Supporting Information

Hetero-Metal Cations Control of CuO Nanostructures and

Their High Catalytic Performance for CO Oxidation

Hongwen Huang, Liqiang Zhang, Kewei Wu, Qing Yu, Ru Chen, Hangsheng Yang, Xinsheng $Peng^{a,b}*$ and Zhizhen Ye^{a,b}*

^aState Key Laboratory of Silicon Materials, ^a Address, State Key Laboratory of Silicon Materials, ^bCyrus Tang Center for Sensor Materials and Application, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, P. R.

* Corresponding Author. Email: pengxinsheng@zju.edu.cn; yezz@zju.eud.cn

Contents:

Figure S1: Raman spectrum of Zn2Cu2 sample prepared at 25 °C.

Table S1: ICP-MS results of Zn2Cu2, Zn4Cu2 and Zn6Cu2 samples prepared at 25 °C.

Figure S2: TEM images of Cu2, Zn2Cu2, Zn4Cu2 and Zn6Cu2 samples prepared at 25 °C.

Figure S3: Size distributions along two perpendicular directions for Cu2, Zn2Cu2, Zn4Cu2 and Zn6Cu2 samples prepared at 25 °C.

Table S2: The characteristic parameters of Cu2, Zn2Cu2, Zn4Cu2 and Zn6Cu2 samples prepared at 25 $^{\circ}$ C.

Table S3: The characteristic parameters of as-prepared Cu2, Zn2Cu2, Zn4Cu2 and Zn6Cu2 samples prepared at 35 °C.

Figure S4: SEM images for Zn2Cu2 samples prepared at 20 °C, 25 °C, 30 °C and 50 °C.

Table S4: The characteristic parameters of Zn2Cu2 samples prepared at 20 $^{\circ}$ C, 25 $^{\circ}$ C, 30 $^{\circ}$ C and 50 $^{\circ}$ C.

Table S5: pH values of our sample solutions without adding 1.6 mmol AE aqueous solution at 25 $^{\circ}$ C.

Figure S5: SEM images of Ag2Cu2, Mg2Cu2, Al2Cu2 prepared at 25 °C and EDS spectrum of Al2Cu2.

Table S6: The characteristic parameters of Cu2, Zn2Cu2, Ag2Cu2, Mg2Cu2 and Al2Cu2 samples prepared at 25 °C.

Figure S6: UV-Vis spectrum of Cu2 nanosheets prepared at 25 $^{\circ}$ C and the plot of $(\alpha hv)^{1/2}$ vs photon energy for the absorption spectrum of Cu2 nanosheets.

Figure S7: Photograph of Tyndall effect for Cu2 solution prepared at 25 °C and Uv-vis absorption of Evans Blue solutions after mixing the 80 ml Cu2 solution products.

Figure S8: FTIR spectrum of Cu2 nanosheets prepared at 25 °C.

Figure S9: Cu2p XPS spectrum of Cu2 nanosheets prepared at 25 °C.

Table S7: Detailed reaction rates of catalytic CO oxidation at different temperatures.

Figure S10: XRD pattern and SEM image of Cu2 sample after 6 hours' catalytic reaction.

Figure S11: Nitrogen adsorption-desorption isotherms at 77K of Zn4Cu2 prepared at 25 °C.



Figure S1. Raman spectrum of Zn2Cu2 sample prepared at 25 °C.

Table S1: ICP-MS results of Zn2Cu2, Zn4Cu2 and Zn6Cu2 samples prepared at 25 °C.

Sample	Ratio of Zn^{2+}/Cu^{2+} (× 10 ⁻³)
Zn2Cu2	4.1755
Zn4Cu2	5.0935
Zn6Cu2	7.176



Figure S2. TEM images of Cu2 (a), Zn2Cu2 (b), Zn4Cu2 (c) and Zn6Cu2 (d) samples prepared at 25 °C, respectively. Scale bar equals 100 nm.



Figure S3. Size distribution along two perpendicular directions (the short axis and the long axis were denoted). Histograms for Cu2 (a), Zn2Cu2 (b), Zn4Cu2 (c) and Zn6Cu2 (d) samples prepared at 25 °C, respectively.

Table S2: The characteristic parameters of the samples prepared at 25 °C. In this table, the long axis size and the short axis size was obtained by the above histograms based on analyzing more than 100 particles. And we chose the central size to calculate the ratio. Noticeably, reaction time was defined as time interval from the moment of mixing solutions to that of finished reaction, which is gained by observing the color of prepared solution owing to remarkably difference (from light blue to tawny).

Sample	Long axis size	Short axis	Ratio of long axis size	Reaction time	
	(nm)	size (nm)	/ short axis size	(hour)	
Cu2	320±40	200±40	1.6	12	
Zn2Cu2	180±40	150±40	1.2	26	
Zn4Cu2	400±40	360±40	1.1	54	
Zn6Cu2	420±40	400±40	1.05	96	

Table S3: The characteristic parameters of the samples prepared at 35 °C.

Sample	Long axis size	Short axis	Ratio of long axis size	Reaction time	
	(nm)	size (nm)	/ short axis size	(hour)	
Cu2	240±40	140±40	1.71	6	
Zn2Cu2	200±40	130±40	1.54	12	
Zn4Cu2	220±40	150±40	1.47	17	
Zn6Cu2	280±40	220±40	1.27	23	



Figure S4. SEM images for Zn2Cu2 prepared at 20 $^{\circ}$ C (a), 25 $^{\circ}$ C (b), 30 $^{\circ}$ C (c) and 50 $^{\circ}$ C (d), respectively.

Temperature	Long axis	Short axis Ratio of the long a		s Reaction time			
(°C)	(nm)	(nm)	/the short axis	(hour)			
20	250±40	220±40	1.14	38			
25	180±40	150±40	1.2	26			
30	230±40	150±40	1.53	14			
50	280±40	150±40	1.87	3			

Table S4: The characteristic parameters of Zn2Cu2 samples at 20, 25, 30, 50 °C, respectively.

Table S5: pH values of our sample solutions without adding 1.6 mmol AE aqueous solution at 25 $^{\circ}$ C.

Solution	PH value		
Cu2	4.91±0.01		
Zn2Cu2	5.29 ± 0.01		
Zn4Cu2	5.36 ± 0.01		
Zn6Cu2	5.43±0.01		



Figure S5. SEM images of Ag2Cu2 (a), Mg2Cu2 (b) and Al2Cu2 (c) prepared at 25 $^{\circ}$ C, respectively. (d) EDS elemental analysis spectrum of the red dotted line box in Figure S5c. (Note that: K_{sp}(AgOH)=-8.17; K_{sp}(Mg(OH)₂)=-11.15; K_{sp}(Al(OH)₃)=-33.45.

Readinty representes studinty constants for corresponding metal hydroxide.								
Samples	K _{sp}	K _{stability}	Product	Reaction	Ratio of the			
				time (hours)	long axis to			
					the short			
					axis			
Cu2	-19.32 (Cu(OH) ₂)	13.68(Cu(OH) ₂)	CuO	12	1.6			
Zn2Cu2	-16.76 (Zn(OH) ₂)	11.1(Zn(OH) ₂)	CuO	26	1.2			
Ag2Cu2	-8.17 (AgOH)	2.0(AgOH)	CuO	13	1.52			
Mg2Cu2	-11.15 (Mg(OH) ₂)	5.1 (Mg(OH) ₂)	CuO	20	1.36			
Al2Cu2	-33.45 (Al(OH) ₃)		Al-compound					

Table S6: The characteristic parameters of Cu2, Zn2Cu2, Ag2Cu2, Mg2Cu2 and Al2Cu2 samples prepared at 25 $^{\circ}$ C, respectively. K_{sp} means the solubility product of corresponding metal hydroxide; K_{stability} represents stability constants for corresponding metal hydroxide.



Figure S6. (a) UV-Vis absorption spectrum of Cu2 nanosheets prepared at 25 $^{\circ}$ C and (b) the plot of $(\alpha hv)^{1/2}$ vs photon energy for the absorption spectrum of Cu2 nanosheets.



Figure S7. (a) Photograph of Tyndall effect for Cu2 nanosheet solution prepared at 25 $^{\circ}$ C and (b) UV-Vis absorption curves of original Evans Blue solutions and after filtering the mixture of EB and the 80 ml Cu2 nanosheet solution.



Figure S8. FTIR spectrum of Cu2 nanosheets prepared at 25 °C.



Figure S9. Cu2p XPS spectrum of Cu2 nanosheets prepared at 25 °C.

Somelo	Reaction rates of catalytic CO oxidation (mmol _{co} g ⁻¹ catalysth ⁻¹)							
Sample	50 °C	80 °C	100 °C	120 °C	150 °C	160 °C	180 °C	200 °C
Cu2	0.3866	/	1.77	3.33	19.54	27.16	41.89	47.77
Zn4Cu2	0.20	0.27	0.31	0.41	4.36	/	12.73	25.29
CuO	0.30	/	0.33	0.30	0.36	/	0.41	1.35
powder								

Table S7: Detailed reaction rates of catalytic CO oxidation at different temperatures. "/" denotes blank data.



Figure S10. (a) XRD pattern and (b) SEM image of Cu2 sample after 6 hours' catalytic reaction.



Figure S11. Nitrogen adsorption-desorption isotherms at 77K of Zn4Cu2 prepared at 25 °C.