

Electronic Supplementary Information

Synergetic catalysis of bimetallic copper-cobalt nanosheets for direct synthesis of ethanol and higher alcohols from syngas

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1. Figures

Fig. S1 XRD patterns of the $\text{Cu}_x\text{Co}_y\text{Al}$ with different Cu/Co mole ratios (x/y) of (a) 1:2; (b) 1:1; (c) 2:1; (d) 4:1; (e) 8:1.

Fig. S2 XRD patterns of the (a) CuCoAl, (b) Cu/CoAl, (c) Co/CuAl and (d) CuCo/Al-IM catalysts (A) after reduction and (B) after 12 h reaction.

Fig. S3 SEM-EDX elemental mapping images for O, Cu, Co, Al, and C of the CuCoAl-LDH precursor.

Fig. S4 SEM images of (A) Cu/CoAl, (B) Co/CuAl and (C) CuCoAl catalysts.

Fig. S5 HAADF-STEM images of the reduced (A) Cu/CoAl, (B) Co/CuAl and (C) CuCo/Al-IM catalysts and the corresponding elemental EDX maps of Cu, Co and Al.

Fig. S6 TEM images of the spent (A) CuCoAl and (B) CuCo/Al-IM catalysts after 72 h reaction.

Fig. S7 The CO conversion and products selectivity for (A) $\text{Cu}_2\text{Co}_1\text{Al}$ and (B) CuCo/Al-IM catalysts with reaction time on stream at $T=270\text{ }^\circ\text{C}$, $P=2.5\text{ MPa}$, $\text{GHSV}=7500\text{ h}^{-1}$ and $\text{H}_2/\text{CO}=2/1$.

Fig. S8 Anderson-Schulz-Flory (ASF) plots for the distributions of hydrocarbons and alcohols obtained for (A) CuCoAl, (B) Cu/CoAl, (C) Co/CuAl and (D) CuCo/Al-IM.

Fig. S9 (A) N_2 adsorption-desorption isotherms and (B) pore size distribution curves

of the (a) CoAl, (b) CuAl, (c) Cu/CoAl, (d) Co/CuAl, (e) CuCoAl and (f) CuCo/Al-IM catalysts.

Fig. S10 XPS spectra of (A) Cu 2p and (B) Co 2p for calcined CuCoAl catalyst.

2. Tables

Table S1 Lattice parameters for different $\text{Cu}_x\text{Co}_y\text{Al-LDH}$.

Table S2 The catalytic performance for the bimetallic CuCo catalysts at a close CO conversion level.

Table S3 The XPS and XAES data of copper in reduced catalysts.

Table S4 Quantitative analysis about the surface Co species concentration from XPS spectra.

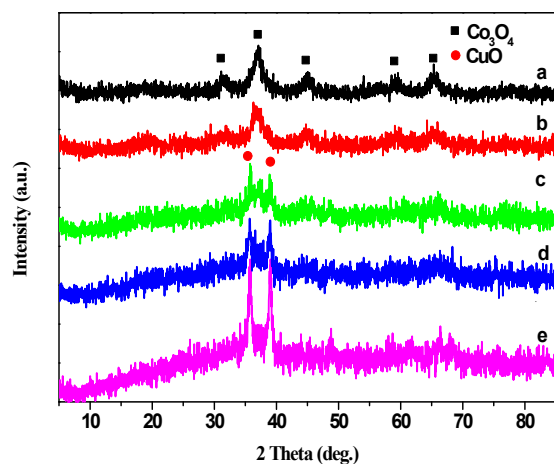


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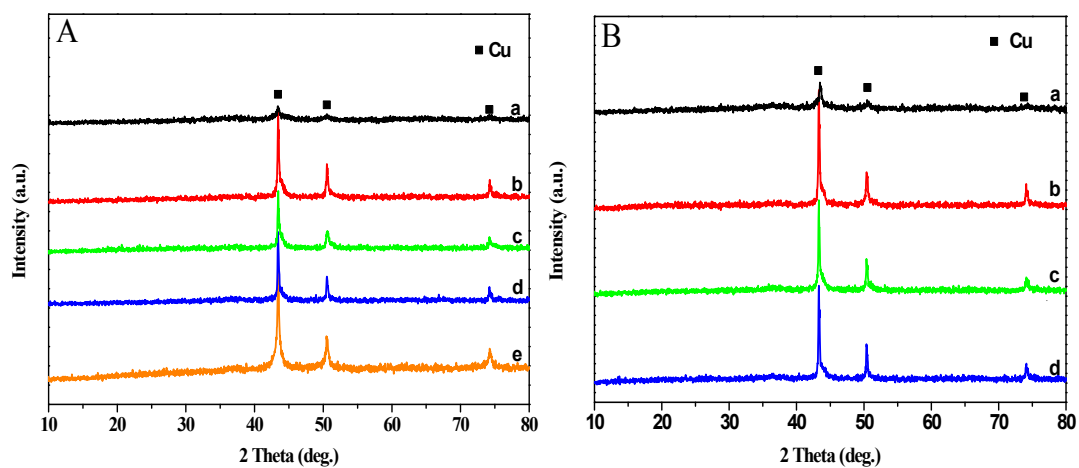


Fig. S2 XRD patterns of the (a) CuCoAl, (b) Cu/CoAl, (c) Co/CuAl, (d) CuCo/Al-IM and (e) CuAl catalysts (A) after reduction and (B) after 12 h reaction.

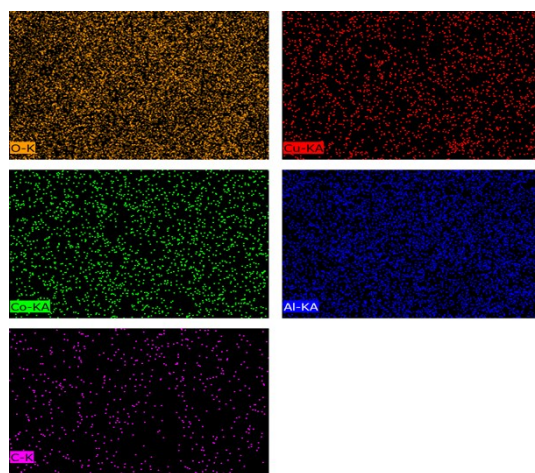


Fig. S3 SEM-EDX elemental mapping images for O, Cu, Co, Al, and C of the CuCoAl-LDH precursor.

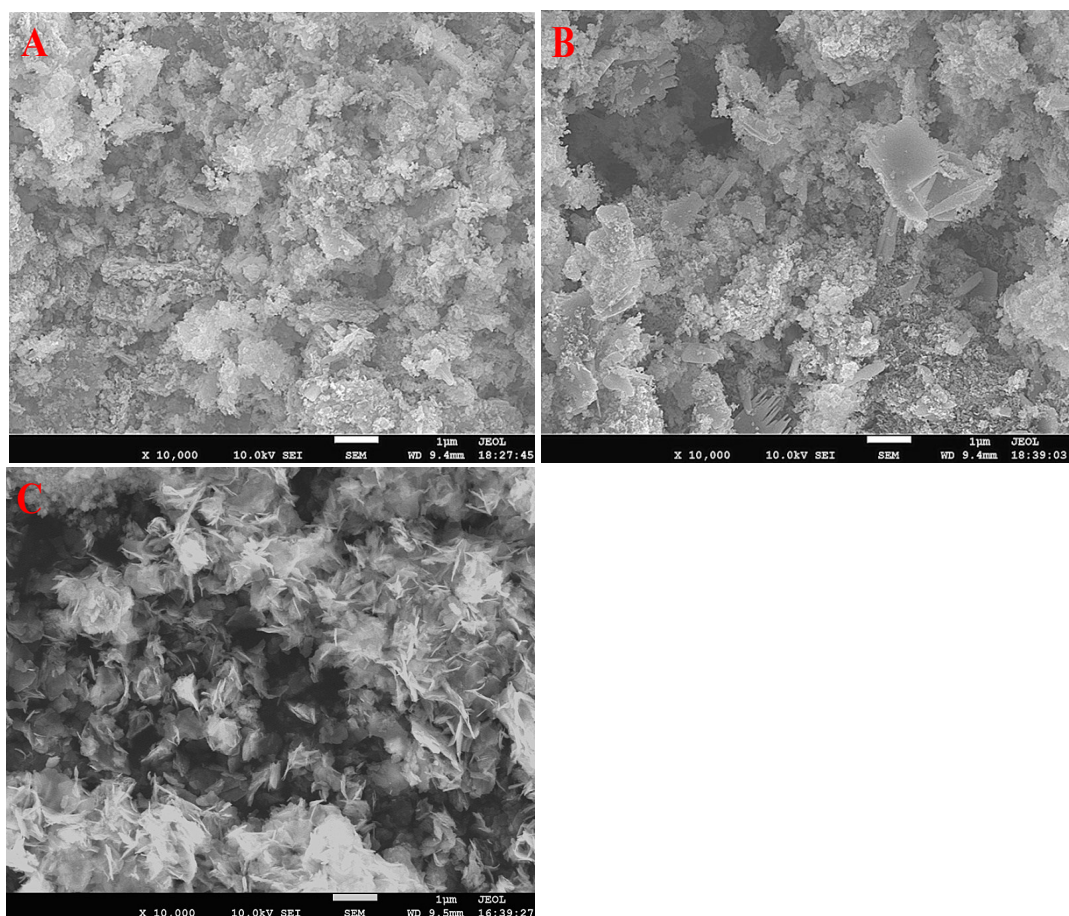


Fig. S4 SEM images of (A) Cu/CoAl, (B) Co/CuAl and (C) CuCoAl catalysts.

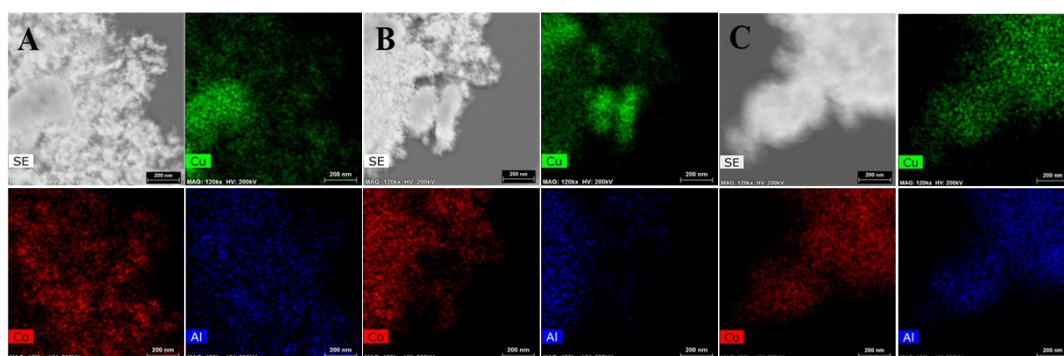


Fig. S5 HAADF-STEM images of the reduced (A) Cu/CoAl, (B) Co/CuAl and (C) CuCoAl/Al-IM catalysts and the corresponding elemental EDX maps of Cu, Co and Al.

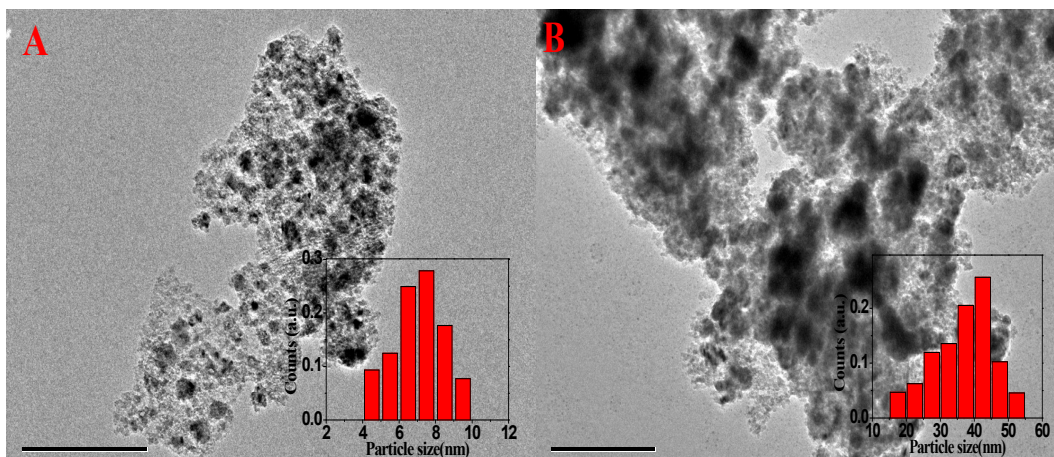


Fig. S6 TEM images of the spent (A) CuCoAl and (B) CuCo/Al-IM catalysts after 72 h reaction.

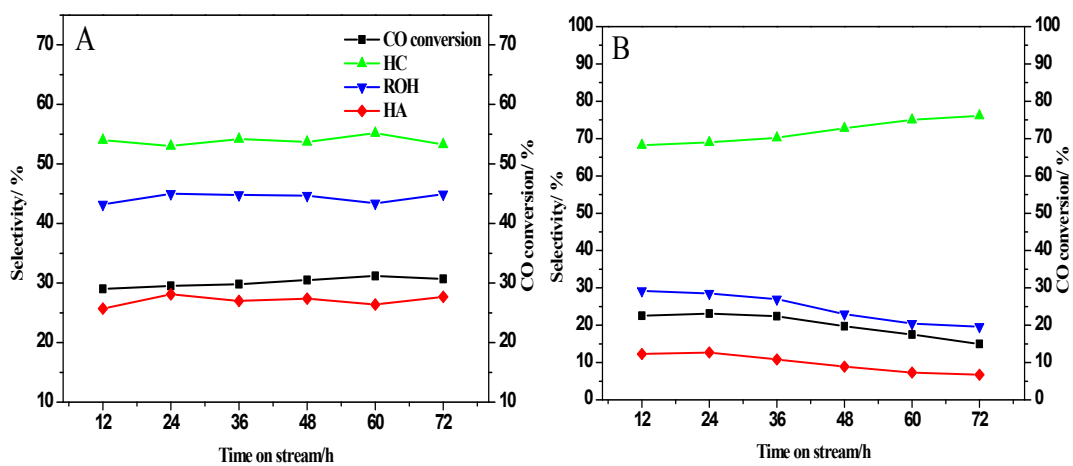
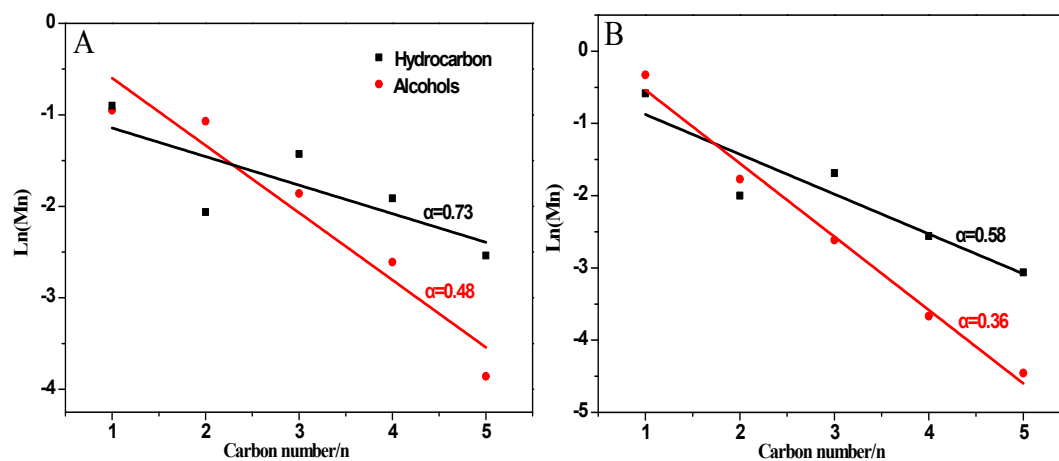


Fig. S7 The CO conversion and products selectivity for (A) $\text{Cu}_2\text{Co}_1\text{Al}$ and (B) CuCo/Al-IM catalysts with reaction time on stream at $T=270^\circ\text{C}$, $P=2.5\text{MPa}$, $\text{GHSV}=7500\text{ h}^{-1}$ and $\text{H}_2/\text{CO}=2/1$.



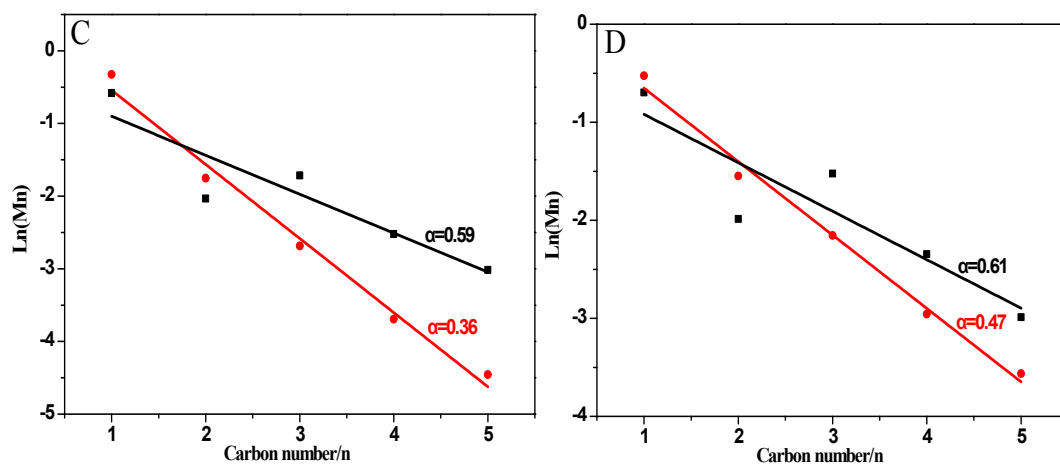


Fig. S8 Anderson-Schulz-Flory (ASF) plots for the distributions of hydrocarbons and alcohols obtained for (A) CuCoAl, (B) Cu/CoAl, (C) Co/CuAl and (D) CuCo/Al-IM.

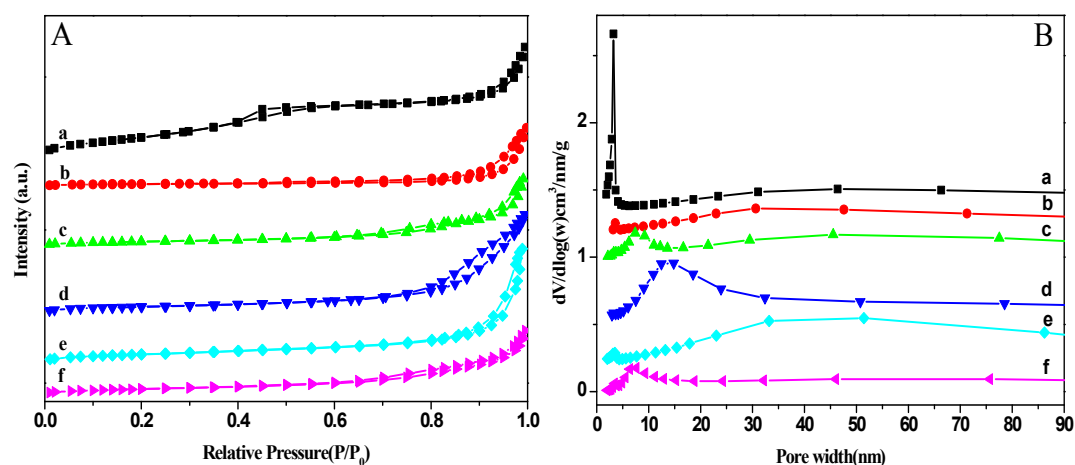


Fig. S9 (A) N_2 adsorption-desorption isotherms and (B) pore size distribution curves of the (a) CoAl, (b) CuAl, (c) Cu/CoAl, (d) Co/CuAl, (e) CuCoAl and (f) CuCo/Al-IM catalysts.

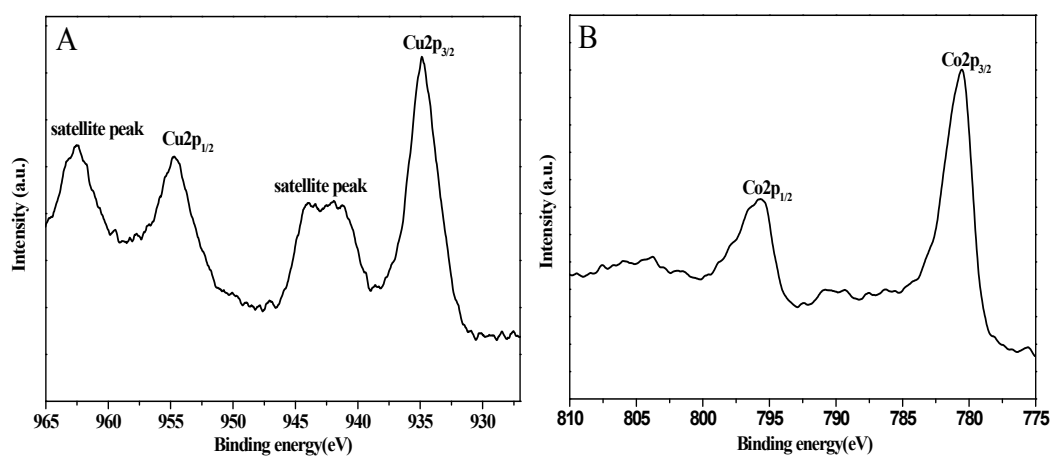


Fig. S10 XPS spectra of (A) Cu 2p and (B) Co 2p for calcined CuCoAl catalyst.

Tables

Table S1 Lattice parameters for different $\text{Cu}_x\text{Co}_y\text{Al-LDH}$.

Catalysts	a (nm)	c (nm)
CoAl-LDH	0.3072	2.246
$\text{Cu}_1\text{Co}_2\text{Al-LDH}$	0.3072	2.252
$\text{Cu}_1\text{Co}_1\text{Al-LDH}$	0.3070	2.247
$\text{Cu}_2\text{Co}_1\text{Al-LDH}$	0.3068	2.263
$\text{Cu}_4\text{Co}_1\text{Al-LDH}$	0.3064	2.246
$\text{Cu}_8\text{Co}_1\text{Al-LDH}$	-	2.241
CuAl-LDH	-	2.240
Cu/CoAl-LDH	-	2.045
Co/CuAl-LDH		2.068

Table S2 The catalytic performance for the bimetallic CuCo catalysts at a close CO conversion level.

Catalyst	CO Conv. (%)	C-Balance(%)	Selectivity (C mol %)					Alcohols distribution (C mol %)				
			CH_4	C_2+H	DME	CO_2	ROH	MeOH	EtOH	PrOH	BuOH	C_5+OH
$\text{Cu}_1\text{Co}_2\text{Al}$	28.9	99.0	31.1	37.6	1.2	3.8	26.3	45.3	30.3	15.3	7.8	1.3
$\text{Cu}_1\text{Co}_1\text{Al}$	28.5	98.2	24.7	35.6	1.3	1.9	36.5	42.9	30.7	15.8	9.2	1.4
$\text{Cu}_2\text{Co}_1\text{Al}$	29.2	101.6	22.1	32.3	1.1	0.5	44.0	40.7	34.3	15.6	7.3	2.1
$\text{Cu}_4\text{Co}_1\text{Al}$	25.7	99.7	24.4	35.3	2.4	1.3	36.6	49.4	32.3	12.3	4.3	1.7
$\text{Cu}_8\text{Co}_1\text{Al}$	26.8	100.8	35.6	29.5	0.4	4.0	30.5	57.5	25.9	9.5	4.9	2.2
Cu/CoAl	25.2	99.6	39.1	33.0	1.5	2.4	24.0	64.7	20.4	9.2	4.7	1.0
Co/CuAl	22.7	100.3	38.5	30.9	1.2	2.0	27.4	66.4	19.2	8.9	4.1	1.4
CuCo/Al-IM	23.0	99.9	35.0	35.1	0.6	0.7	28.6	59.1	21.2	11.6	5.2	2.9

Table S3 The XPS and XAES data of copper in reduced catalysts.

Samples	BE(Cu 2p _{3/2})	KE(CuL ₃ VV)	α'(Cu)
	(eV)	(eV)	(eV)
CuAl	932.9	917.5	1850.4
CuCoAl	933.7	917.3	1851.0
Cu/CoAl	932.8	917.5	1850.3
CuCo/Al-IM	932.9	917.8	1850.7

Table S4 Quantitative analysis about the surface Co species concentration from XPS spectra.

Samples	Surface Co species concentration		
	Co ²⁺	Co ³⁺	Co ⁰
CuAl	-	-	-
CuCoAl	0.50	0.33	0.17
Cu/CoAl	0.70	0.26	0.04
CuCo/Al-IM	0.32	0.61	0.07
CoAl	0.29	0.71	0