Supplemental Materials

Strong metal-support interactions between gold nanoparticles and ZnO nanorods in CO oxidation

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Chemicals:

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%), hexadecyltrimethylammonium bromide (CTABr, 99+%), hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O, for analysis ACS) and ethylenediamine (C₂H₄(NH₂)₂, EDA, 99%) were purchased from Acrös. Sodium hydroxide pellets (NaOH) and ethanol (EtOH, 99.9%) were purchased from J. T. Baker. Sodium borohydride (NaBH₄, 98%) and sodium carbonate (Na₂CO₃, anhydrous) were bought from Alfa and OSAKA, respectively. All chemicals were used without further purifications.

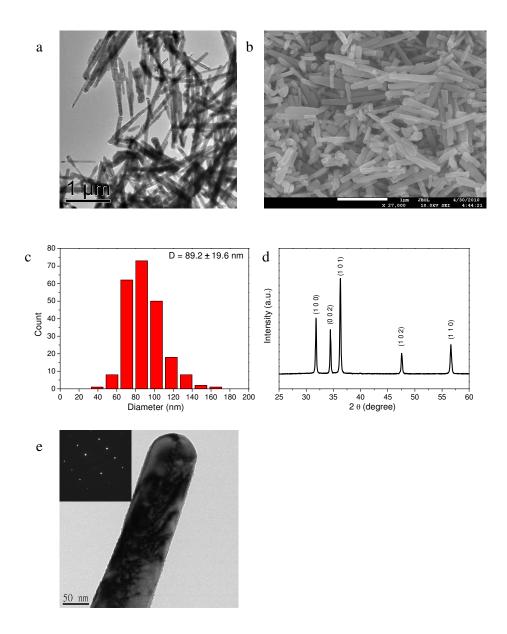


Figure S1 Basic nature of the ZnO nanorods: TEM image (a); SEM image (b); diameter distribution determined by the SEM images (c); XRD pattern (d); selected area electron diffraction patterns from an arbitrarily selected single ZnO nanorod (e).

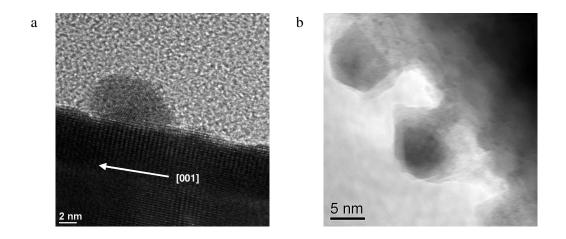


Figure S2 HRTEM images of Au/ZnO-nanorod pretreated at 200 $^{\circ}$ C (a) and 300 $^{\circ}$ C (b) under oxygen atmosphere, respectively.

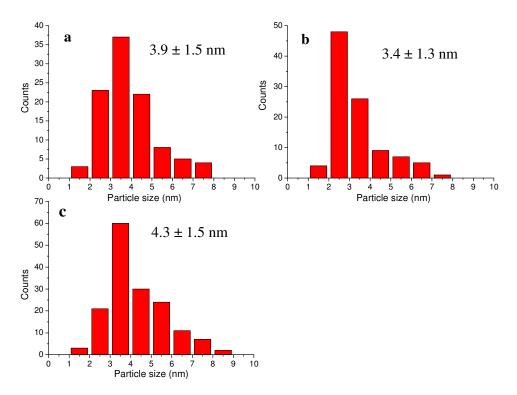


Figure S3 Size distribution of gold nanoparticles supported on ZnO nanorods pretreated under oxygen atmosphere at 200 $^{\circ}$ C (a), 300 $^{\circ}$ C (b) and followed by further pretreatment under hydrogen gas flow at 300 $^{\circ}$ C (c).

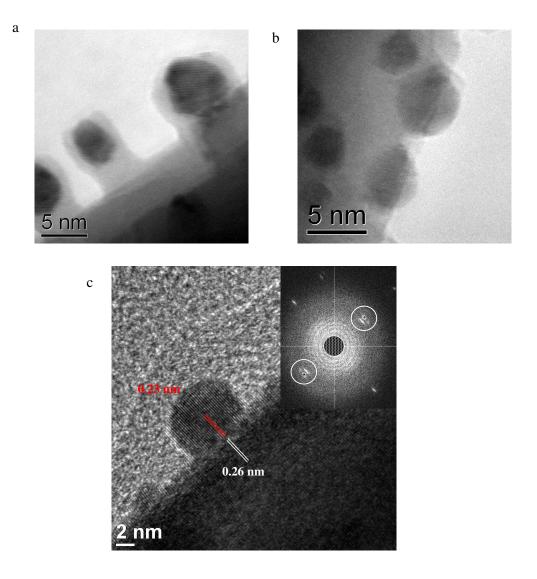


Figure S4 HRTEM images of Au/ZnO-nanorod pretreated at 300 $^{\circ}$ C in H₂ (99.999% H₂, flow rate: 30 mL•min⁻¹).

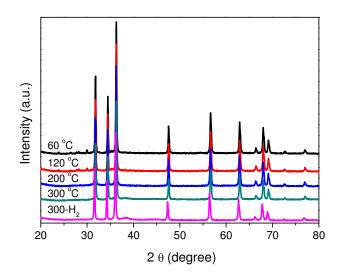


Figure S5 XRD patterns of Au/ZnO-nanorods pretreated under oxygen atmosphere at 60 $^{\circ}$ C, 120 $^{\circ}$ C, 200 $^{\circ}$ C, 300 $^{\circ}$ C and followed by further pretreatment under hydrogen gas flow at 300 $^{\circ}$ C.

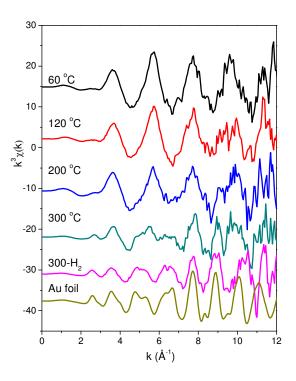


Figure S6 The k³-weighted EXAFS spectra at Au L_{III}-edge for 20Au/ZnO-nanorods pretreated under oxygen atmosphere at 60 °C, 120 °C, 200 °C, 300 °C and followed by further pretreatment under hydrogen gas flow at 300 °C. The noise level ratio increased when k > ~11.0 Å⁻¹. Therefore, $\Delta k = 3.1 - 11.1$ Å⁻¹ was used for Au foil and 20Au/ZnO-nanorod pretreated under O₂ atmosphere at various temperatures, while $\Delta k = 2.9 - 10.8$ Å⁻¹ was used for 20Au/ZnO-nanorod pretreated under H₂ atmosphere at 300 °C.

Au/ZnO-nanorod	XPS Au_{4f} and Zn_{3p} peak				
(pretreatment temperature)	Au ⁰ (atom%)	Au ⁺ (atom%)	Au ³⁺ (atom%)	Au/Zn (surface	
60	62.3	14.5	23.2	atomic ratio) 0.65	
120	74.8	13.3	11.9	0.56	
200	74.5	13.3	12.2	0.52	
300	80.6	14.3	5.1	0.30	
300-H ₂	97.3	2.7	0	0.32	

 Table S1 XPS analysis results of the Au/ZnO-nanorod catalysts.

The Au/ZnO-nanorod was pretreated under oxygen atmosphere at 60, 120, 200, 300 $^{\circ}$ C and followed by further pretreatment under hydrogen gas flow at 300 $^{\circ}$ C.

SMSI	Classical SMSI	O-SMSI	R-SMSI
Treatment	H ₂ -reduction	O ₂ -oxidation	H ₂ -reduction
Adsorption	reduced H ₂ , CO adsorption	reduced CO adsorption	reduced CO adsorption
Encapsulation	Yes, T > Ti	Yes, T > Ti	No, alloy, epitaxial interaction and sinking into the support
Activity	T > Ti, reduced activity	T > Ti, reduced activity	T > Ti, reduced activity
Electron transfer	substrate-to-metal	metal-to-substrate	substrate-to-metal
Reversibility	Yes	Yes	Yes

Table S2 Contrasts between classical SMSI with that of Au/ZnO.