

Sheet-like Morphology CuO/Co₃O₄ Nanocomposites for Enhanced Catalysis in Hydrogenation of CO₂ to Methanol

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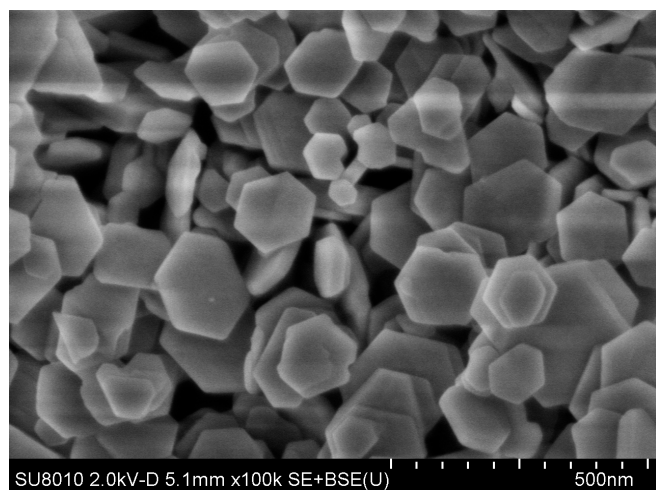


Figure S1. SEM image of Co(OH)_2 .

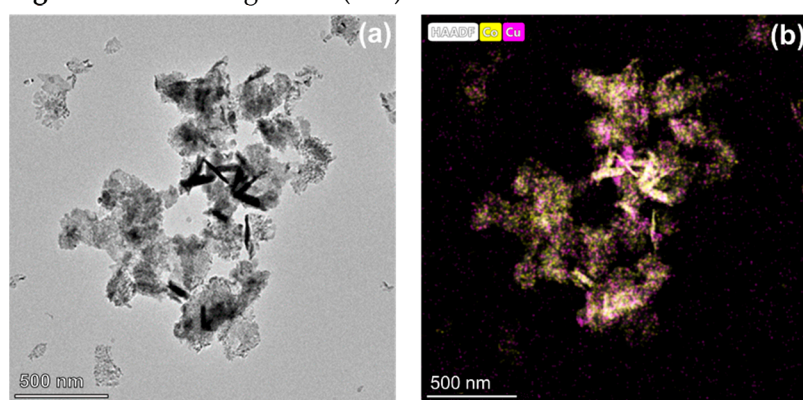


Figure S2. (a) STEM image of $\text{CuO/Co}_3\text{O}_4\text{-IM}$; (b) EDX elemental mappings of $\text{CuO/Co}_3\text{O}_4\text{-IM}$ yellow represents Co, and purple represents Cu.

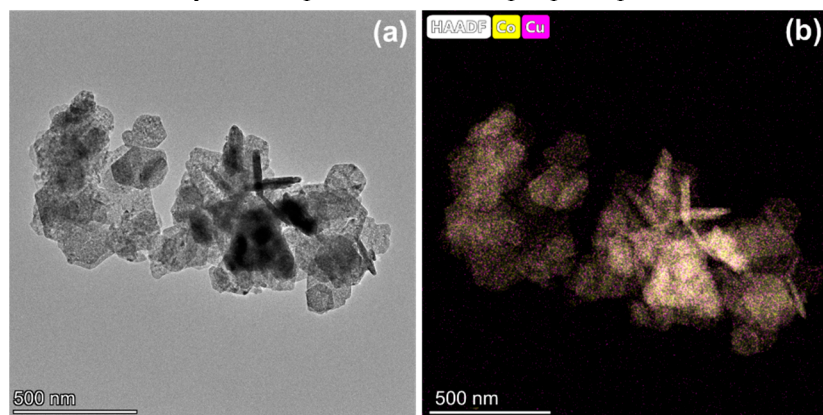


Figure S3. (a) STEM image of $\text{CuO/Co}_3\text{O}_4\text{-IE}$; (b) EDX elemental mappings of $\text{CuO/Co}_3\text{O}_4\text{-IE}$ yellow represents Co, and purple represents Cu.

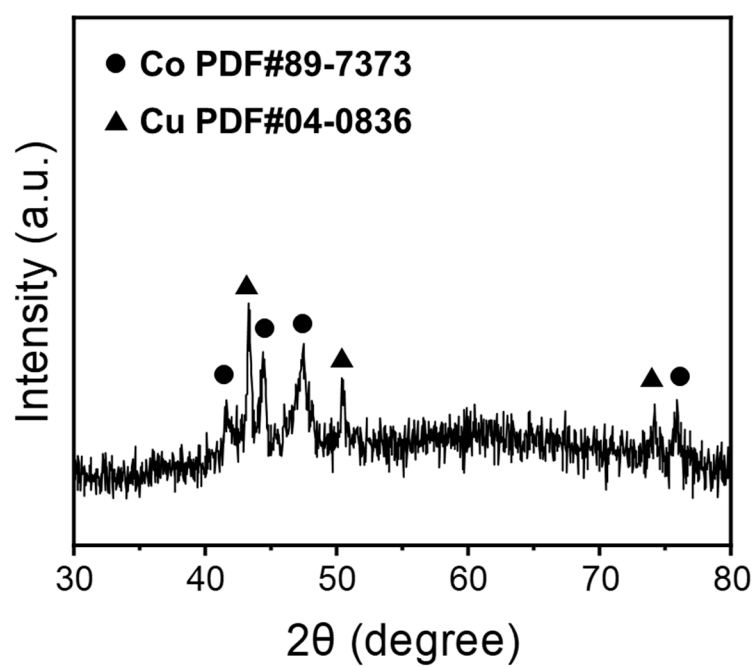


Figure S4. XRD patterns of CuO/Co₃O₄-IE spent catalyst.

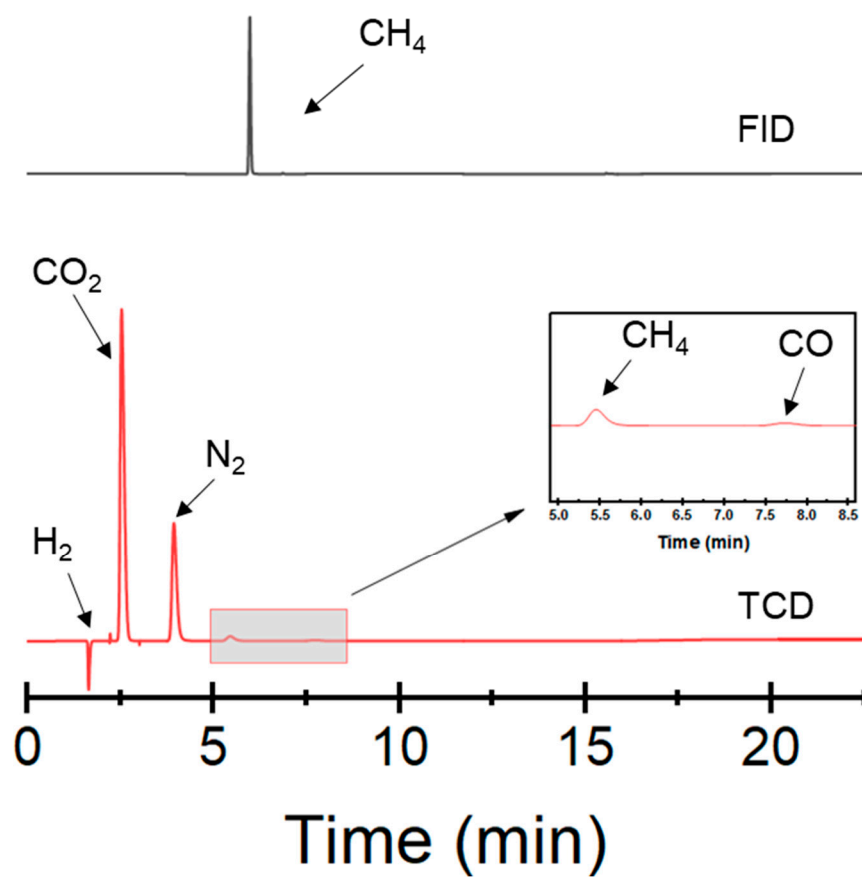


Figure S5. Agilent GC 7890B chromatogram of gas phase products of CO₂ Hydrogenation catalyzed by CuO/Co₃O₄-IE.



Figure S6. Agilent GC 4890D chromatogram of liquid phase products of CO₂ Hydrogenation catalyzed by CuO/Co₃O₄-IE.

Table S1. The results of XPS Co 2p_{3/2} for CuO/Co₃O₄-IE, CuO/Co₃O₄-IM and Co₃O₄ catalysts.

Catalysts	Co 2p _{3/2} Binding Energy (eV)	
	Co ³⁺	Co ²⁺
Co ₃ O ₄	779.9	781.5
1CuO/4Co ₃ O ₄ -IM	779.5	780.9
1CuO/4Co ₃ O ₄ -IE	779.4	780.8

Table S2. XPS O 1s fitting peak data of the different catalysts.

Catalysts	O (%)	O _c /O _T ^a	O _d /O _T ^a	O _i /O _T ^a
Co ₃ O ₄	71.1%	8.9%	36.6%	54.5%
1CuO/4Co ₃ O ₄ -IM	66.8%	11.2%	29.5%	59.1%
1CuO/4Co ₃ O ₄ -IE	65.3%	5.6%	31.0%	63.4%

Table S3. The results of XPS O 1s for CuO/Co₃O₄-IE, CuO/Co₃O₄-IM and Co₃O₄ catalysts.

Catalysts	O 1s Binding Energy (eV)		
	O _{lattice}	O _{defect}	O _{chemisorbed}
Co ₃ O ₄	530.0	531.3	533.1
1CuO/4Co ₃ O ₄ -IM	529.8	531.5	533.2
1CuO/4Co ₃ O ₄ -IE	529.8	531.8	533.6

Table S4. X-ray photoelectron spectroscopy surface elemental concentrations (at.%) as well as the relative surface concentration of the elements.

Catalysts	Co%	Cu%	O%
Co ₃ O ₄	70.5	0	29.5
1CuO/4Co ₃ O ₄ -IM	65.3	11.7	23.0
1CuO/4Co ₃ O ₄ -IE	65.0	6.3	28.7

Table S5. Chemisorption amounts of CO and H₂ over CuO/Co₃O₄-IE, CuO/Co₃O₄-IM and Co₃O₄ catalysts.

Catalysts	CO ₂ -TPD	H ₂ -TPD
	CO ₂ uptake ($\mu\text{mmol}\cdot\text{g}_{\text{cat}}^{-1}$)	H ₂ uptake ($\mu\text{mmol}\cdot\text{g}_{\text{cat}}^{-1}$)
Co ₃ O ₄	501.1	374.2
1CuO/4Co ₃ O ₄ -IM	450.3	302.1
1CuO/4Co ₃ O ₄ -IE	393.7	258.6

Table S6. State of art Co-Cu catalysts for methanol synthesis by CO₂ hydrogenation.

Catalysts	T (°C)	p (MPa)	MeOH Selectivity(%)	MeOH STY
5Cu5CoZ ^[1]	190	3	76.1	0.62 mmol·g _{cat} ⁻¹ ·h ⁻¹
1CuO/4Co ₃ O ₄ -IE	250	2	36.1	1.23 mmol·g _{cat} ⁻¹ ·h ⁻¹

1. Din, I.U.; Alotaibi, M.A.; Alharthi, A.I.; Al-Shalwi, M.N.; Alshehri, F. Green Synthesis Approach for Preparing Zeolite Based Co-Cu Bimetallic Catalysts for Low Temperature CO₂ Hydrogenation to Methanol. *Fuel* **2022**, 330, 125643.