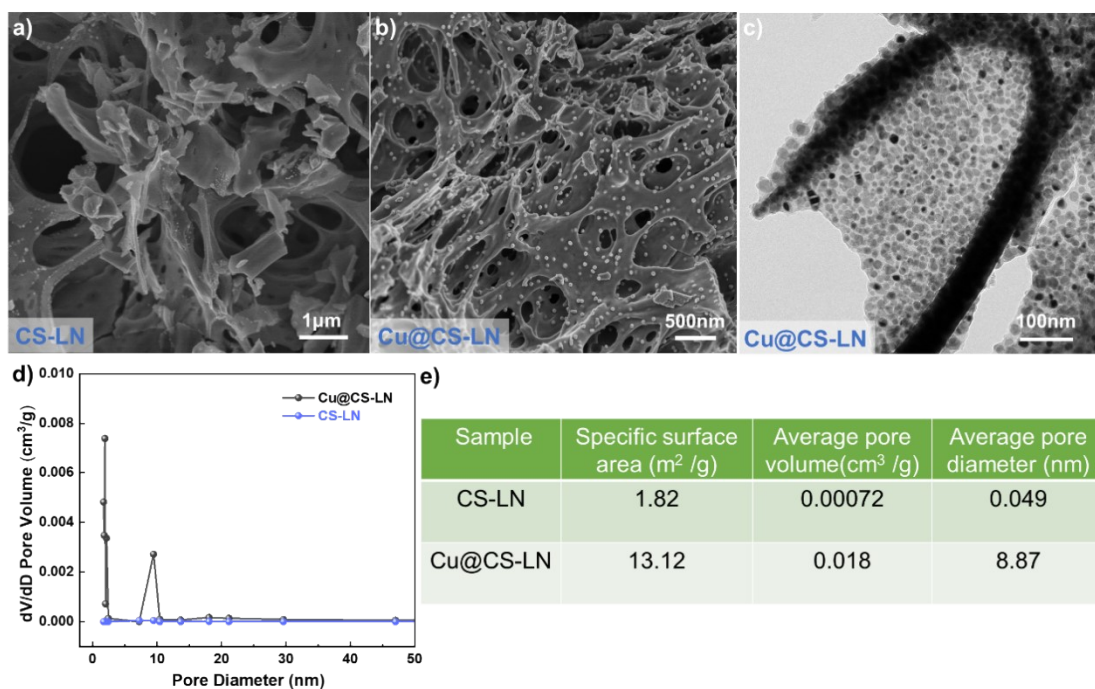# Chitosan-Lignin Carbon Framework Encapsulated Cu Catalyst Facilitates Base-free Hydrogen Evolution from Methanol/Water

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Sample	Specific surface area (m² /g)	Average pore volume(cm³ /g)	Average pore diameter (nm)
CS-LN	1.82	0.00072	0.049
Cu@CS-LN	13.12	0.018	8.87

Fig. S1 SEM image of CS-LN composite(a) and Cu@CS-LN(b); (c) TEM of Cu@CS-LN; (d) Pore size distribution of CS-LN and Cu@CS-LN; (e) the specific surface area, average pore volume, and average pore size of the CS-LN support and Cu@CS-LN.

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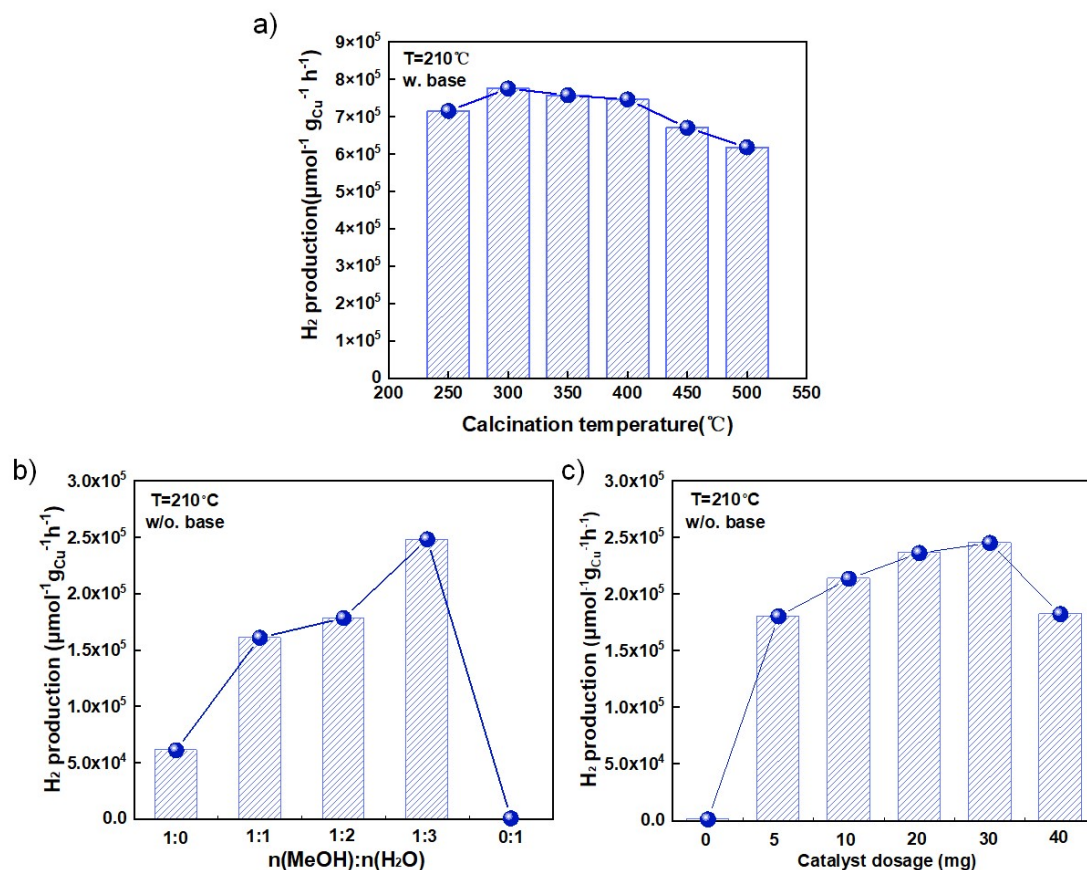
Fig. S2 The hydrogen production rate of (a) various calcination temperatures (250-500°C) with 5 wt% NaOH; (b) various molar ratio of MeOH to H_2O; (c) various dosage of Cu@CS-LN catalyst. Reaction conditions: 210 °C, 2 MPa, N_2.

Table S1. The generation of H_2 via aqueous phase methanol reforming over M@CS-LN (M=Ni, Fe, Co) catalysts [a]

Entry	Catalyst	Temp (°C)	n_{CH_3OH}:n_{H_2O}	$\mu mol_{H2}\ g_{Cu}^{-1}\ h^{-1b}$	Sel (CO)%
1	**Cu@CS-LN**	210	1：3	$2.5x10^5$	0.22
2	**Ni@CS-LN**	210	1：3	$3.9x10^4$	6.6
3	**Fe@CS-LN**	210	1：3	$6.4.x10^4$	3.9
4	**Co@CS-LN**	210	1：3	$7.4x10^4$	2.1

[a]Reaction conditions: n(MeOH)/n(H_2O) = 1:3, 10 mL of total volume of liquid, 30 mg of activated catalysts, no base, 2 MPa of N_2. [b]Catalytic performance is calculated as the hydrogen production per gram of Cu-catalyst per hour. The unit is $\mu mol_{H2}\ g_{Cu}^{-1}\ h^{-1}$.

Table S2. Catalytic hydrogen evolution activity of aqueous MeOH reforming[a]

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Entry	Catalyst	Temp (°C)	$\mu mol_{H2}\ g_{Cu}^{-1}\ h^{-1\,b}$	Sel (CO)%
1	**Cu@CS-LN**	210	2.5×10^5	0.22
2	**CS-LN**	210	1082	6.2
3	--	210	--	--
4	**Cu/LN**	210	1131	3.9
5	**Cu@CS**	210	1.1×10^5	0.21
6[c]	**Cu@CS-LN**	210	898	1.1
7[d]	**Cu@CS-LN**	210	1.8×10^5	0.002

[a]Reaction conditions: $n(MeOH)/n(H_2O) = 1{:}3$, 10 mL of total volume of liquid, 30 mg of activated catalysts, no base, 2 MPa of N_2. [b]Catalytic performance is calculated as the hydrogen production per gram of Cu-catalyst per hour. The unit is $\mu mol_{H2}\ g_{Cu}^{-1}\ h^{-1}$. [c] Reaction conducted in the air atmosphere. [d] Cu@CS-LN precursor was calcined in N_2 at 500 °C for 2h.

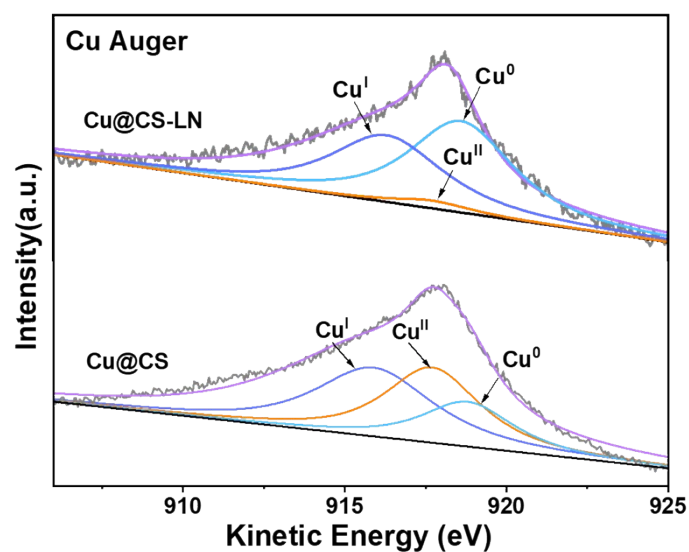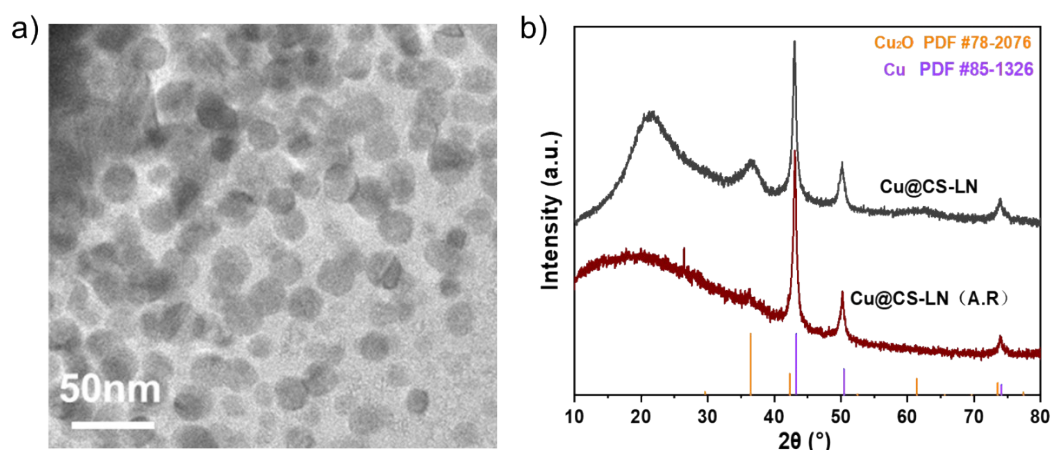**Fig. S3** Cu $L_3M_{45}M_{45}$ Anger spectra of Cu@CS-LN and Cu@CS.

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Table S3. The kinetic energy of Cu LMM peak in XPS and surface Cu^I/Cu^0 ratio of the sets of Cu-containing catalysts. $\%Cu^{II}$ is the percentage of Cu^{II}

Catalyst	Kinetic energy of Cu LMM (eV)			Surface Cu^I/Cu^0 atomic ratio(%)	$\%Cu^{II}$ By fitting
	Cu^0	Cu^I	Cu^{II}		
Cu@CS	918.6	916.7	917.7	196.7	37.0
Cu@CS-LN	918.6	916.4	917.7	78.3	3.4
Cu@CS-LN (A.R.)	918.5	916.5	917.7	68.4	1.0
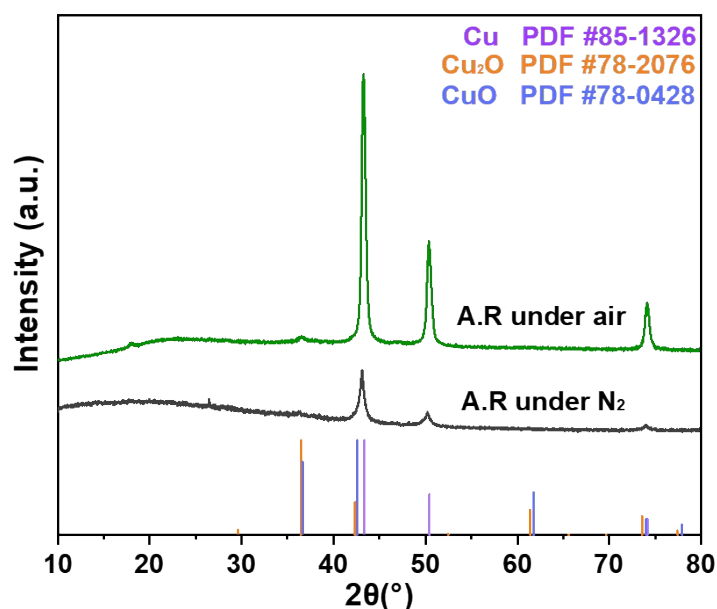
Fig. S4 The XRD patterns of Cu@CS-LN catalysts after reaction (A.R) under N_2/air atmosphere. Reaction conditions: $n(MeOH)/n(H_2O)$ = 1:3, 10 mL of total volume of liquid, 30 mg of activated Cu@CS-LN catalysts, no base, 210 ^{o}C, 2 MPa of N_2/air.

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Fig. S5 (a) The TEM image after reactions; (b) XRD patterns before and after reaction over Cu@CS-LN catalyst in the hydrogen production of aqueous MeOH reforming under optimal reaction.

Table S4. Correlation between the reactivity of APRM and the contact angle of catalysts

| Entry	Catalyst	Contact angle(º)	$\mu mol_{H2} \; g_{Cu}^{-1} \; h^{-1a}$
1	**Cu@CS-LN**	55.3±2.4	2.5×10^5
2	**CS-LN**	68.2±1.2	1082
3	**CS**	117.1±4.2	272

Reaction conditions: n(MeOH)/n(H₂O) = 1:3, 10 mL of total volume of liquid, 30 mg of activated catalysts, no base, 210 °C, 2 MPa of N₂. [a]Catalytic performance is calculated as the hydrogen production per gram of Cu-catalyst per hour. The unit is $\mu mol_{H2} \; g_{Cu}^{-1} \; h^{-1}$. [b]The hydrogen production rate decreases remarkably with rise of contact angle, verifying that improving catalyst wettability could promote activity for APR of methanol.

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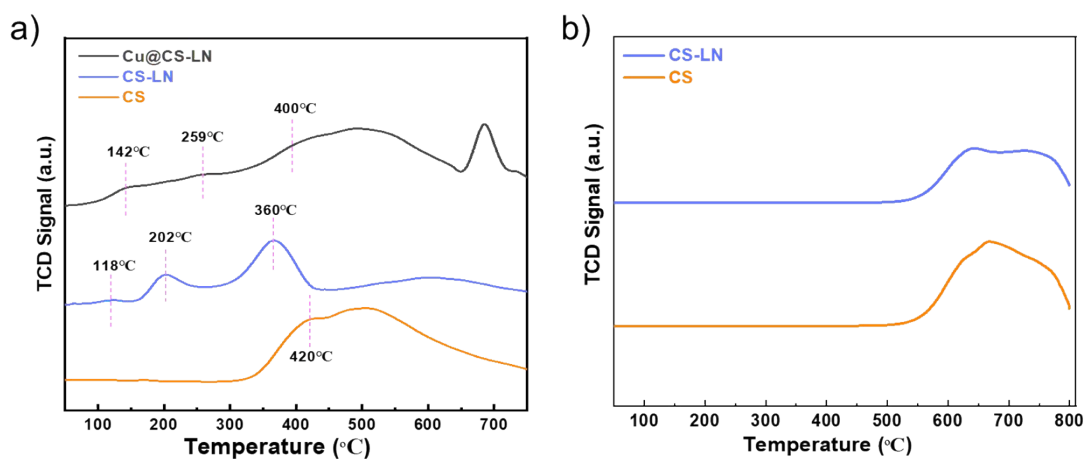
Fig. S6 Temperature-programmed desorption (TPD) experiment (a) with methanol over CS, CS-LN, and Cu@CS-LN (b) without methanol over CS and CS-LN.
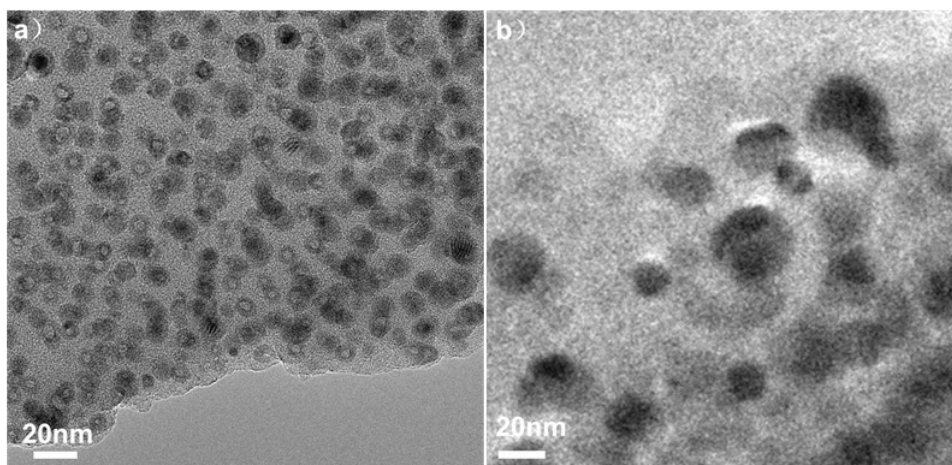
Fig. S7 The TEM image of Cu/CS-LN (a) before reaction (with particle size of 11.2±1.7nm) and (b) after reaction (with particle size of 20.6±1.2nm).

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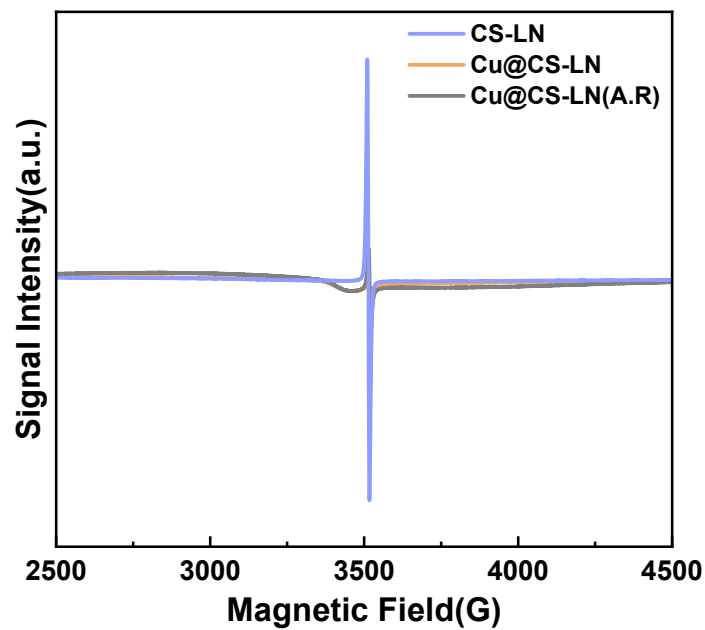
Fig S8. EPR spectra of CS-LN and Cu@CS-LN before and after reaction. The spectra of Cu@CS-LN almost overlapped with that of pure carbon framework CS-LN, ruling out the existence of Cu^{II} in the copper species.

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