Supporting information for

Structure, morphology and catalytic properties of pure and alloyed Au-ZnO hierarchical nanostructures

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Content:

Experimental Procedures

Synthesis of the Au seeds

Au NCs were prepared according to the procedure reported by Peng et al.[1] 1 mmol *tert*-butylamine-borane complex (97%, Sigma-Aldrich) was dissolved in oleylamine (80-90%, Acros Organics, 2 mL) and 1,2,3,4-tetrahydronaphthalene (tetralin, Acros Organics, 2 mL) by sonication. This solution was swiftly injected into a solution of $HAuCl_4$ (200 mg) in 20 mL oleylamine (80-90%, Acros Organics) and 20 mL 1,2,3,4-tetrahydronaphthalene (tetralin, Acros Organics) kept at RT (~22 °C). Reduction occurred almost immediately as evidenced by a change in color from orange to dark red, but reaction was left stirring in air for 1 h. Then, the flask was sealed and flushed with N_2, and temperature increased to 60 °C. At this point, 100 µL of 1-dodecanethiol (>98%, Sigma-Aldrich) were slowly added. At the end of the addition (~3 minutes), flask was cooled and opened to air. Particles were then purified by three rounds of precipitation in isopropanol/ethanol 3/1 (40 mL) and centrifugation (8000 rpm, 3 minutes) with dissolution in hexanes after each step. Finally, particles were dissolved in hexane at a concentration of Au of ~5 mg mL^{-1}.

Synthesis of Au@ZnO structures

2 mL of the Au seeds were mixed with 1 mmol of Zn acetate dihydrate (>98%, Sigma-Aldrich) and 2 mmol of oleic acid (90%, Sigma-Aldrich) in 1-octadecene (12.5 mL). Hexanes from the Au solution was slowly removed at RT under vacuum, and mixture was then further evacuated at 80 °C for 30 minutes. The flask was then flushed with N_2, and temperature ramped to 300 °C, at which point 4 mmol of dried and degassed oleylamine (70%, Sigma-Aldrich) from the glovebox were injected. The reaction was left at 300 °C for 1 hour, then cooled to RT and Au@ZnO structures purified following the same steps as reported above for the Au seeds.

Synthesis of Au/Cd-ZnO structures

The synthesis was the same as described above for Au@ZnO, but Au/Cd seeds prepared as reported by Guardia *et al.*[2] were utilized instead of pure Au. Reaction was left at 300 °C for 5 minutes, then cooled to RT and purified as above.

Synthesis of pure ZnO

The synthesis was the same as described above for Au@ZnO, but without Au seeds.

Characterization techniques

TEM characterization was performed on a JEOL JEM 1400 operating at 120 kV, and on a Jeol JEM 2100 operating at 200 kV. Samples were prepared using 300 mesh carbon-coated Cu grids (Ted Pella, Inc.). UV-Vis spectra were recorded in transmission mode on a Cary 5000 spectrophotometer at 2 nm spectral bandwidth. XRD patterns were obtained on a Rigaku Smartlab diffractometer; patterns were measured in the 2θ range of 20-85 ° (Cu K_α radiation, $\lambda = 1.5418$ Å).

Catalytic characterization

Steady state rates of CO oxidation reaction were measured in a ¼-inch, quartz, tubular reactor, using 0.10 g of catalyst. All measurements were conducted at atmospheric pressure, with the partial pressures of CO and O_2 being 25 and 12.5 torr, respectively, and the balance being He. The total flow rate of the gas mixture was maintained at 120 mL min^{-1}. Before testing, each sample was activated by heating to 320 °C at 5 °C min^{-1} in the reaction mixture before cooling back to the desired reaction temperature. The composition of the reactor effluent was determined using an on-line gas chromatograph equipped with a HayeSep-D column and a thermal conductivity detector. All reported rates were measured with conversions below 15 % in order to ensure differential conditions.

The water-gas shift (WGS) experiments were performed with a similar setup in a ¼-inch, quartz, tubular reactor, using 100 mg of catalyst. Water was introduced to the reactor by saturation of a He carrier gas flowing through deionized water. The reactant partial pressures were fixed at 25 torr CO and 25 torr H_2O with a total flow rate of 120 ml min^{-1}. In determining reaction rates, conversions of CH_4 or CO were kept well below 10% so that differential conditions could be assumed. Products were analyzed using an on-line gas chromatograph (SRI8610C) equipped with a Hayesep Q column and a TCD detector.

Figure S1: TEM images of several batches of Au@ZnO structures prepared with same reaction conditions that demonstrate the reproducibility of the synthesis method.

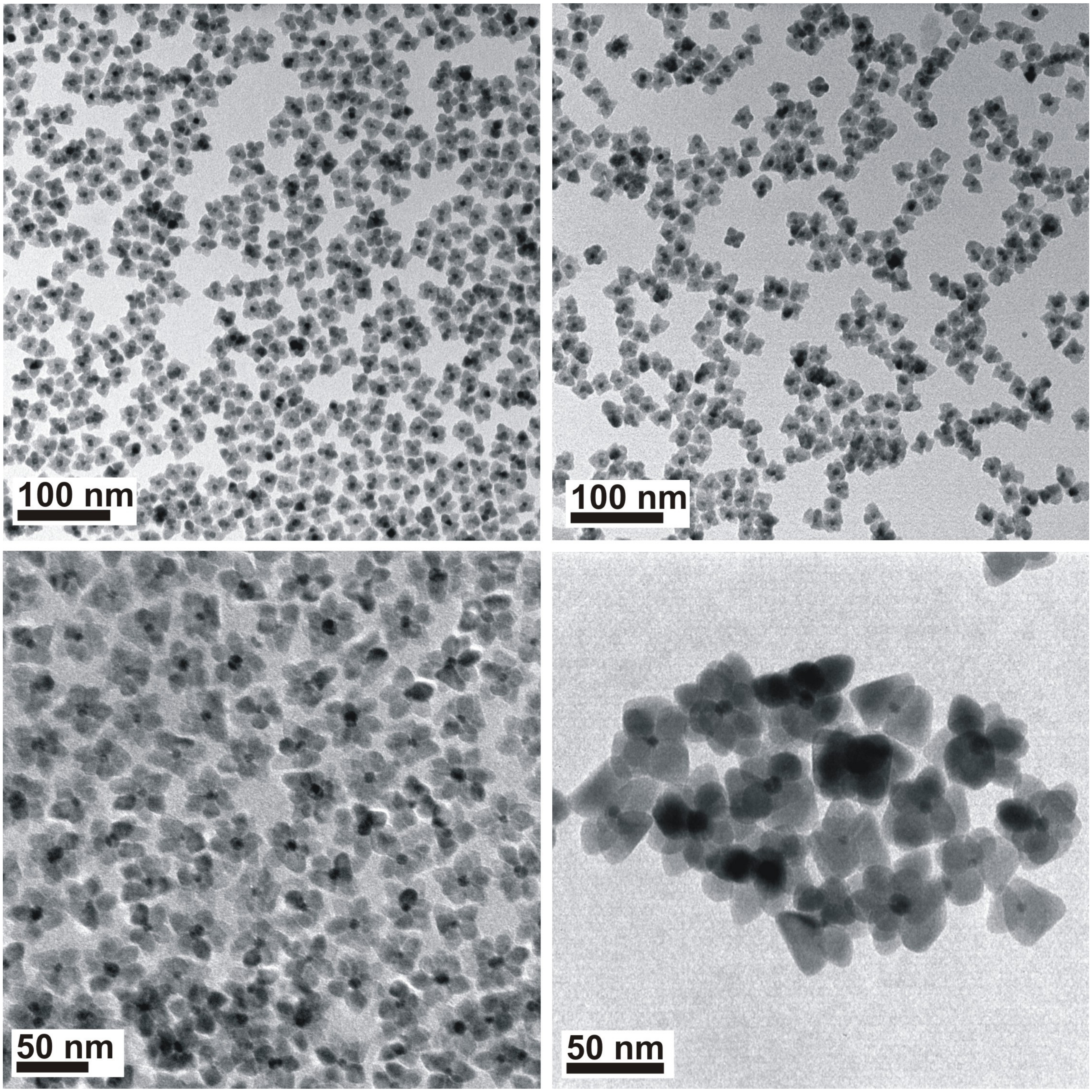


Figure S2: X-ray diffraction patterns of pure ZnO, Au@ZnO and Au/Cd-ZnO structures. For the Au/Cd@ZnO sample, a weak peak at ~40 ° 2θ demonstrates the formation of Au_2Cd intermetallic.

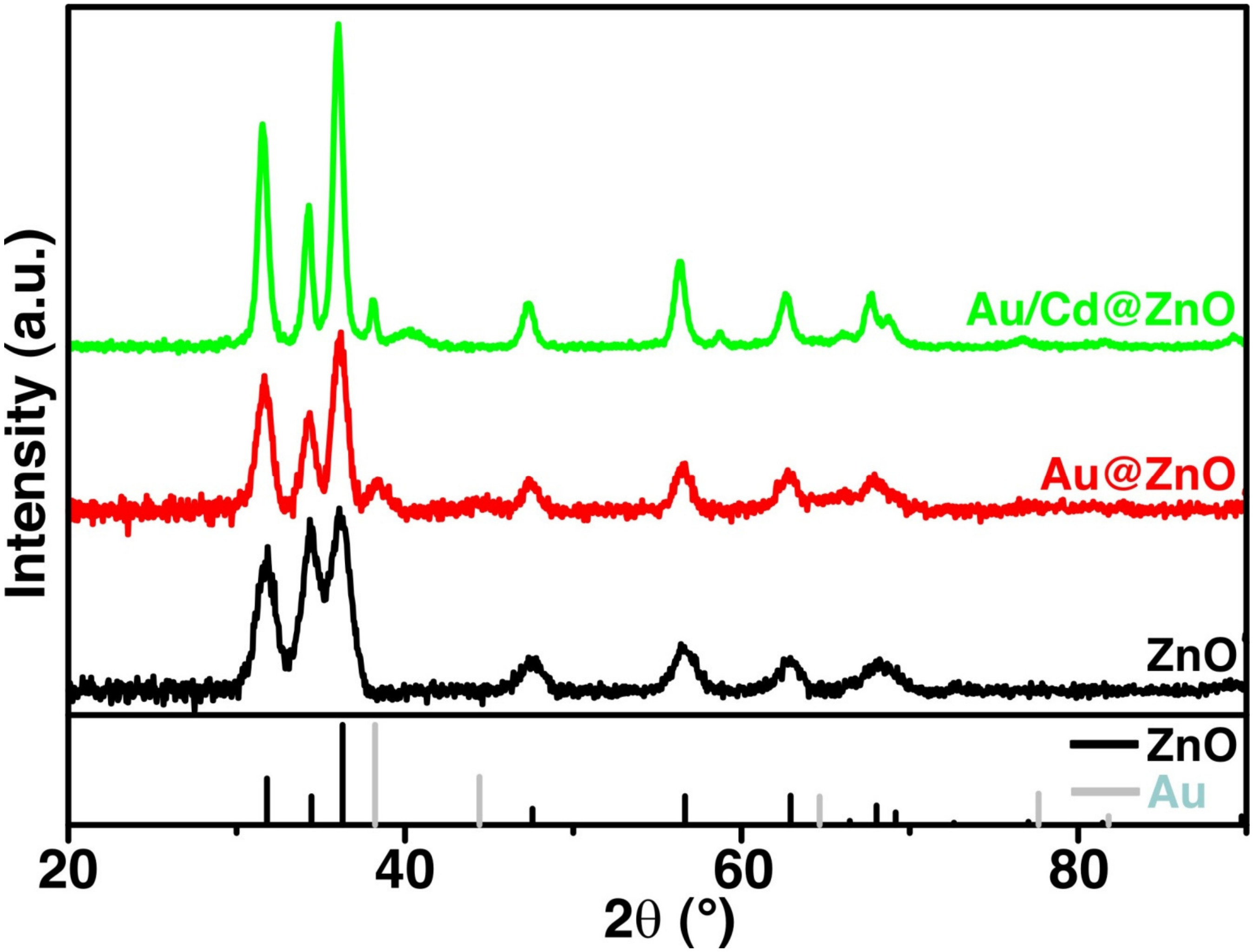


Figure S3: representative TEM images of the starting Au (a) and Au/Cd (b) seeds. The difference in crystallinity should be noticed, with pure Au rich in twinning defects and Au/Cd being single crystalline.

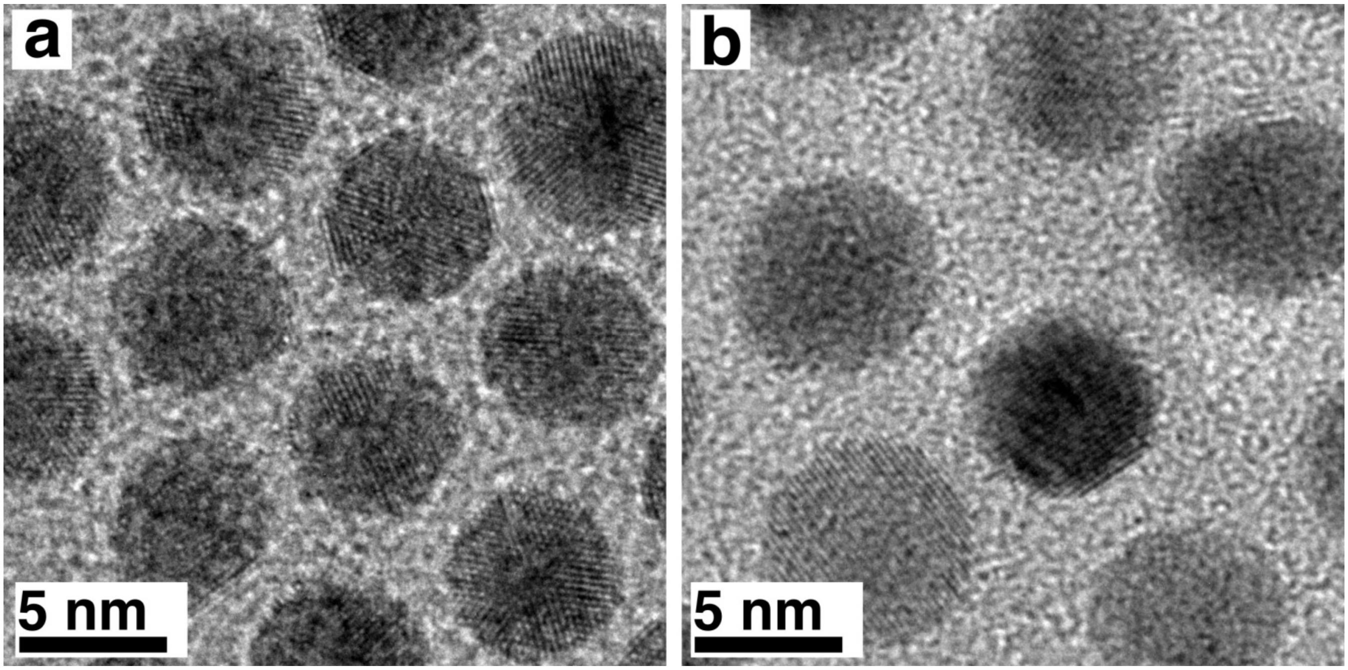
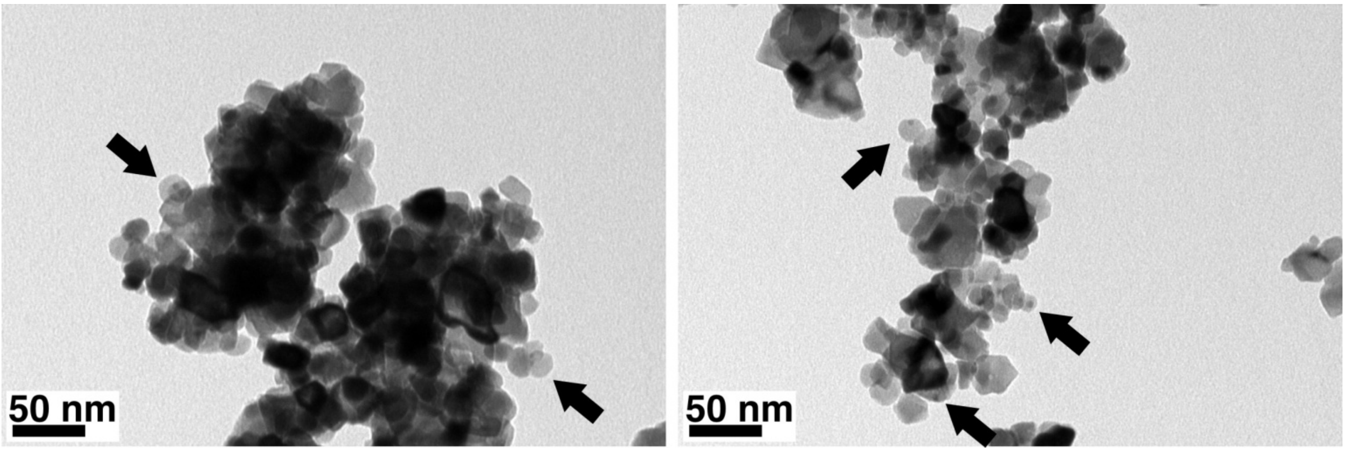


Figure S4: representative TEM images of Au@ZnO-Al_2O_3 after catalytic reaction. Arrows point to structures where the core-shell system is still intact.



References

1. S. Peng, Y. Lee, C. Wang, H. Yin, S. Dai, and S. Sun, *Nano Research*, 2008**, 1**, 229-234.
2. P. Guardia, K. Korobchevskaya, A. Casu, A. Genovese, L. Manna, and A. Comin, *ACS Nano*, 2013**, 7**, 1045-1053.