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Electronic Supplementary Information

2 Title: A Facile One-Pot Synthesis of CaO/CuO Hollow Microspheres

3 Featuring Highly Porous Shells for Enhanced CO₂ Capture in Combined

4 Ca-Cu Looping Process via a Template-Free Synthesis Approach

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1. Experimental

60 Performance test

In this work, the CO_2 capture performance and redox characteristics of the assynthesized CaO/CuO composites were assessed in a bench-scale fixed-bed reactor, as illustrated in Fig. S1. In a typical test, approximately 1 g of sample was supported by quartz wool in the center of a tubular quartz reactor, which had an inner diameter of 25 mm, a wall thickness of 2.5 mm and a length of 600 mm. The tubular quartz reactor was placed inside an electrically-heated programmable tube furnace. The flow rates of different gases were controlled using accurate mass flow controllers (MFCs).

The cycling experiment started once the sample was heated to 850 °C with a heating 68 rate of 10 °C/min under a N2 flow of 1500 mL/min. The calcination/reduction reaction 69 was conducted for 10 min in an atmosphere of 20 vol.% CH₄ (N₂ balance, a total volume 70 flow of 1500 mL/min). The calcination/reduction temperature was selected as 850 °C, 71 because it was high enough to achieve completely decompose CaCO₃, considering the 72 pronounced dilution effect of steam generated in the reduction reaction (as shown in 73 Eq. S1). The dilution effect of steam is even more pronounced when H_2 is selected as 74 the reducing gaseous fuel (as shown in Eq. S2). The oxidation reaction was carried out 75 at 600 - 700 °C for 5 min in an atmosphere of 21 vol.% O_2 (N₂ balance, a total volume 76 77 flow of 1500 mL/min), and the subsequent carbonation reaction was performed at the same temperature for another 5 min in an atmosphere of 15 vol.% CO₂ (N₂ balance, a 78 total volume flow of 1500 mL/min). The heating step (i.e., when transitioning from the 79 oxidation step to the calcination/reduction step) of the cycling experiment was 80 performed in an atmosphere of 20 vol.% CH₄ (N₂ balance, a total volume flow of 1500 81 mL/min) with a heating rate of 10 °C/min, while the cooling step was conducted in an 82 atmosphere of N₂ (a total volume flow of 1500 mL/min) with a cooling rate of 10 83 °C/min. The duration for each step, i.e., calcination/reduction, oxidation and 84 carbonation, was determined by our preliminary experiments, respectively. The 85 calcination/reduction, oxidation and carbonation reactions were repeated a specified 86 number of times. The O₂ and CO₂ concentrations during the oxidation and carbonation 87

reactions were measured online by a flue gas analyzer (NOVA PLUS, MRU Germany),respectively.

$$4CuO+CH_4 \rightarrow CO_2+2H_2O+4Cu \tag{S1}$$

(S2)

91
$$H_2+CuO \rightarrow H_2O+Cu$$

90

Note that N₂ should not be present in the calcination/reduction reactor, because the 92 presence of N2 dilutes the CO2 stream and, thus, a concentrated CO2 stream cannot be 93 obtained at the outlet of the calcination/reduction reactor. Also, the presence of N₂ 94 significantly lowers the decomposition temperature of CaCO₃, thus the tests conducted 95 are unrealistic and do not reflect the performance of sorbents under realistic conditions. 96 97 Consequently, an extremely harsh condition was employed in this work, which aims to emulate a real process as closely as possible and thus assess the real carbonation and 98 redox characteristics of the materials. At this condition, the calcination/reduction 99 reaction was conducted for 10 min at a higher temperature of 940 °C in an atmosphere 100 of 20 vol.% CH₄ (CO₂ balance, a total volume flow of 1500 mL/min), in which N₂ was 101 replaced by CO₂ as the balance gas without changing the volume ratio. The oxidation 102 reaction and the carbonation reaction were performed at the same conditions mentioned 103 above (i.e., oxidation reaction: 650 °C, 5 min, 21 vol.% O2 (N2 balance, a total volume 104 flow of 1500 mL/min); carbonation reaction: 650 °C, 5 min, 15 vol.% CO₂ (N₂ balance, 105 a total volume flow of 1500 mL/min)). The heating step of this experiment was 106 107 performed in an atmosphere of 20 vol.% CH₄ (CO₂ balance, a total volume flow of 1500 mL/min) with a heating rate of 10 °C/min, while the cooling step was conducted 108 in an atmosphere of N₂ (a total volume flow of 1500 mL/min) with a cooling rate of 10 109 110 °C/min. To the best of our knowledge, such extremely harsh conditions have not been 111 employed before. In previous work, the calcination/reduction reaction was commonly conducted under an atmosphere of pure CH₄ or CH₄ diluted by N₂ with various CH₄/ 112 N₂ volume ratios at a temperature range of 750-800 °C,¹⁻⁶ which ignored the presence 113 of CO₂ generated during the reaction process and, thus, was unrealistic. 114

In this work, CO_2 uptake capacity (i.e., C_N) and O_2 uptake capacity (i.e., O_N) were used to characterize the CO_2 capture performance and redox characteristics of the 117 sorbent, respectively, as follows:

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$$C_{N} = \frac{\int_{0}^{t} \left(c_{CO_{2}}^{in} - c_{CO_{2}}^{out}(t) \right) dt \cdot Q \cdot M_{cO_{2}}}{22.4 \cdot m_{0}}$$
(S3)

119
$$O_N = \frac{\int_0^{y} \left(c_{O_2}^{in} - c_{O_2}^{out}(y) \right) dy \cdot Q \cdot M_{O_2}}{44.8 \cdot m_0}$$
(S4)

where C_N (in g_{CO2}/g_{material}) means the CO₂ uptake capacity of the sample in the Nth cycle; 120 $c_{CO_2}^{in}$ (in %) represents the CO₂ inlet concentration; $c_{CO_2}^{out}(t)$ (in %) denotes the CO₂ 121 122 outlet concentration at time t; t (in s) is the carbonation time; Q (in L/s) means the total gas flow rate; M_{CO2} (in g/mol) is the molar mass of CO₂; m_0 (in g) represents the mass 123 of sample. O_N (in $g_{O2}/g_{material}$) means O_2 uptake capacity of the sample in the Nth cycle; 124 $c_{O_2}^{in}$ (in %) represents the O₂ inlet concentration; $c_{O_2}^{out}(y)$ (in %) denotes the O₂ outlet 125 concentration at time y; y (in s) is the oxidation time; and M_{O2} (in g/mol) is the molar 126 mass of O₂. 127

2. Result



132 Fig. S2. Morphology of CaO/CuO(1)-0.4-180-24. (a) SEM image; (b) HAADF-STEM image.



Fig. S3. TEM image of CaO/CuO(1)-0.24-180-12.

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138 Fig. S4. SEM image of CaO/CuO(1)-0.24*. This composite was synthesized without

139 hydrothermal treatment and the other synthesis parameters were kept the same as

- 140 CaO/CuO(1)-0.24-180-24.
- 141



Fig. S5. SEM image of CaO/CuO(1)-0.24-180-24*. This composite was synthesized

144 in the absence of glycine whereas the other synthesis parameters were kept the same

145 as CaO/CuO(1)-0.24-180-24.

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- 148
- Fig. S6. SEM image of CaO/CuO(1)-0.24-120-24.



- 157 respectively. (a) CO₂ capture performance; (b) redox characteristics.
- 158



- **Fig. S9.** TEM image of CaO/CuO(1)-0.24-180-24 after five repeated cycles.



163 Fig. S10. SEM images of broken CaO/CuO(1)-0.24-180-24 after ten repeated cycles.



166 Fig. S11. Pore size distributions of CaO/CuO composites before and after the repeated

cycles.

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Fig. S12. XRD patterns of CaO/CuO hollow microspheres (CaO/CuO(1)-0.4-180-24)
during the repeated calcination/reduction, oxidation and carbonation cycles. (Reaction
conditions: calcination/reduction temperature: 850 °C; oxidation and carbonation

- temperature: 650 °C)
- 174

Sample	Synthesis method	Ca ²⁺ molar concentration (mol/L)	Hydrothermal temperature (°C)	Hydrothermal duration (h)
CaO/CuO(1)-0.04-180-24	Template-free synthesis	0.04	180	24
CaO/CuO(1)-0.08-180-24	Template-free synthesis	0.08	180	24
CaO/CuO(1)-0.24-180-24	Template-free synthesis	0.24	180	24
CaO/CuO(1)-0.4-180-24	Template-free synthesis	0.4	180	24
CaO/CuO(1)-0.24-180-6	Template-free synthesis	0.24	180	6
CaO/CuO(1)-0.24-180-12	Template-free synthesis	0.24	180	12
CaO/CuO(1)-0.24-180-18	Template-free synthesis	0.24	180	18
CaO/CuO(1)-0.24-120-24	Template-free synthesis	0.24	120	24
CaO/CuO(1)-0.24-180-24* a	Template-free synthesis	0.24	180	24
CaO/CuO(1)-0.24* b	Template-free synthesis	0.24	/	/
CaO/CuO(1)-0.24-CP	Co-precipitation	0.24	/	/
CaO/CuO(1)-0.24-WM	Wet mixing	0.24	/	/

 Table S1. Summary of CaO/CuO composites synthesized in this work

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a: CaO/CuO(1)-0.24-180-24* denotes CaO/CuO composites synthesized in the absence
of glycine, whereas the other synthesis parameters were kept the same as CaO/CuO(1)0.24-180-24.

b: CaO/CuO(1)-0.24* denotes CaO/CuO composites synthesized without hydrothermal
treatment, whereas the other synthesis parameters were kept the same as CaO/CuO(1)0.24-180-24.

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183 **Table S2.** CO₂ capture performance of CaO/CuO composites reported in previous

work and synthesized in this work

	Reaction condition	Cycle	CO ₂ uptake		Reactor ^a
Sample			$(g_{CO2}/g_{material})$		
		number	Initial	Final	-
core-shell structured CaO- CuO/MgO@Al ₂ O ₃ ⁷	cal/red: 750 °C, 15 vol.% CH ₄ (N ₂ bal.), 8 min car: 750 °C, 15 vol.% CO ₂ (N ₂ bal.), 10 min	30	0.05	0.08	TGA
CaO/CuO pellet supported with cement ⁶	cal/red: 875 °C, CH ₄ , 10 min car: 650 °C, 20 vol.% CO ₂ (N ₂ bal.), 15 min	16	0.06	0.02	TGA
Core-in-shell structured CaO- CuO pellets ⁸	cal/red: 850 °C, 66.5 vol.% (H ₂ bal.), 15 min car: 650 °C, 15 vol.% CO ₂ , 4 vol.% O ₂ (N ₂ bal.), 15 min	12	0.11	0.07	FBR
CaO/CuO composite supported with MgO ⁴	cal/red: 750 °C, 10 vol.% CH ₄ (N ₂ bal.), 20 min car: 750 °C, 40 vol.% CO ₂ , 5.4 vol.% O ₂ , (N ₂ bal.), 40 min	15	0.15	0.10	TGA
CaO/CuO composite ³	cal/red: 800 °C, 15 vol.% CH ₄ (N ₂ bal.), 10 min car: 650 °C, 15 vol.% CO ₂ (N ₂ bal.), 10 min	4	0.06	0.05	TGA

CaO/CuO cal/red: 800 °C, 15 vol.% CH ₄					
composite	(N ₂ bal.), 10 min	1	0.26	0.20	
supported with	car: 650 °C, 15 vol.% CO ₂ (N ₂	4	0.20	0.20	IGA
MgO ³	bal.), 10 min				
CaO/CuO	cal/red: 950 °C, 15 vol.% CH ₄				
composite	(N ₂ bal.), 10 min	4	0.11	0.00	
supported with	car: 750 °C, 15 vol.% CO ₂ (N ₂	4	0.11	0.09	IUA
MgO ³	bal.), 10 min				
	cal/red: 750 °C, 10 vol.% CH ₄				
CaO/CuO	(N ₂ bal.), 20 min	15	0.27	0.19	TGA
composite ²	car: 750 °C, 40 vol.% CO ₂ , 5.4	15	0.27	0.18	
	vol.% O ₂ (N ₂ bal.), 40 min				
Core-in-shell CaO-	cal/red: 800 °C CH4 10 min				
CuO pellets		2	0.25	0.15	TCA
supported with	car: 600 °C, 20 vol.% CO ₂ (N ₂	3	0.23	0.13	IUA
cement ¹	bal.), 12 min				
	cal/red: heating step from 650				
nanostructured	°C to 800 °C, 15 vol.% CH ₄				
CaO/CuO	$(N_2 bal.)$, 15 min	(N ₂ bal.), 15 min 40		0.17	TGA
composite9	car: 650 °C, 15 vol.% CO ₂ (N ₂				
	bal.), 30 min				
CaO/CuO hollow	cal/red: 850 °C, 20 vol.% CH ₄				
microspheres	(N ₂ bal.), 10 min	20	0.21	0.15	EDD
synthesized in this	synthesized in thiscar: 650 °C, 15 vol.% CO_2 (N2workbal.), 5 min		0.21	0.13	ΓΔΚ
work					

185 a: Reactor is divided into thermogravimetric analyzer (TGA) and fixed bed reactor

186 (FBR).

187

190) synthesis methods					
	Somula	CO ₂ uptake (CO ₂ uptake (g _{CO2} /g _{material})			
	Sample	First cycle	10 th cycle	Decline fate (%)		
	CaO/CuO(1)-0.24-WM	0.15	0.05	66.7		
	CaO/CuO(1)-0.24-CP	0.17	0.07	58.8		
	CaO/CuO(1)-0.24-180-24	0.21	0.15	28.6		
	CaO/CuO(1)-0.4-180-24	0.19	0.13	31.6		

Table S3. CO₂ capture performance of CaO/CuO composites prepared by different

Table S4. Porosity characterizations of CaO/CuO composites before and after



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	As-synthesized		After ten cycles (calcined/reduced state)	
Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Surface area (m ² /g)	Pore volume (cm ³ /g)
CaO/CuO(1)-0.24-CP	16.7	0.027	4.6	0.019
CaO/CuO(1)-0.24-WM	14.7	0.023	2.1	0.013
CaO/CuO(1)-0.24-180-24	33.9	0.031	7.8	0.024
CaO/CuO(1)-0.4-180-24	24.0	0.043	6.6	0.019

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