Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supplementary Material

A self-triggered carboxymethyl chitosan hydrogel for convenient sustained release ClO_2 gas with environmental stability and long-term antimicrobial effect

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Table. S1. The sample preparation proportion

Sample's name	Content (W/V)
CMCS-Zn	CMCS:8%, $Zn(NO_3)_2 \cdot 6H_2O$: 10%
CMCS-Zn@$NaClO_2$-20	CMCS:8%, $Zn(NO_3)_2 \cdot 6H_2O$: 10%, NaClO2: 20%
CMCS-Zn@$NaClO_2$-30	CMCS:8%, $Zn(NO_3)_2 \cdot 6H_2O$: 10%, NaClO2: 30%
CMCS-Zn@$NaClO_2$-40	CMCS:8%, $Zn(NO_3)_2 \cdot 6H_2O$: 10%, NaClO2: 40%

Sample's name	Stage	pH
$Zn(NO_3)_2 \cdot 6H_2O$	Before Cross-link	5±0.1
CMCS@$NaClO_2$-20	Before Cross-link	13.1±0.2
CMCS@$NaClO_2$-30	Before Cross-link	13.3±0.1
CMCS@$NaClO_2$-40	Before Cross-link	13.5±0.1
CMCS-Zn@$NaClO_2$-20	Cross-linked	4.0±0.1
CMCS-Zn@$NaClO_2$-30	Cross-linked	4.2±0.1
CMCS-Zn@$NaClO_2$-40	Cross-linked	4.4±0.1

Table. S2. The pH values of different samples and different stage

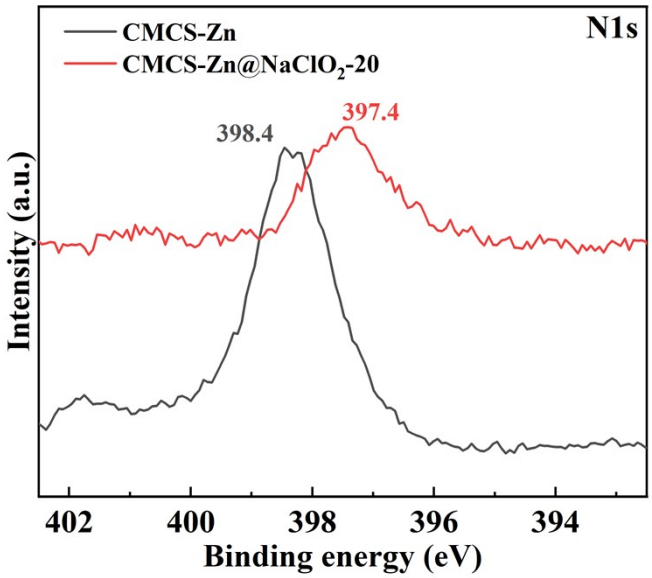


Fig. S1. XPS spectra of CMCS-Zn and CMCS-Zn@$NaClO_2$-20: N 1s peaks

Table S3. Summary of the atomic % data of XPS

	C 1s	N 1s	Cl 2p	O 1s	Zn 2p
Atomic (%)	38.31	4.21	13.97	39.60	3.91

NaClO2 content (%)	34.65

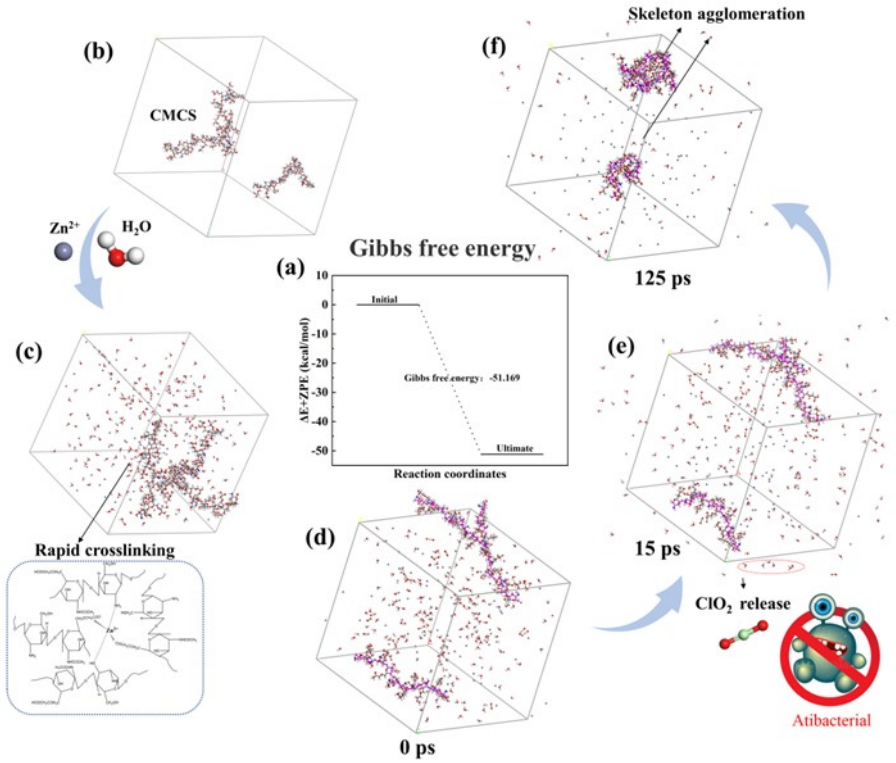


Fig. S2. (a) Gibbs free energy changes image. (b-c) Simulation snapshot of CMCS, Zn2+ and water molecules in the system. (d-f) Snapshots of aggregation behaviours at various simulation times (0ps/15ps/125ps).

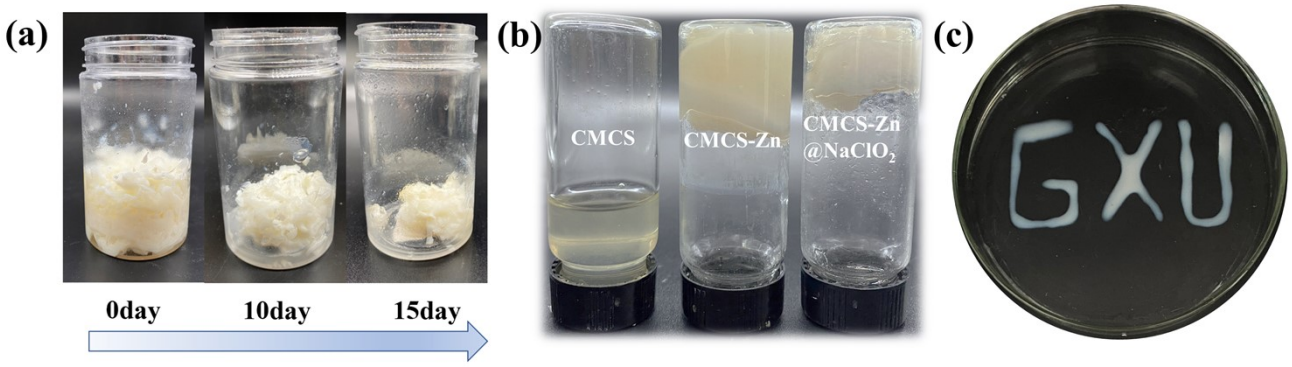


Fig. S3. (a) Changes in the appearance of CMCS-Zn@$NaClO_2$. (b) Adhesion state diagram. (c) Rapid cross-linking pattern "GXU".

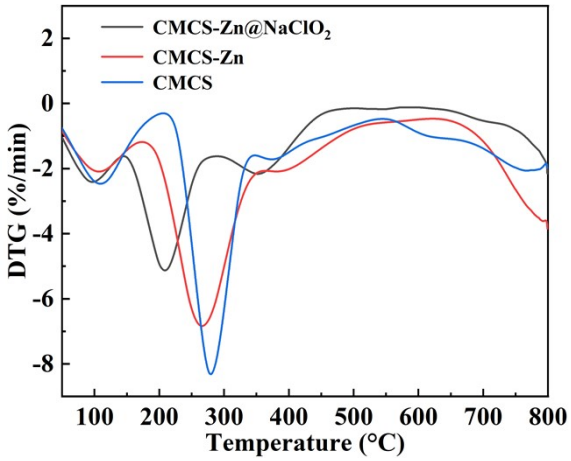
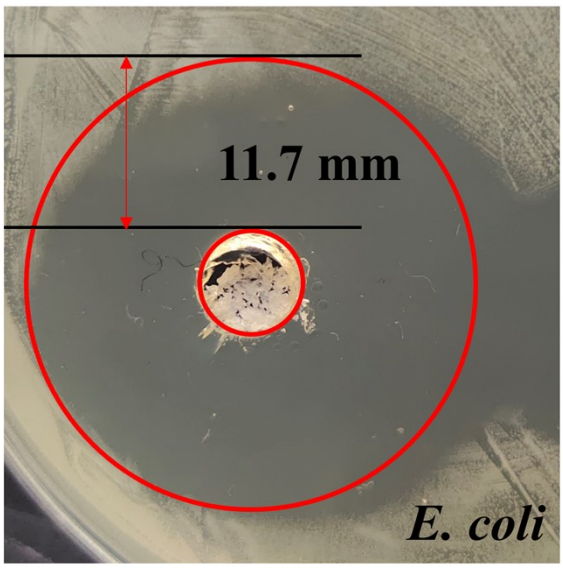


Fig. S4. DTG curve of CMCS, CMCS-Zn and CMCS-Zn@$NaClO_2$

Table S3. Comparison with reported antibacterial materials

	Inhibition zone diameter (mm)						
	HKUST-1@CMCS	PLT@Ag-MOF-Vanc	CEO nanoemulsion	HA-DA/rGO3/Doxy	PBVT4	Ag-MOFs@CMFP	CMCS-Zn@$NaClO_2$
E. coli	5.2	—	—	3.9	—	7.2	16.2
S. aureus	4.9	22.1	—	3.2	6.6	4.6	16.6
A. niger	—	—	23.74	—	—	14.1	17.6
Reference	Huang et al., 2020	Huang et al., 2021	Pongsumpun et al., 2020	Liang et al., 2019	Ge et al., 2019	Zhang et al., 2022	★ This work



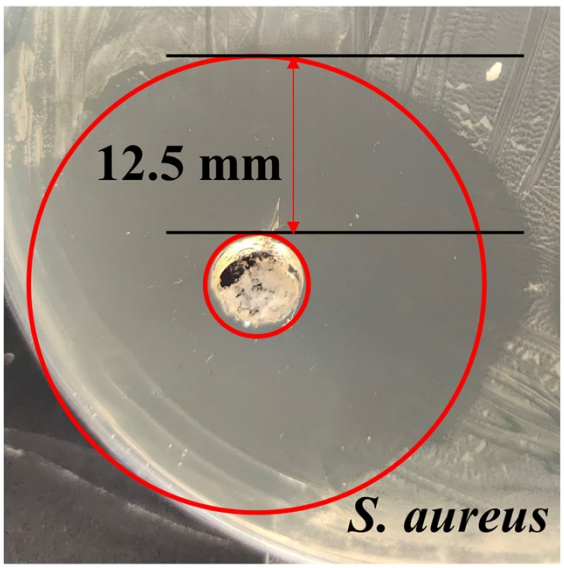


Fig. S5. Inhibition zone test against *E. coli* and *S. aureus* of CMCS@$NaClO_2$.

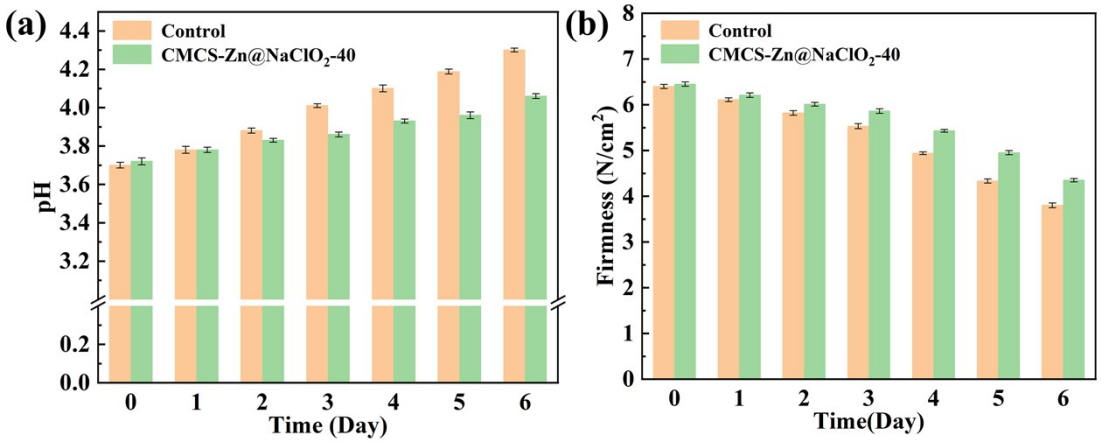


Fig. S6. The (a) pH and (b) firmness of blueberry.

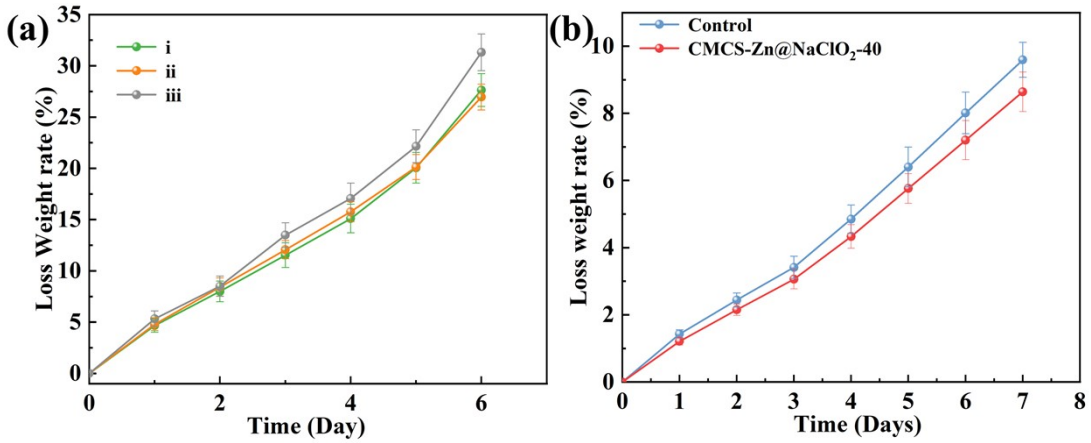


Fig. S7. Loss weight of (a) strawberry and (b) blueberry. (i) CMCS-Zn@$NaClO_2$-20; (ii) CMCS-Zn@$NaClO_2$-40; (iii) control.

Table S4. Comparison with reported ClO_2 release materials

Materials	ClO_2 release rate	Antibacterial properties	Preparation	Reference
Sodium polyacrylate, cross-linked polyacrylic acid resin, cross-linked polyvinyl alcohol, vinyl acetate, etc.	5.0-8.0 mg/h	-	※Required reagent type>10; ※Complex preparation	Patent CN101810874A; (CN101810874B)
Sodium carboxymethyl cellulose	1-50 mg/kg	※Effective sterilization days: 84%	※Required reagent type>10; ※Complex preparation	Meng et al., 2020. (10.13386/j.issn1002-0306.2020.16.005)
Poly (acrylic acid) gels	0.01-0.18 mg/g	※Against *Enterococcus faecalis*	※Preparation time>12h	Palcsó et al., 2019. (https://doi.org/10.1016/j.msec.2019.01.043)
Carboxymethyl chitosan	4.5-39.6 $mg \cdot L^{-1}/h$ (Wide concentration range under control)	※Kill bacteria rate on *E. coli* and *S. aureus* >99.9% ※Effective sterilization days: 100%	※Required reagent type=3 ※Preparation time<3h	This work