

## Electronic Supplementary Material

# Facile synthesis of hierarchical flower-like Ag/Cu<sub>2</sub>O and Au/Cu<sub>2</sub>O nanostructures and enhanced catalytic performance in electrochemical reduction of CO<sub>2</sub>

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### Products *FEs* calculation

After the quantification, the Faradaic efficiencies (*FEs*) toward each CO<sub>2</sub> reduction product were calculated as

$$i_{H_2 \text{ or } CO} = V_{H_2 \text{ or } CO} \times q \times \frac{2Fp_0}{RT}$$

$$FE_{H_2 \text{ or } CO} = \frac{i_{H_2 \text{ or } CO}}{i_{\text{total}}} \times 100$$

$$FE_{HCOOH} = \frac{z n F}{Q} \times 100$$

where  $V_{H_2 \text{ or } CO}$  is volume concentration of H<sub>2</sub> or CO quantified by GC,  $q$  is flow rate of CO<sub>2</sub>,  $i_{\text{total}}$  is measured average current,  $F$  is Faradaic constant (96485.3 C/mol),  $p_0$  is pressure,  $T$  is room temperature and  $R$  is ideal gas constant (8.314 J • mol<sup>-1</sup> • K<sup>-1</sup>),  $z$  is the amount of the product,  $n$  is the number of moles of electrons to participate in the Faradaic reaction quantified by NMR, and the  $Q$  is the total charge applied during the electrolysis process.

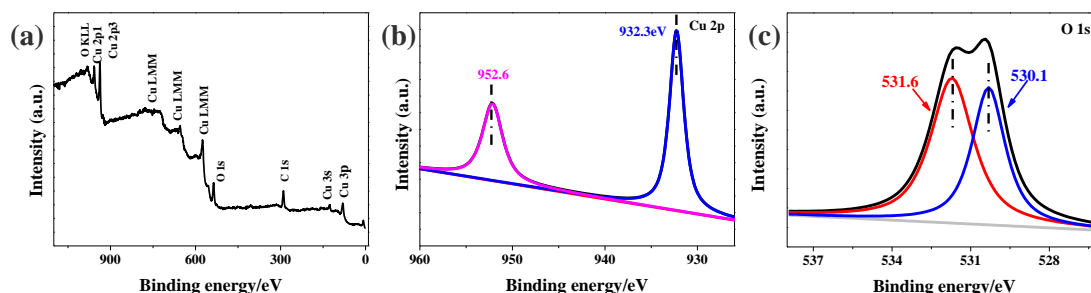


Fig. S1 XPS survey spectrum of Cu<sub>2</sub>O (a), Cu 2p (b), and O 1s (c)

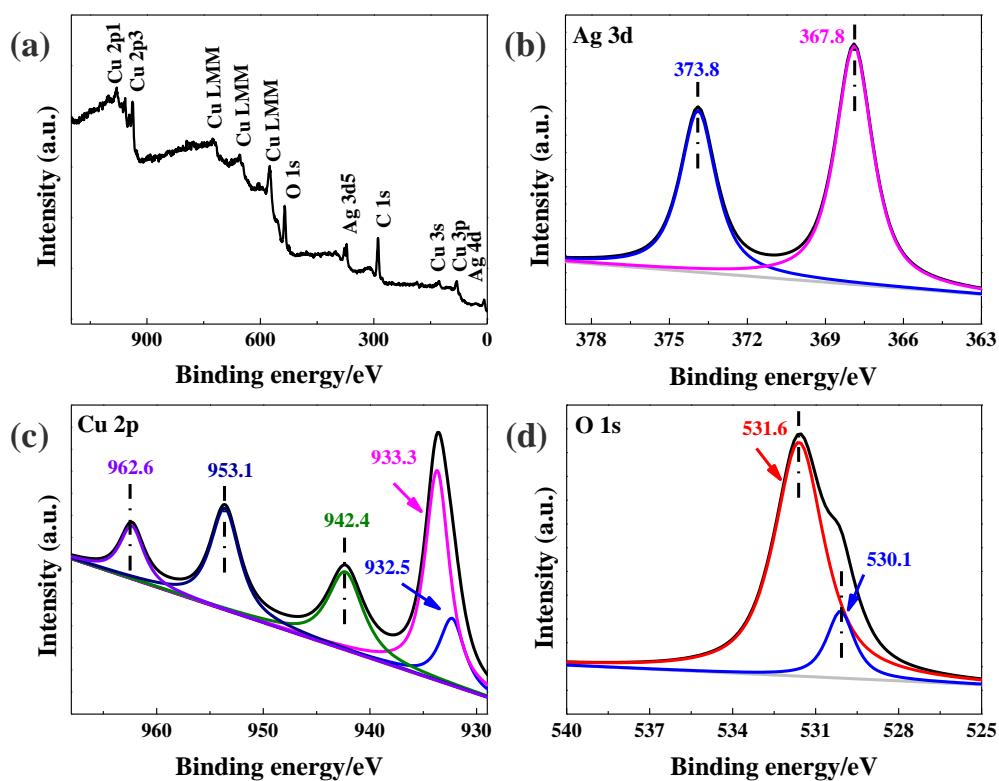


Fig. S2 XPS survey spectrum of  $\text{Ag}_{0.25}/\text{Cu}_2\text{O}$  composite (a), Ag 3d (b), Cu 2p (c), and O 1s (d)

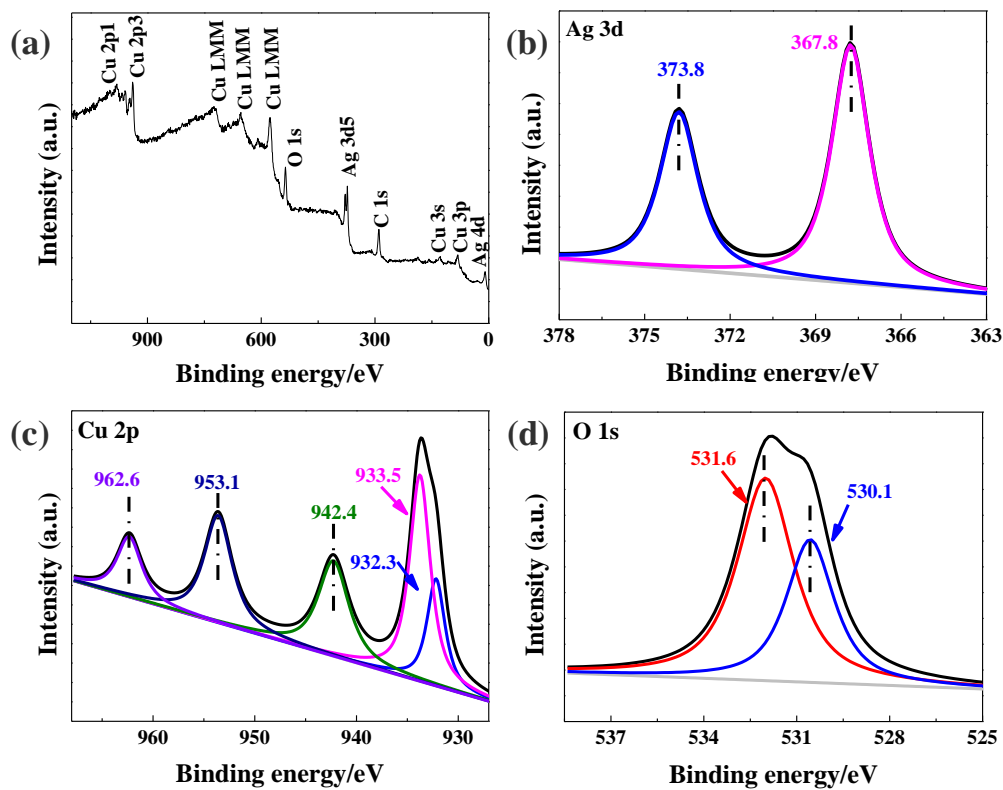
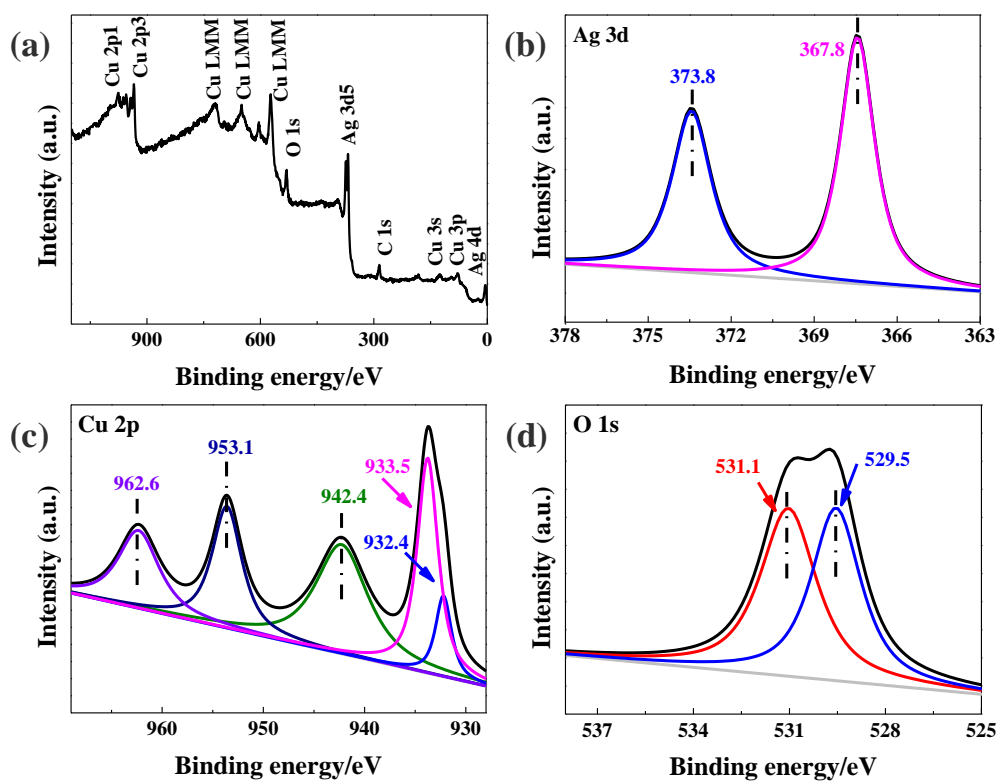
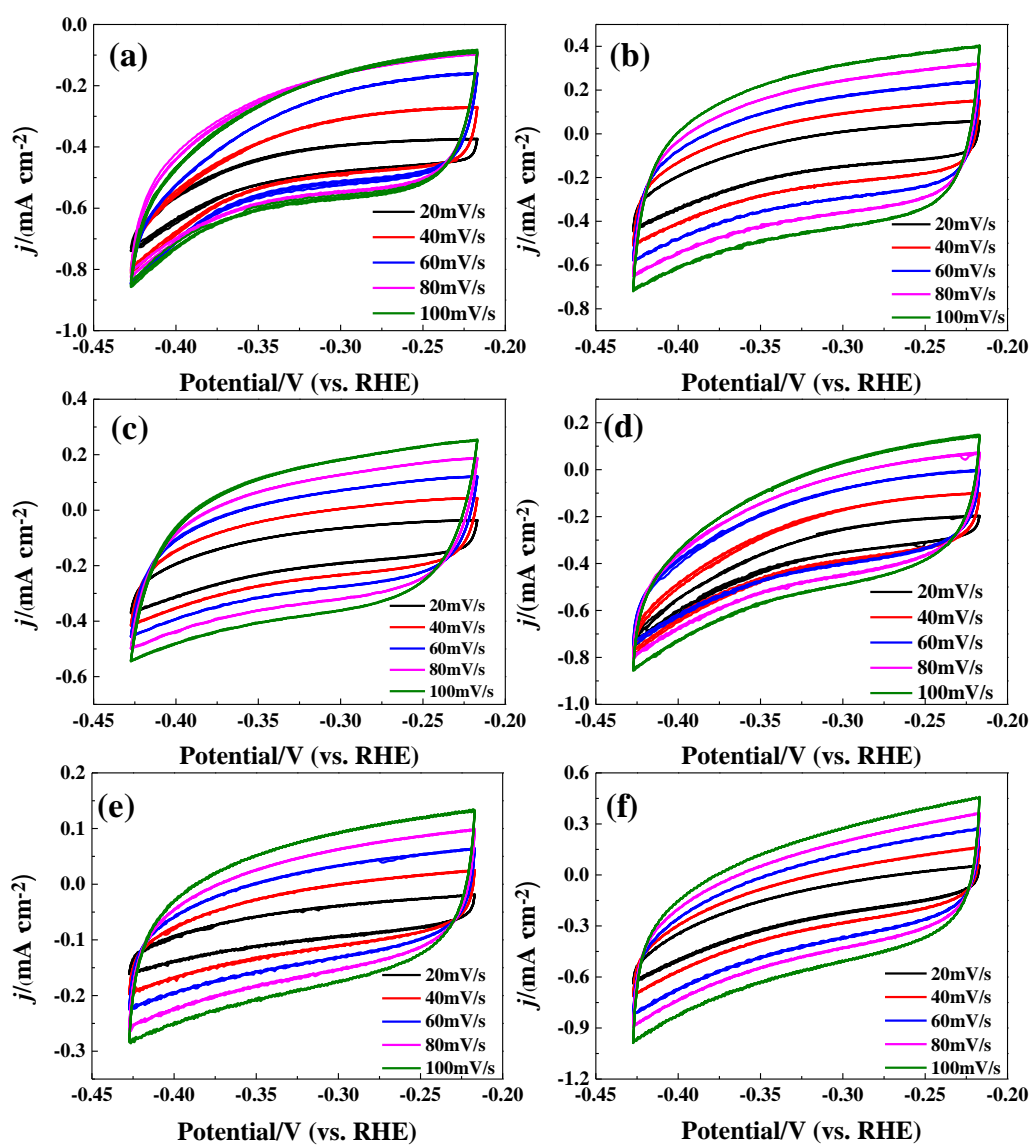


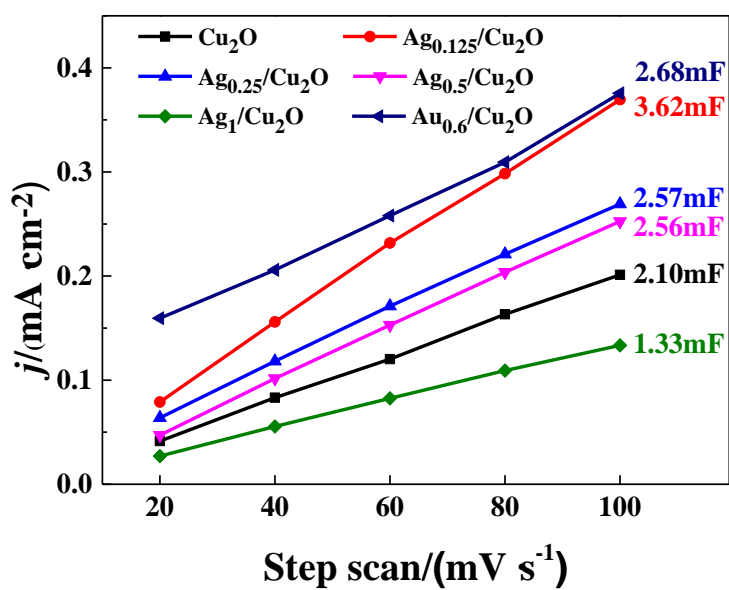
Fig. S3 XPS survey spectrum of  $\text{Ag}_{0.5}/\text{Cu}_2\text{O}$  composite (a), Ag 3d (b), Cu 2p (c), and O 1s (d)



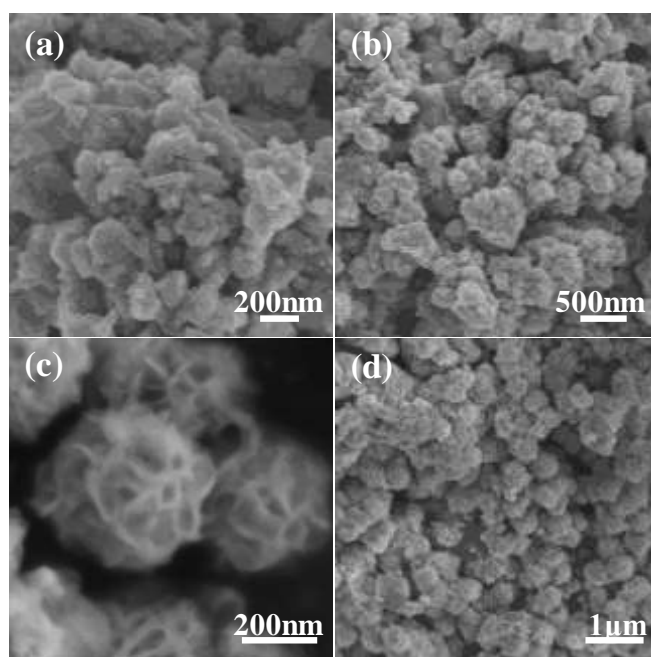
**Fig. S4** XPS survey spectrum of Ag<sub>1</sub>/Cu<sub>2</sub>O composite (a), Ag 3d (b), Cu 2p (c), and O 1s (d)



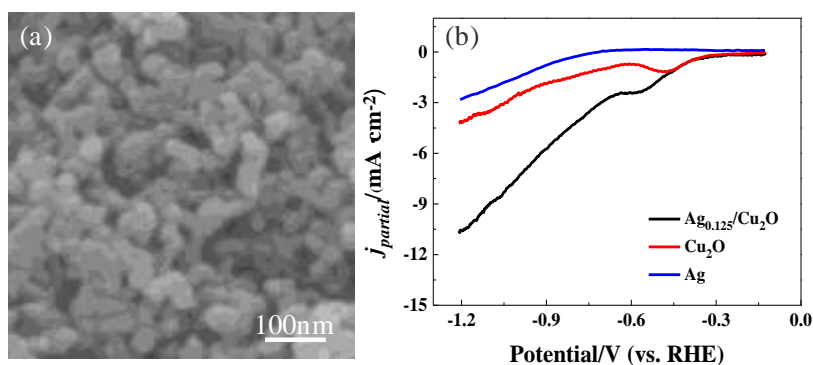
**Fig. S5** Cyclic voltammograms at various scan rates for (a)  $\text{Cu}_2\text{O}$ , (b)  $\text{Ag}_{0.125}/\text{Cu}_2\text{O}$ , (c)  $\text{Ag}_{0.25}/\text{Cu}_2\text{O}$ , (d)  $\text{Ag}_{0.5}/\text{Cu}_2\text{O}$ , (e)  $\text{Ag}_1/\text{Cu}_2\text{O}$ , and (f)  $\text{Au}/\text{Cu}_2\text{O}$



**Fig. S6** The linear relationship between the current density and scan rate



**Fig. S7** SEM images of the used catalysts after 5 h reduction at -1.0V in  $\text{CO}_2$ -saturated 0.1 M  $\text{KHCO}_3$  solution (a) and (b) for  $\text{Cu}_2\text{O}$ , (c) and (d) for  $\text{Ag}_{0.125}/\text{Cu}_2\text{O}$



**Fig. S8** (a) SEM image of as-prepared Ag nanoparticles, (b) Partial current density of CO<sub>2</sub> reduction on three samples

**Table S1** Summary of compositions of Ag/Cu<sub>2</sub>O composites based on XPS results

Sample	Cu	Ag	O	Atom Ratio
				Ag/Cu
Cu <sub>2</sub> O	38.2	/	61.8	/
Ag <sub>0.125</sub> /Cu <sub>2</sub> O	38.9	3.5	57.6	0.09
Ag <sub>0.25</sub> /Cu <sub>2</sub> O	29.0	6.3	64.7	0.22
Ag <sub>0.5</sub> /Cu <sub>2</sub> O	30.1	9.7	60.2	0.32
Ag <sub>1</sub> /Cu <sub>2</sub> O	27.6	11.8	60.6	0.43

**Table S2** Summary of representative catalysts for electrochemical reduction of CO<sub>2</sub>

Catalyst	Electrolyte	Experimental Conditions	Faradaic efficiency (%)				Ref.
			H <sub>2</sub>	CO	HCOOH	Others	
Dendritic Ag <sub>x</sub> Cu <sub>100-x</sub>	0.5 M KHCO <sub>3</sub>	-1.3 V (vs. SCE)	28.6	43.9	--	--	[1]
Cubic Cu <sub>2</sub> O@Au Nanocomposites	0.1 M KHCO <sub>3</sub>	-1.0 V (vs. RHE)	51.3	30.1	--	CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub>	[2]
Au thin layers on polycrystalline Cu	0.1 M KHCO <sub>3</sub>	-1.0 V (vs. RHE)	41	58	1	--	[3]
AuCu Nanoparticles	0.1 M KHCO <sub>3</sub>	-0.77 V (vs. RHE)	42	52	5	--	[4]
Au <sub>3</sub> Cu bimetallic nanoparticles	0.1 M KHCO <sub>3</sub>	-0.7 V (vs. RHE)	35	62	3	--	[5]
Flower-like Ag/Cu <sub>2</sub> O	0.1 M KHCO <sub>3</sub>	-1.0 V (vs. RHE)	30	55	15	--	Our work
Flower-like Au/Cu <sub>2</sub> O	0.1 M KHCO <sub>3</sub>	-1.0 V (vs. RHE)	28	65	7	--	Our work

### References:

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