

Electronic Supplementary Information

Metal-Support Interaction Induced ZnO Overlayer in Cu@ZnO/Al₂O₃ Catalysts toward Low-Temperature Water Gas Shift Reaction

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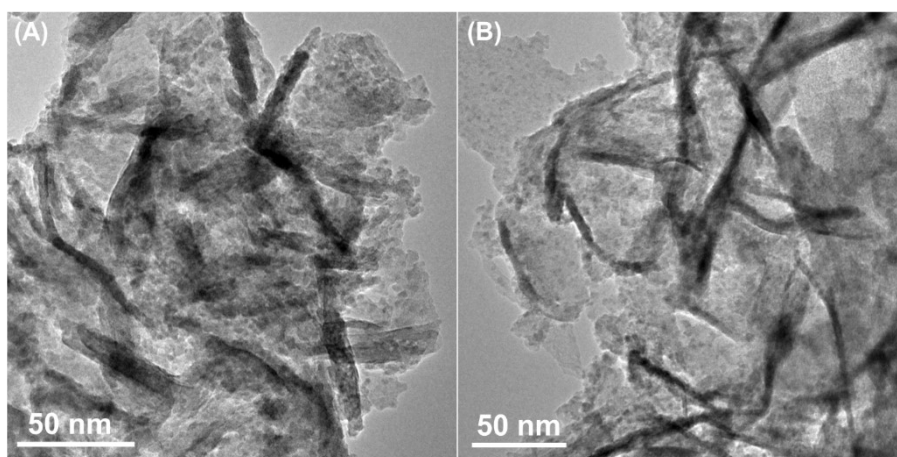


Figure S1. (A–B) TEM images of $\text{Cu}_2\text{Zn}_1\text{Al-LDHs}$.

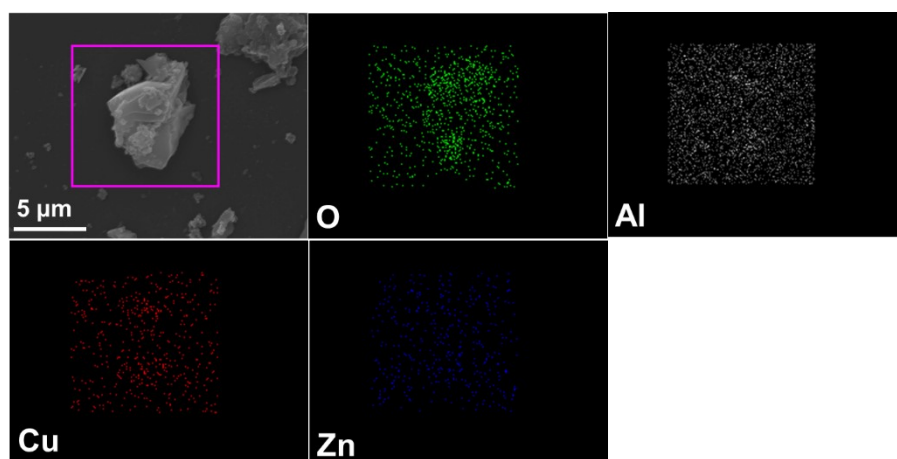


Figure S2. SEM image of $\text{Cu}_2\text{Zn}_1\text{Al-LDHs}$ and the corresponding element EDS mapping of Cu, Zn, Al, and O.

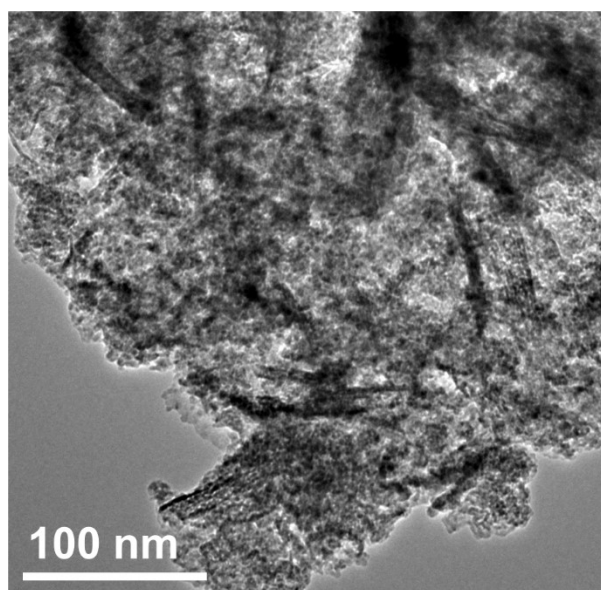


Figure S3. TEM images of Cu@ZnO/Al₂O₃-300R.

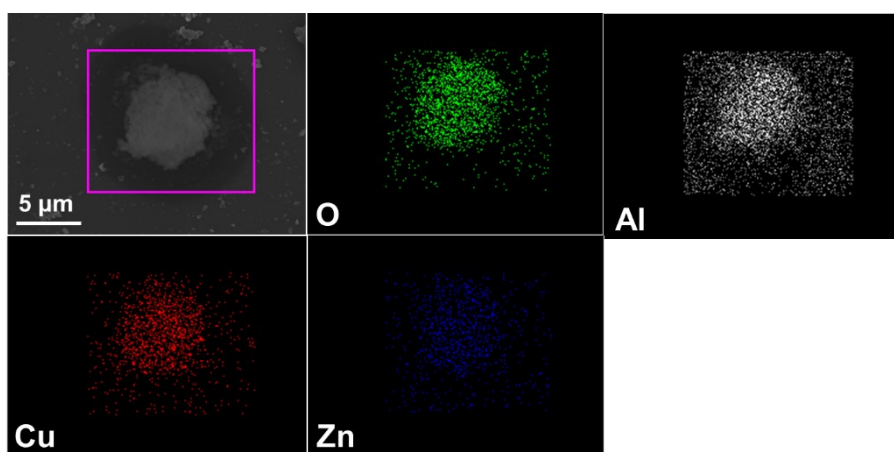


Figure S4. SEM image of Cu@ZnO/Al₂O₃-300R and the corresponding element EDS mapping of Cu, Zn, Al, and O.

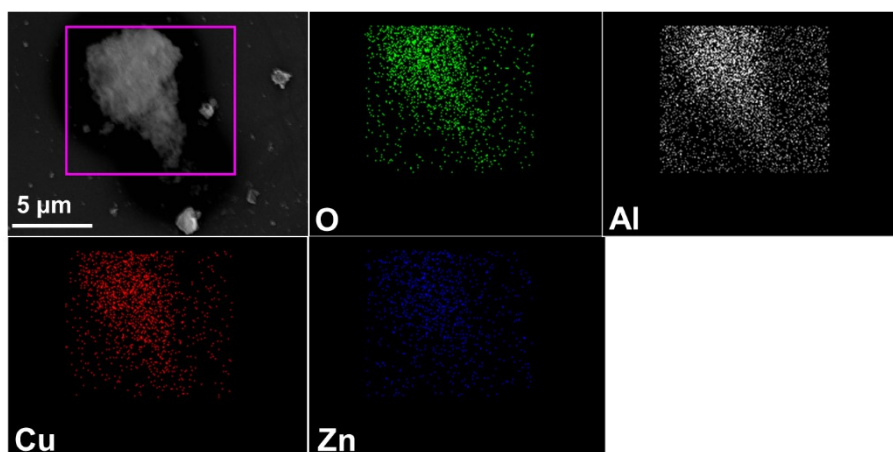


Figure S5. SEM image of Cu@ZnO/Al₂O₃-350R and the corresponding element EDS mapping of Cu, Zn, Al, and O.

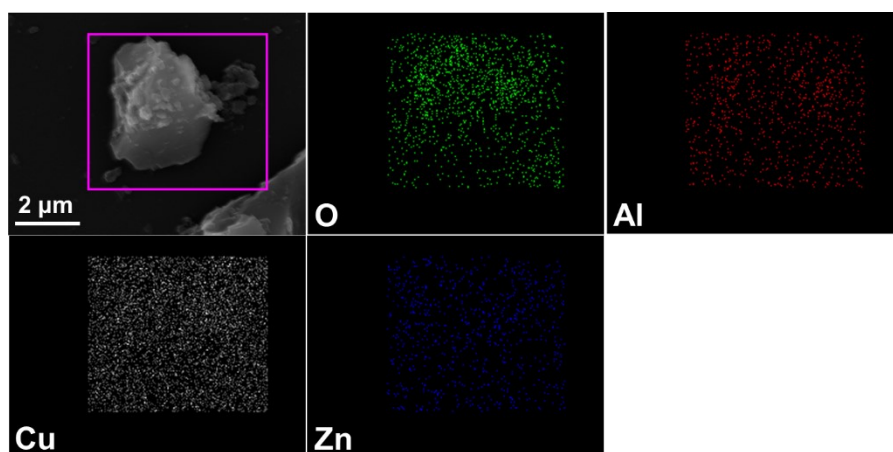


Figure S6. SEM image of Cu@ZnO/Al₂O₃-400R and the corresponding element EDS mapping of Cu, Zn, Al, and O.

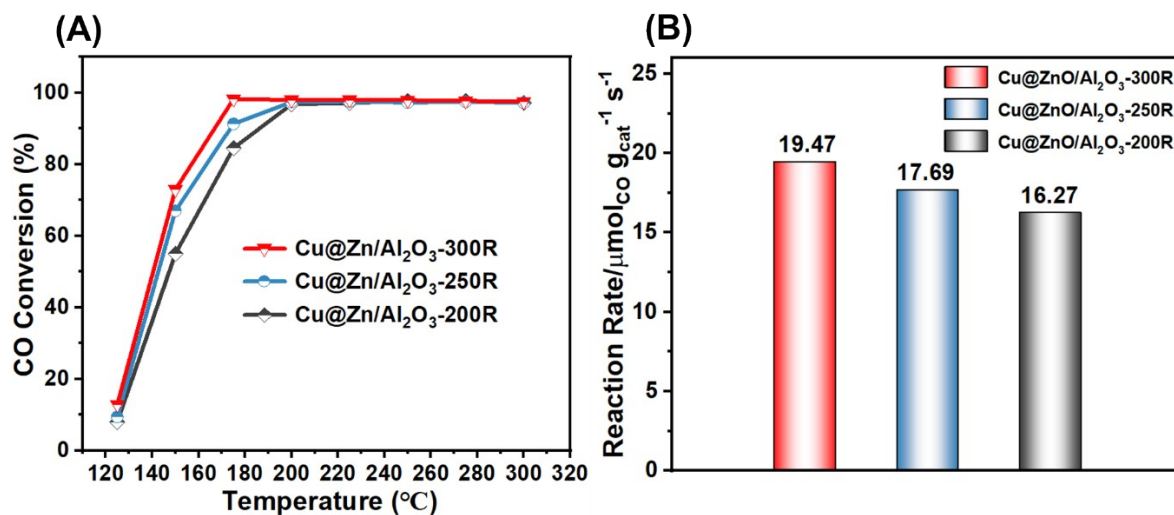


Figure S7. (A) CO conversion as a function of reaction temperature over the Cu@ZnO/Al₂O₃ catalysts (WGS reaction conditions: 6% CO, 25% H₂O, 69% Ar; WHSV: 15700 mL g_{cat}⁻¹ h⁻¹). (B) Reaction rates of Cu@ZnO/Al₂O₃-300R, Cu@ZnO/Al₂O₃-250R and Cu@ZnO/Al₂O₃-200R catalysts at 175 °C.

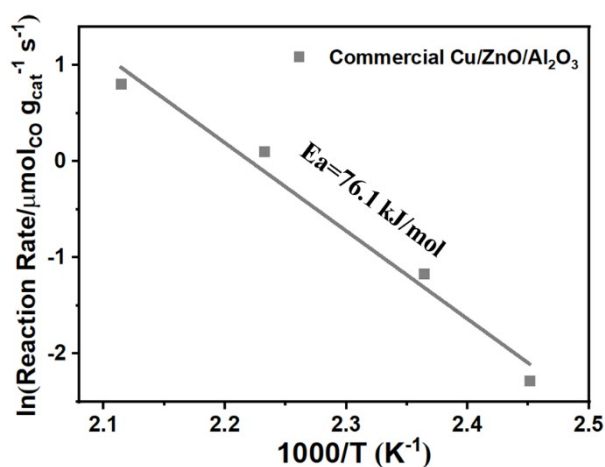


Figure S8. Arrhenius plots of WGS reaction over the commercial Cu/ZnO/Al₂O₃ catalyst. (WGS reaction conditions: 6% CO, 25% H₂O, 69% Ar)

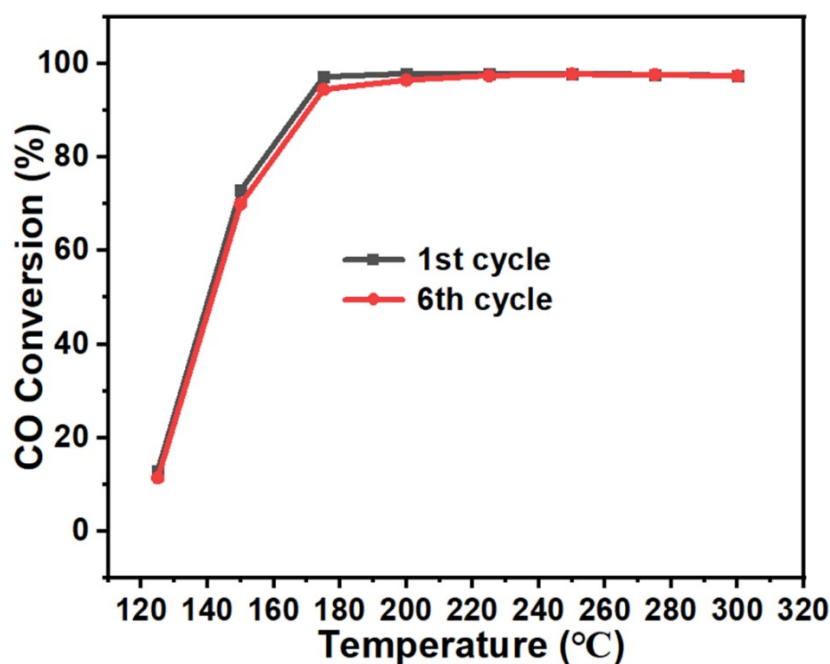


Figure S9. CO conversion as a function of reaction temperature over the Cu@ZnO/Al₂O₃-300R catalyst (WGS reaction conditions: 6% CO, 25% H₂O, 69% Ar; WHSV: 15700 mL g_{cat}⁻¹ h⁻¹).

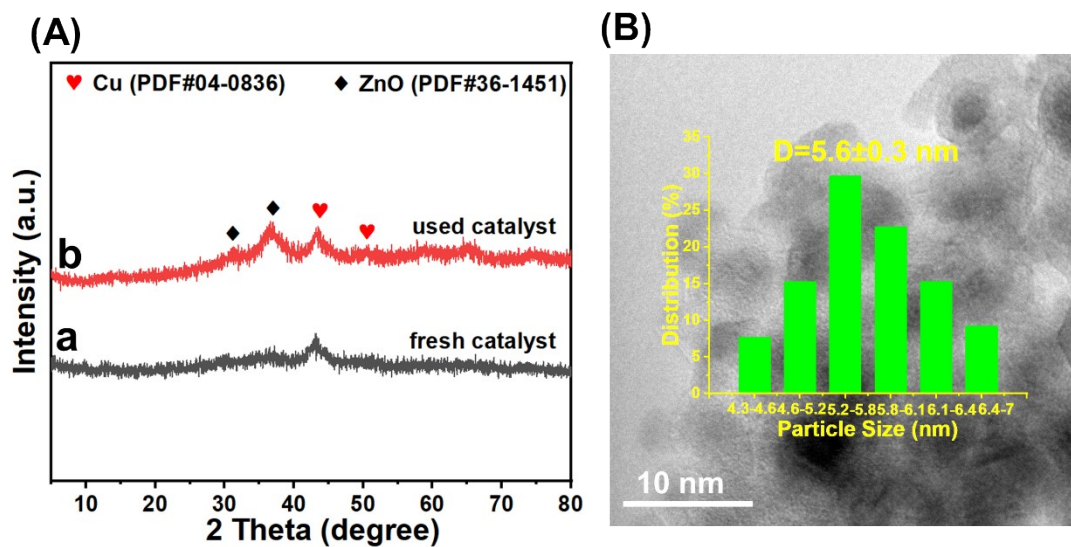


Figure S10. (A) XRD patterns of the Cu@ZnO/Al₂O₃-300R catalyst: (a) the fresh catalyst (b) the used catalyst after five cycles test. (B) TEM images of the used Cu@ZnO/Al₂O₃-300R catalyst after five cycles test.

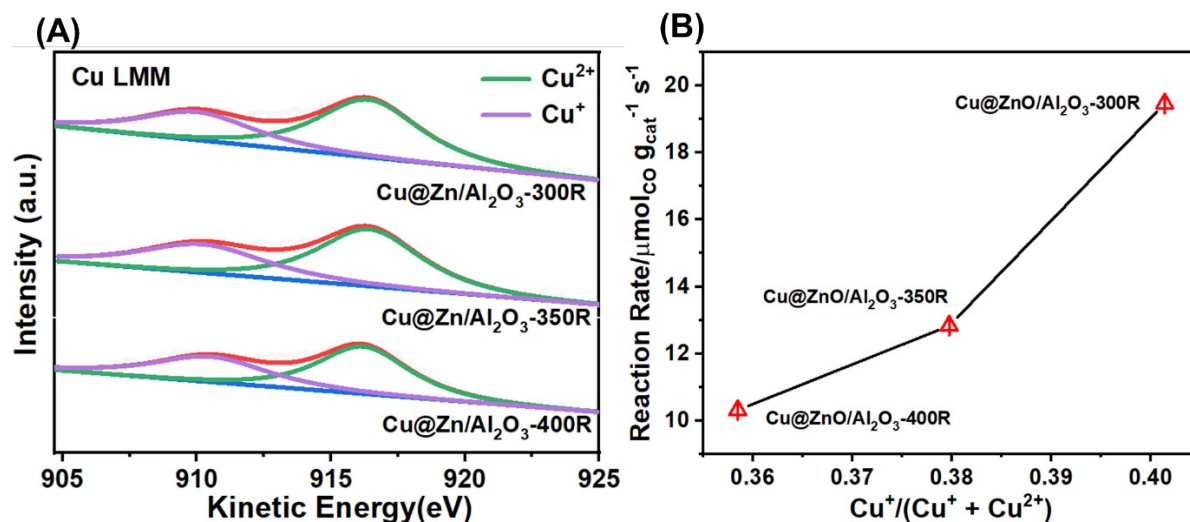


Figure S11. (A) XAES spectra of Cu LMM for Cu@ZnO/Al₂O₃-300R, Cu@ZnO/Al₂O₃-350R, and Cu@ZnO/Al₂O₃-400R. (B) Reaction rate as a function of surface Cu⁺ concentration.

Table S1. Physicochemical properties of Cu@ZnO/Al₂O₃-300R catalyst before and after five cycles test

catalysts	Cu species content ^a (wt %)	Zn species content ^a (wt %)	Al species content ^a (wt %)	Cu crystallite size ^b (nm)	mean Cu particle size ^c (nm)
Cu@ZnO/Al ₂ O ₃ -300R (fresh)	27.5	13.9	47.1	7.6	5.4
Cu@ZnO/Al ₂ O ₃ -300R (used)	27.1	13.6	47.0	7.9	5.6

^a Element content was determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES). ^b Crystallite size of Cu was determined by XRD with the Scherrer equation. ^c Mean particle size of Cu was determined by TEM.

Table S2. Physicochemical properties of Cu@ZnO/Al₂O₃-300R catalyst before and after stability test

catalysts	Cu species content ^a (wt %)	Zn species content ^a (wt %)	Al species content ^a (wt %)	Cu crystallite size ^b (nm)	mean Cu particle size ^c (nm)
Cu@ZnO/Al ₂ O ₃ -300R (fresh)	27.5	13.9	47.1	7.6	5.4
Cu@ZnO/Al ₂ O ₃ -300R (used)	27.7	14.3	47.4	8.0	5.8

^a Element content was determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES). ^b Crystallite size of Cu was determined by XRD with the Scherrer equation. ^c Mean particle size of Cu was determined by TEM.

Table S3. Comparison of catalytic performances for WGS over various catalysts

Catalyst	Reaction Temperature (°C)	Reaction Condition	Reaction Rate ($\mu\text{mol}_{\text{CO}} \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1}$)	Ref.
Cu@ZnO/Al ₂ O ₃ -300R	175	6%CO-25%H ₂ O-Ar	19.47	This work
Cu@ZnO/Al ₂ O ₃ -350R	175	6%CO-25%H ₂ O-Ar	12.83	This work
Cu@ZnO/Al ₂ O ₃ -400R	175	6%CO-25%H ₂ O-Ar	10.31	This work
Cu/ZnO/Al ₂ O ₃	175	6%CO-25%H ₂ O-Ar	3.58	This work
Cu _{8.9} /CeO ₂	300	10% CO, 20% H ₂ O, balance He	16.7	<i>Catal. Today</i> 2008 , 137, 29
Cu/CeO ₂	200	1.0 vol.% CO, 3.0 vol.% H ₂ O/He	4.0	<i>Nat. Catal.</i> 2019 , 2, 334
ZnO/c-Cu	225	5% CO, 10% H ₂ O, balance Ar	1.2	<i>Nat. Commun.</i> 2017 , 8, 488
Cu/ZnO/La	230	7% CO, 8.5% CO ₂ , 23% H ₂ O, 37.5% H ₂ and 25% N ₂	11.7	<i>J. Catal.</i> 2010 , 273, 73
Ce _{0.75} Cu _{0.1} Ni _{0.15} O _{2-δ}	240	1.3% CO, 35% H ₂ O	2.2	<i>Appl. Catal. B: Environ.</i> 2012 , 123, 367
Cu ₄ Ni ₁₆ /CeLaO _x	275	10% CO, 20% H ₂ O, balance He	15.6	<i>Appl. Catal., A</i> 2010 , 387, 87
Au@TiO _{2-x} /ZnO(H300)	250	6%CO-25%H ₂ O-Ar	15.2	<i>ACS Catal.</i> 2019 , 9, 2707
Au/CeO ₂	150	2%CO-10%H ₂ O-He	2.38	<i>Angew. Chem. Int. Ed.</i> 2008 , 47, 2884
Au/CeFeAl	180	4.5%CO-30%H ₂ O-N ₂	1.98	<i>J. Catal.</i> 2014 , 314, 1