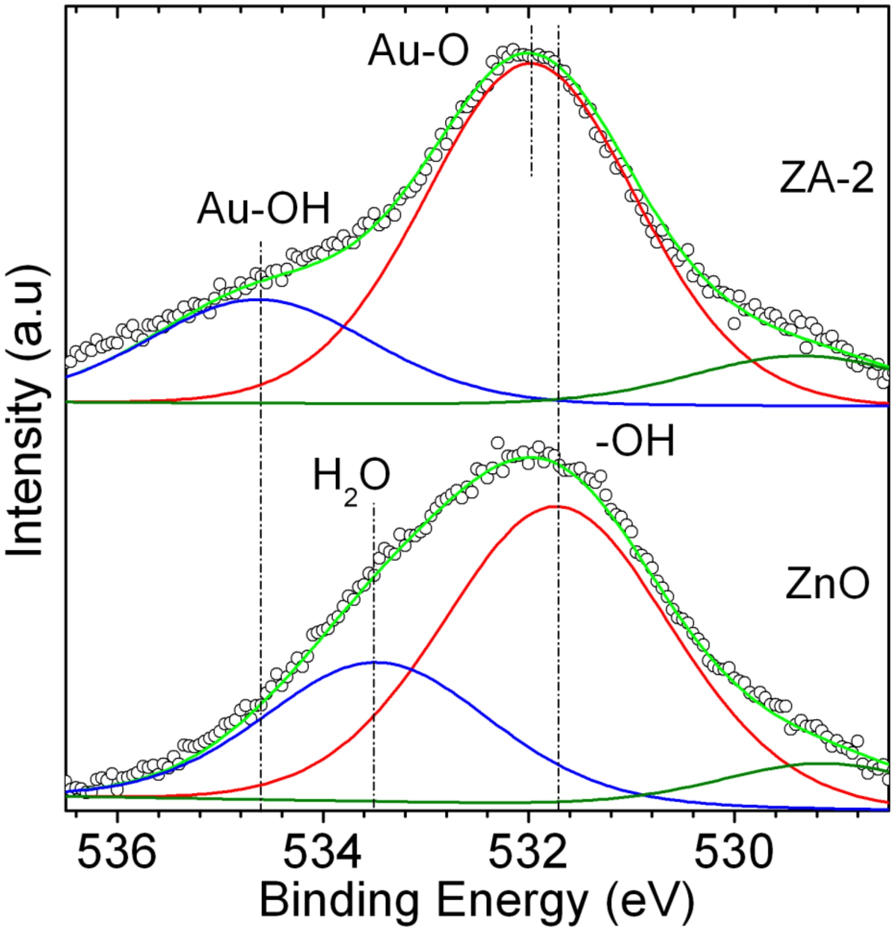

Figure S7. O1s core level XPS in bare ZnO shows the presence of surface hydroxyls and adsorbed H_2O which is converted to Au-O and Au-OH after attachment of Au to ZnO in ZA-2. Thus a corresponding shift of the BE is observed for O1s peaks.

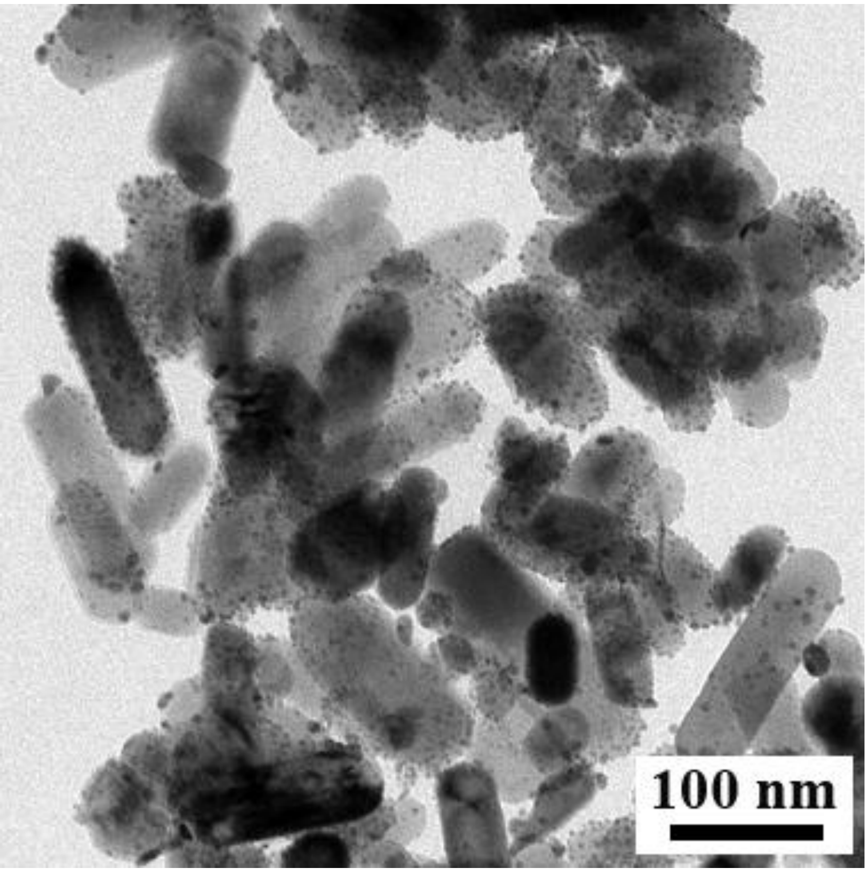

Fig. S8. TEM image of ZA-2 after catalysis showing coarsening of Au at some places, however, the fine particles of 2-3 nm size are retained in the sample in most of the regions indicating the sustained activity of the catalyst even after the destruction of the ionic Au sites.

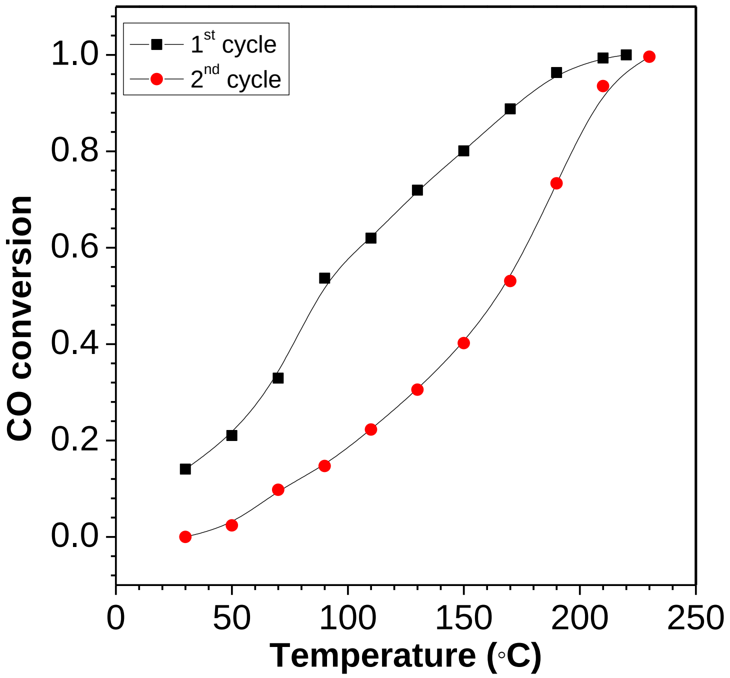

Fig. S9. Variation of CO conversion with temperature at repeated cycles using the catalyst ZA-2. The nature of the curve changes from convex to concave indicating a change in activity and mechanism of CO oxidation due to depletion of the ionic active sites but retention of the fine Au nanoparticles on the ZnO nanorods. The temperature for 100% CO conversion remains almost the same.

References

1. C. Pacholski, A. Kornowski and H. Weller, *Angewandte Chemie International Edition*, 2004, **43**, 4774-4777.