Supporting Information

Surface conversion of CuO-ZnO to ZIF-8 to enhance CO_2 adsorption for CO_2 hydrogenation to methanol

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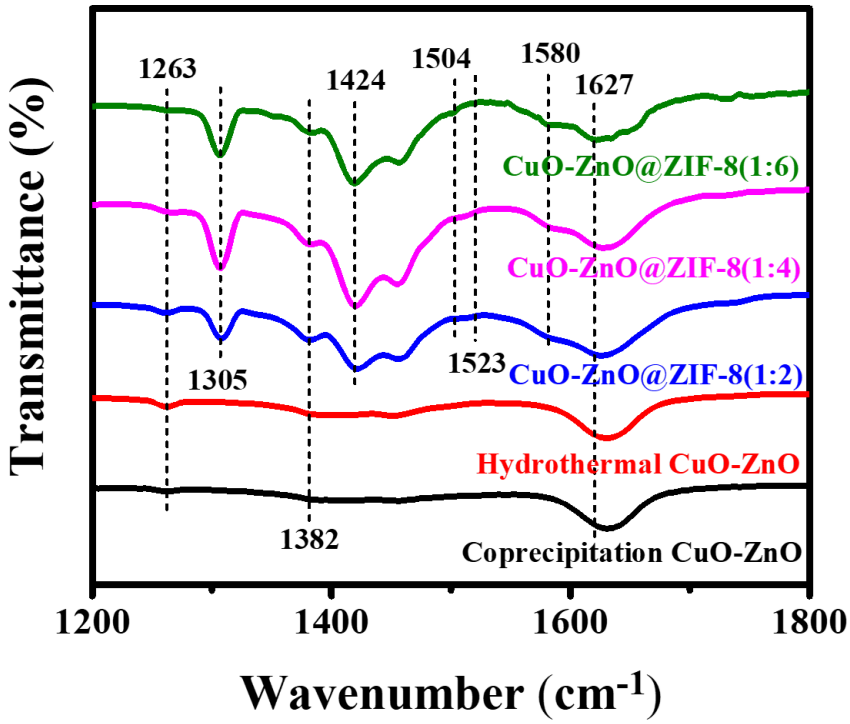

Fig. S1. FTIR spectra of co-precipitated CuO-ZnO, hydrothermal CuO-ZnO and CuO-ZnO@ZIF-8.

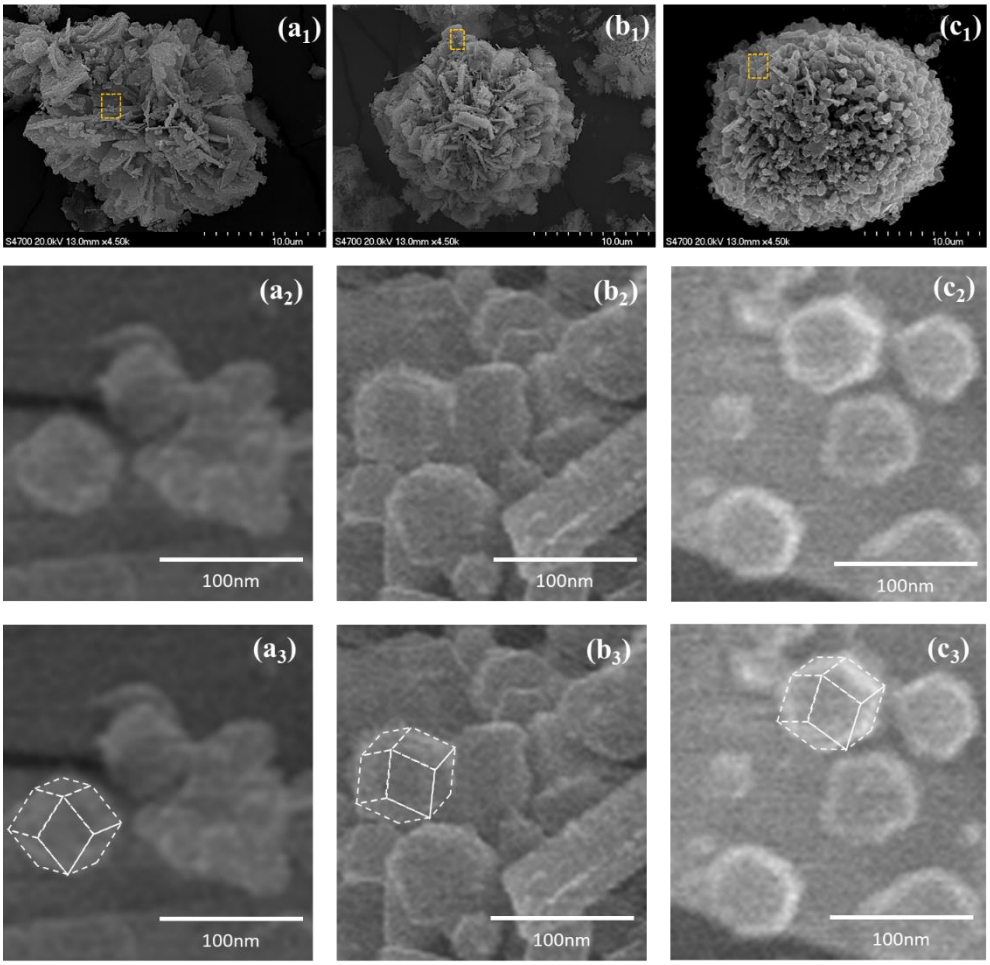

Fig. S2. Low-magnification and high-magnification SEM of image (a) CuO-ZnO@ZIF-8(1:2), (b) CuO-ZnO@ZIF-8(1:4) and (c) CuO-ZnO@ZIF-8(1:6).

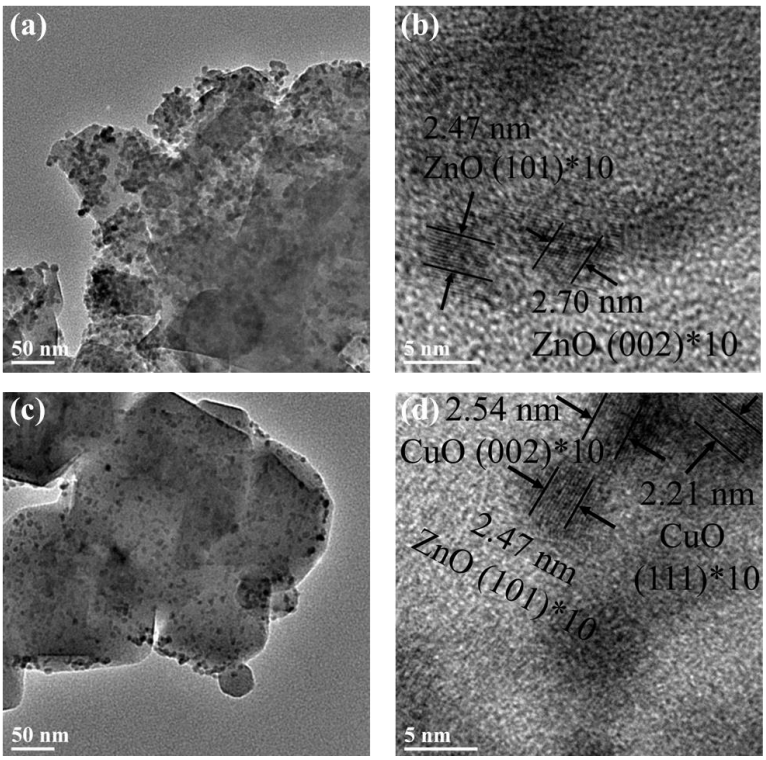

Fig. S3. HRTEM images of CuO-ZnO@ZIF-8 (1:4).

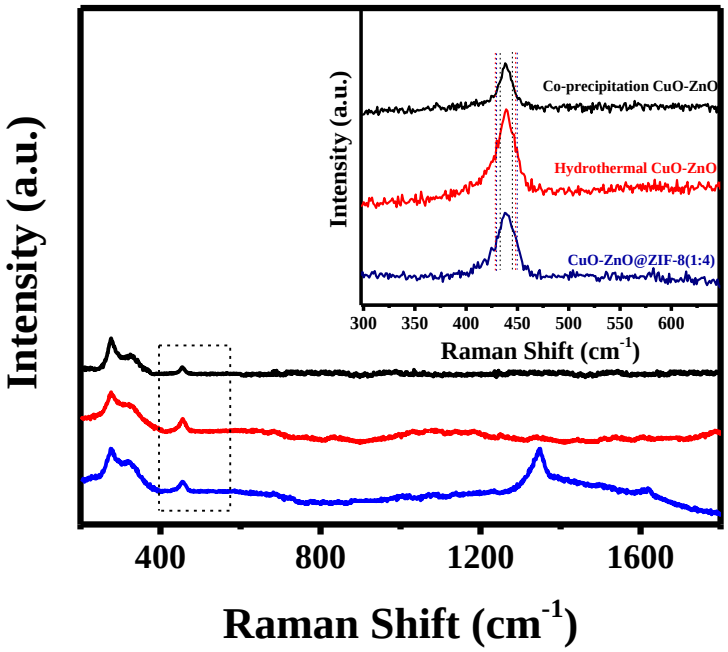

Fig. S4. Raman spectra of co-precipitated CuO-ZnO, hydrothermal CuO-ZnO and CuO-ZnO@ZIF-8(1:4).

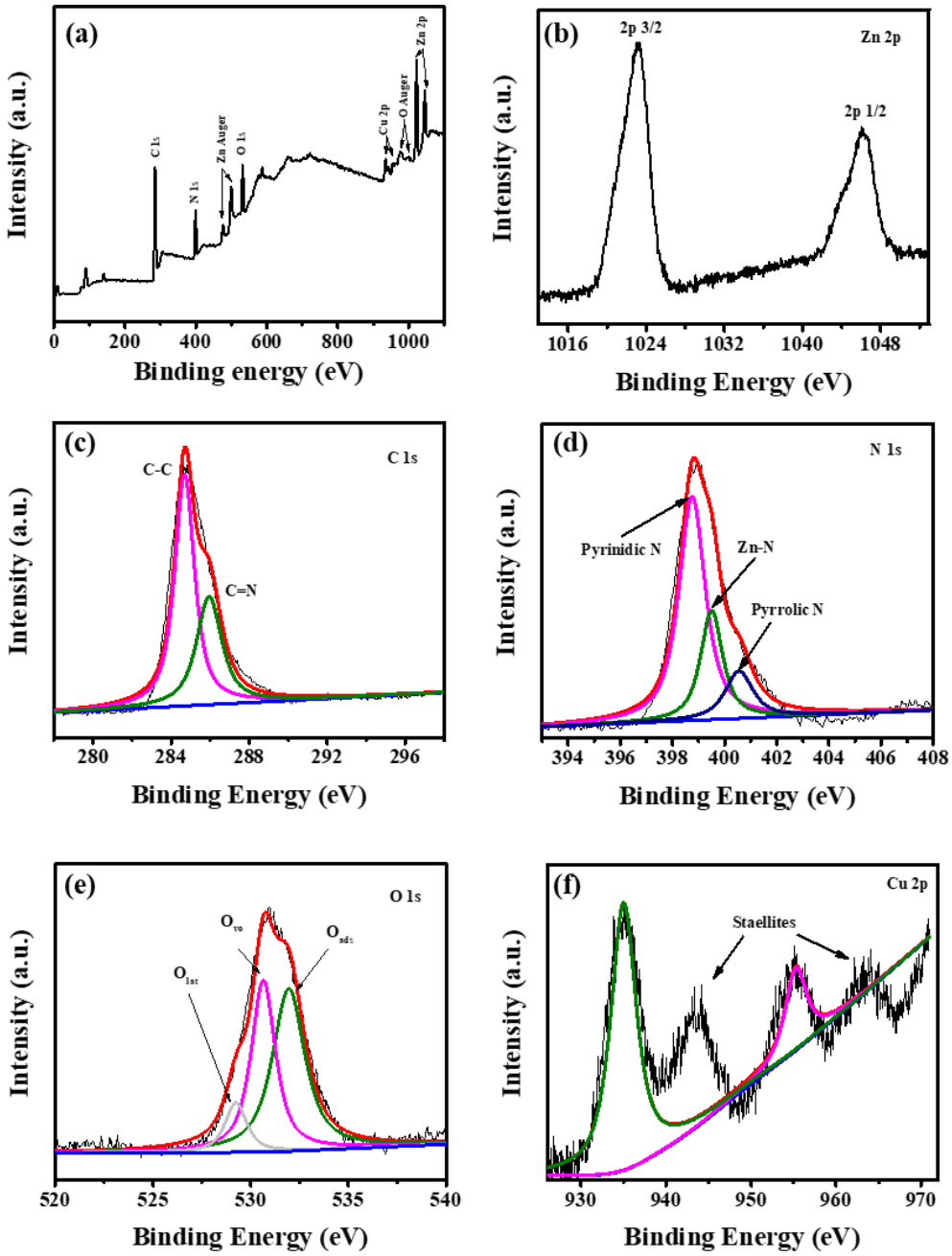

Fig. S5. XPS spectra of CuO-ZnO@ZIF-8(1:4) catalysts: (a) survey XPS spectra of CuO-ZnO@ZIF-8 (b) Zn 2p (c) C 1s(d) N 1s (e) O 1s and (f) Cu 2p.

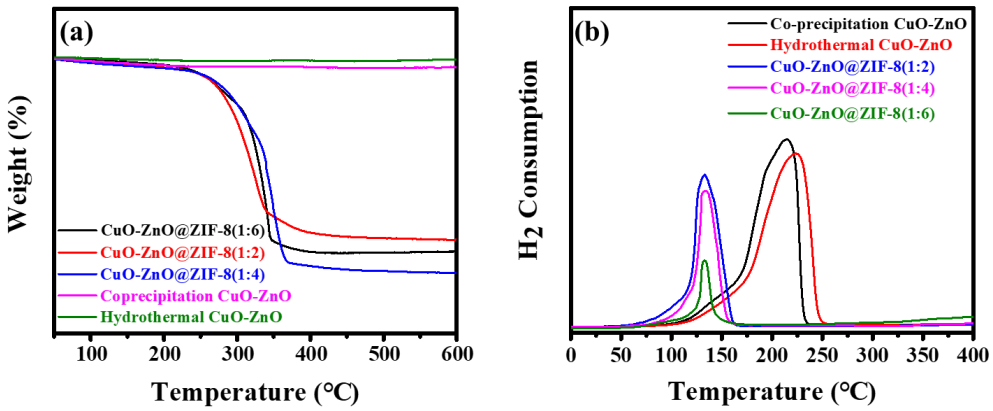

Fig. S6. TG diagrams (a) and TPR patterns (b) of co-precipitated CuO-ZnO, hydrothermal CuO-ZnO and CuO-ZnO@ZIF-8 catalysts.

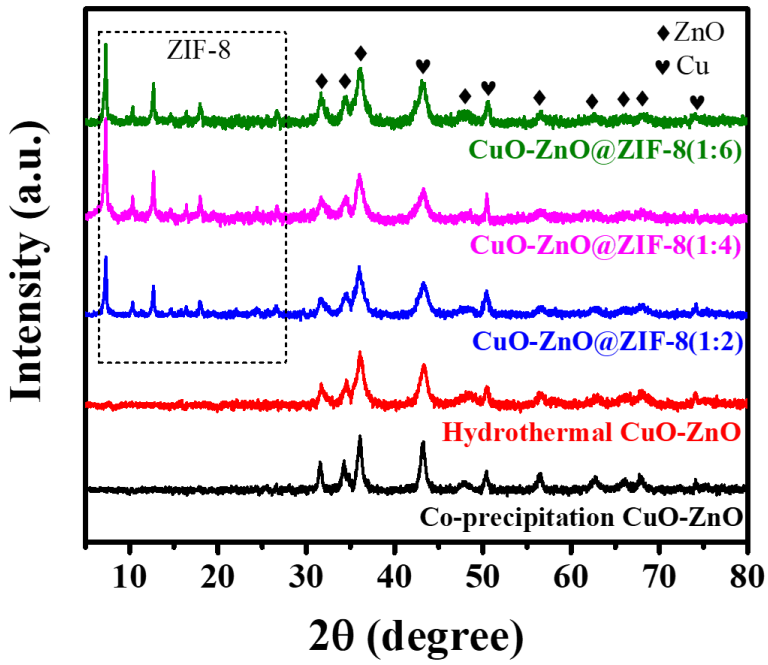

Fig. S7. XRD pattern of co-precipitated CuO-ZnO, hydrothermal CuO-ZnO and CuO-ZnO@ZIF-8 after reaction.

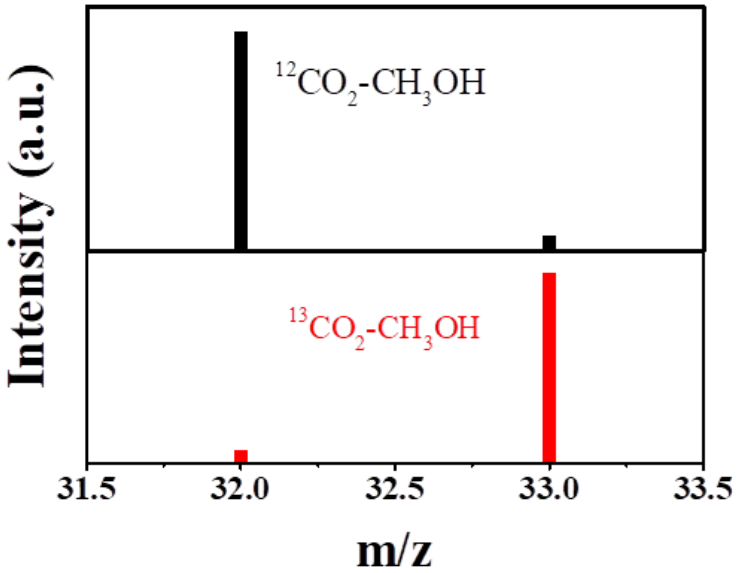

Fig. S8. MS spectra of the CO_2 reduction products of CuO-ZnO@ZIF-8 using $^{12}CO_2$ and $^{13}CO_2$.

Tab. S1.

FTIR spectra of the absorption CO_2 (g) features in ZnO and CuO nanoparticle Surface.

Vibrational Assignment	Bicarbonate				Monodentate carbonate				Bidentate carbonate				Carboxylate	
	ν_3 (O-C-O)$_{as}$		ν_3 (O-C-O)$_s$		ν_3 (O-C-O)$_{as}$		ν_3 (O-C-O)$_s$		ν_3 (O-C-O)$_{as}$		ν_3 (O-C-O)$_s$		ν_3 (O-C-O)$_{as}$	
	ZnO (cm^{-1})	CuO (cm^{-1})	ZnO (cm^{-1})	CuO (cm^{-1})	ZnO (cm^{-1})	CuO (cm^{-1})	ZnO (cm^{-1})	CuO (cm^{-1})	ZnO (cm^{-1})	CuO (cm^{-1})	ZnO (cm^{-1})	CuO (cm^{-1})	ZnO (cm^{-1})	ZnO (cm^{-1})
CuO-ZnO@ZIF-8(1:6)	1627	_	_	1424	1504	_	1382	_	1580	_	1263	1305	1523	_
CuO-ZnO@ZIF-8(1:4)	1627	_	_	1424	1504	_	1382	_	1580	_	1263	1305	1523	_
CuO-ZnO@ZIF-8(1:2)	1627	_	_	1424	1504	_	1382	_	1580	_	1263	1305	1523	_
Hydrothermal CuO-ZnO	1631	_	_	_	_	_	1386	_		_	1263	_	_	_
Coprecipitation CuO-ZnO	1631	_	_	_	_	_	1386	_		_	1263	_	_	_
Range of Frequencies (cm^{-1})[a-e]	1623-1650[a]		1410-1435[a]		1480-1520[a-c]		1380-1395[a]		1553-1644[a,b]		1243-1355[a,b]		1510-1670[a,c,d]	

a. Ref 1; b. Ref, 2; c. Ref. 3 d. Ref. 4; e. Ref. 5

Tab. S2.

The oxygen vacancies relative concentration ratios by XPS (%).

Catalyst	$O_{Vo}/(O_{lat}+ O_{Vo}+ O_{ads})$
Co-precipitation Cu-ZnO	21
Hydrothermal CuO-ZnO	35
CuO-ZnO@ZIF-8 (1:4)	39

References

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