Supplementary Materials of

Green solid-state synthesis of Cu_4O_3/biochar composites with high antimicrobial activity

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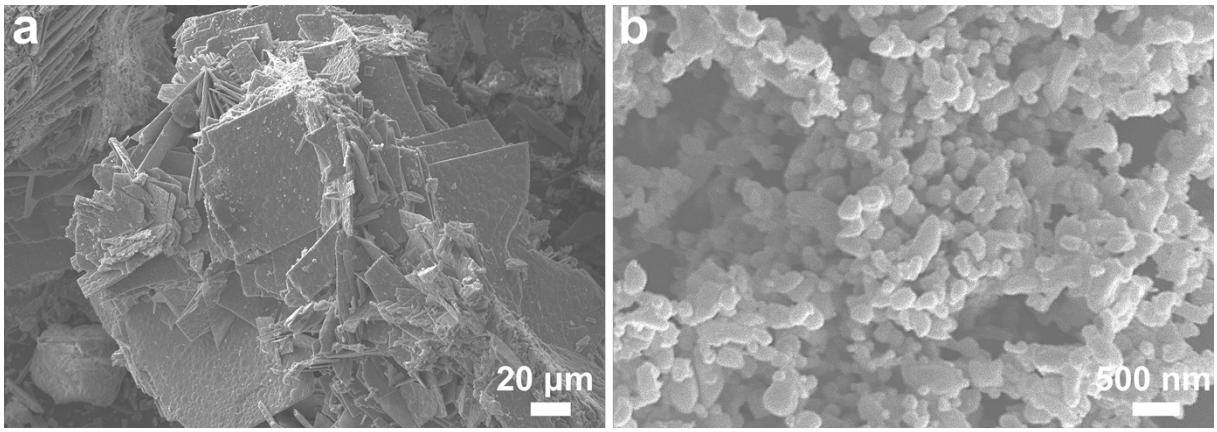

Figure S1. SEM images of copper formate. (a) untreated sample, (b) after the BM-1 process**.**

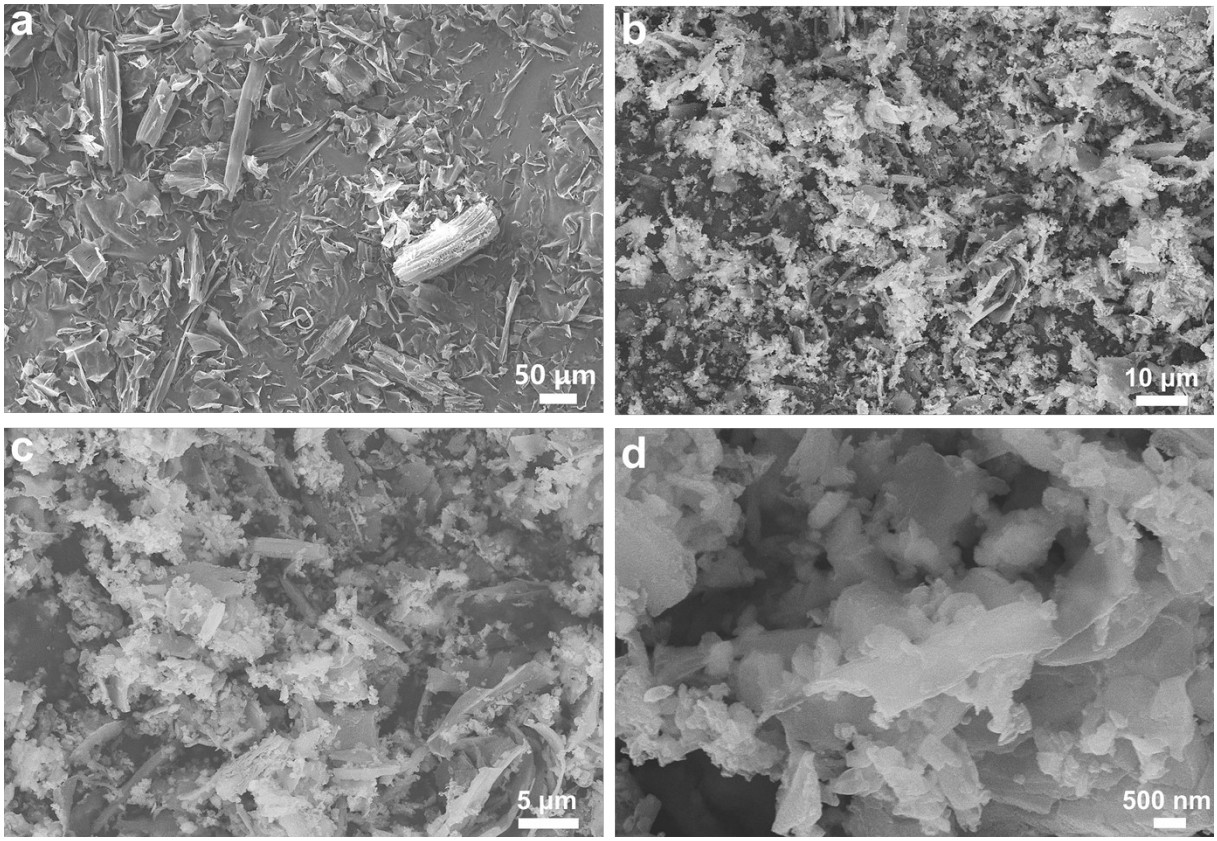

Figure S2. SEM images of (a) CSBC and (b-d) the copper formate/CSBC precursor.

Table S1. The mass ratio of Cu and Cu_4O_3 in the Cu_4O_3/CSBC composite. The results were determined by ICP-OES. The mass ratio of Cu_4O_3 was calculated according to the mass ratio of Cu element (84.1 %) relative to Cu_4O_3.

Sample	**Cu atomic mass ratio (wt.%)**	**Cu_4O_3 mass ratio (wt.%)**
Cu_4O_3/CSBC composite	12.87	15.30

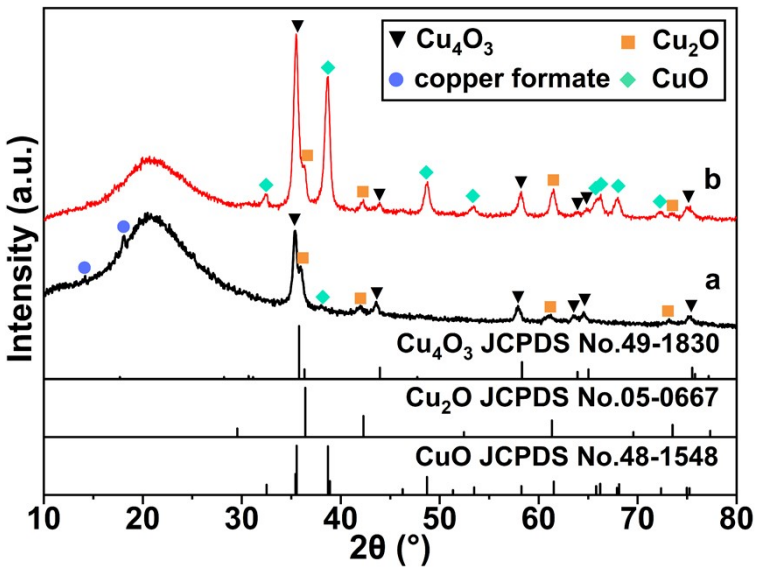

Figure S3. XRD spectra of the sintered product of copper formate/CSBC precursor after the solid-state sintering process at different sintering temperature. (a) sintering at 220 ℃ for 12 min; (b) sintering at 240 ℃ for 12 min.

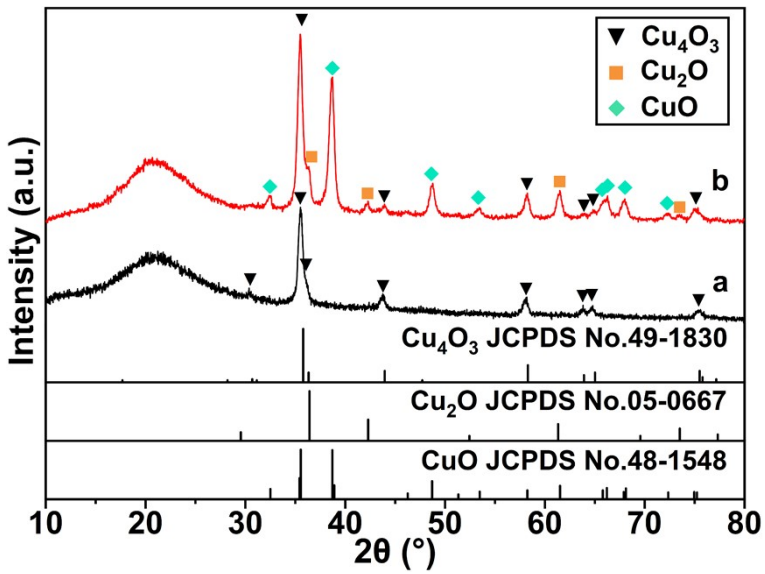

Figure S4. XRD spectra of the sintered products for the CSBC supporting capacity experiments on Cu_4O_3. (a) support amount of 10 wt.% for Cu_4O_3; (b) support amount of 20 wt.% for Cu_4O_3.

Table S2. Optimal processing parameters for preparing Cu_4O_3/biochar composites from various resources: PLBC, CWBC, and BBC.

sample	biomass resource	pyrolysis temperature of biochar (℃)	Cu_4O_3 mass ratio (wt.%)
Cu_4O_3/PLBC composite	palm leaves	300	15
Cu_4O_3/CWBC composite	cedar wood	300	10
Cu_4O_3/BBC composite	bagasse	400	15

Table S3. Processing variables of the controlled experiments, where "√" indicates that the sample underwent the treatment and "×" indicates that the sample did not undergo the treatment.

sample	process		
	BM-2	removal of copper formate	solid-state sintering process
CSBC	×	×	×
BM-CSBC	√	√	×
BM-S-CSBC	√	√	√
Cu_4O_3/CSBC composite	√	×	√

Table S4. MIC values of the Cu_4O_3/CSBC composite against *E. coli*, *S. aureus*, and *MRSA*, respectively.

sample	MIC (μg/mL)		
	E. coli	***S. aureus***	***MRSA***
Cu_4O_3/CSBC composite	5	0.1	0.125

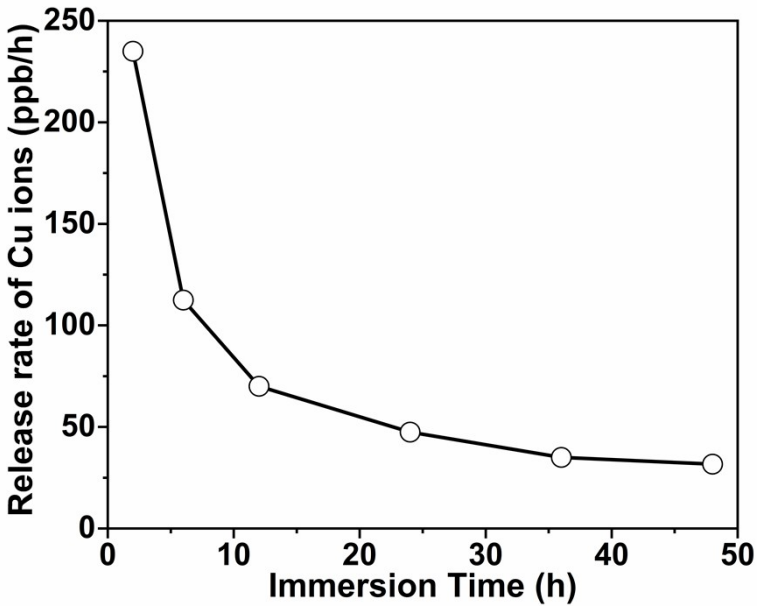

Figure S5. Release rate of Cu ions for the Cu_4O_3/CSBC composite during the 48-hour immersion experiment. The data were analyzed based on the differences in the cumulative release of Cu ions during each test period.

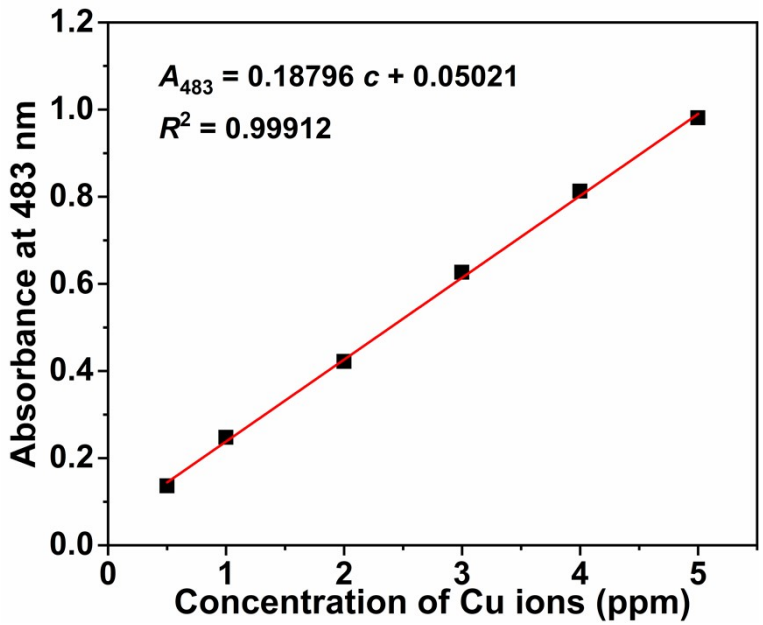

Figure S6. Standard curve between the absorbance of BCS at 483 nm and the concentrations of Cu ions. The linear regression equation was obtained from the standard curve as follows,

$A_{483} = 0.18796\, c + 0.05021$

where A_{483} is the absorbance at 483 nm, and c is the concentration of Cu ions.

Experimental procedure:

Hydroxylamine hydrochloride (20 mg) was added to six portions of the standard solution of $CuSO_4$ (1 mM) to completely reduce Cu^{2+} to Cu^{+}. Then the solution was diluted to 0.5, 1, 2, 3, 4, and 5 ppm of Cu ion concentrations with phosphate buffer solution and water, respectively. 100 μL of BCS solution (5 mM) was added to each solution, and kept for 10 min after shaking. The absorbance of the samples was then detected by UV-vis spectroscopy in the wavelength range of λ = 190-700 nm.

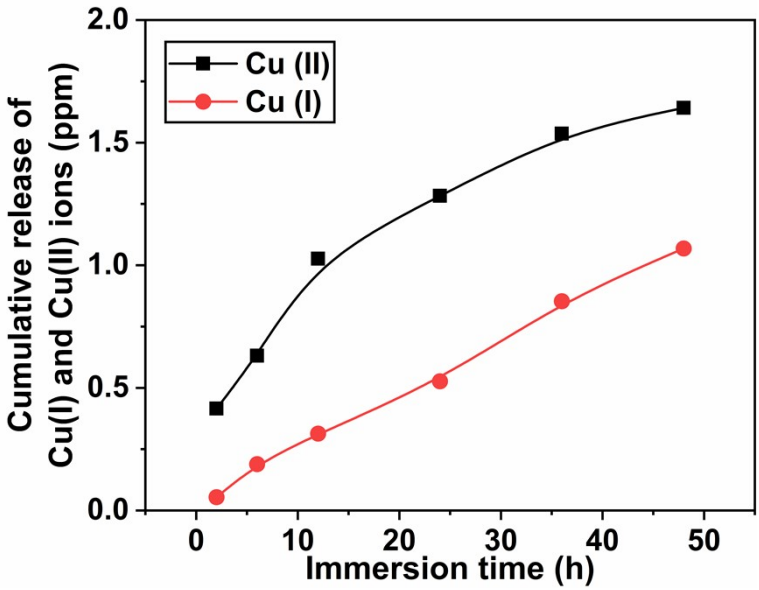

Figure S7. Cumulative release of Cu(I) and Cu(II) ions for the Cu_4O_3/CSBC composite during the 48-hour immersion experiment. The data were obtained as follows,

$$C_{Cu(II)} = C_{Cu} - C_{Cu(I)}$$

where $C_{Cu(II)}$ is the cumulative release of Cu(II) ions, C_{Cu} is the cumulative release of Cu ions obtained from the ICP-OES test, and $C_{Cu(I)}$ is the cumulative release of Cu(I) ions obtained from the linear regression equation: $A_{483} = 0.18796\ c + 0.05021$.

Table S5. Vacancy formation energy of Cu ions on the Cu_4O_3 (101) surface.

Sites	Cu-I	Cu-II-a	Cu-II-b
$E_{\text{defected slab}}$ (eV)	-299.67	-298.25	-298.80
E_{vacancy} (eV)	1.69	3.10	2.55

The vacancy formation energy is calculated by the equation as follows,

$$E_{\text{vacancy}} = E_{\text{defected slab}} + E_{\text{FCC\_Cu}} - E_{\text{perfect slab}}$$

where E_{vacancy} is the vacancy formation energy; $E_{\text{defected slab}}$ is the total energy of surface model with a vacancy, $E_{\text{FCC\_Cu}}$ is the total energy of FCC Cu, -1.63 eV/atom, and $E_{\text{perfect\_slab}}$ is the total energy of (101) surface model, -302.98 eV.

Table S6. Vacancy formation energy of Cu ions on the Cu_4O_3 (100) surface.

sites	Cu-I	Cu-II
$E_{\text{defected slab}}$ (eV)	-291.53	-289.29
E_{vacancy} (eV)	1.83	4.07

The vacancy formation energy is calculated by the equation as follows,

$$E_{\text{vacancy}} = E_{\text{defected slab}} + E_{\text{FCC\_Cu}} - E_{\text{perfect slab}}$$

where E_{vacancy} is the vacancy formation energy; $E_{\text{defected slab}}$ is the total energy of surface model with vacancies, $E_{\text{FCC\_Cu}}$ is the energy of FCC Cu, -1.63 eV/atom, and $E_{\text{perfect\_slab}}$ is the total energy of (100) surface model, -294.99 eV.

Table S7. Intensity ratio of the (202) of Cu_4O_3 and CSBC based on the XRD spectra of the Cu_4O_3/CSBC composite during a 48-hour immersion experiment.

Immersion time	**0 h**	**6 h**	**12 h**	**24 h**	**48 h**
$I_{d(202)}/I_{d(CSBC)}$ (%)	1.28	1.18	1.04	0.91	0.88