SUPPORTING INFORMATION

Synthesis of Microencapsulated Thermal Management Materials via Chitosan Grafting Route for Promoting the Applications in Medical Field

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S1. Thermal management tests and antibacterial examination

S1.1 Thermal management test of zeolite materials

The original zeolite and two modified zeolites by direct physic mixing of the P1-30 microcapsules were chosen for an exothermic experiment. The contents of mixed the P1-30 microcapsules was calculated based on the mass fraction of microcapsules to zeolite. For each test, the amounts of water and zeolite granules were fixed at 1.5 g and 3 g respectively. The sample was packed in medical gauze and placed on a plastic petri dish with a diameter of 2 cm. Then, the water was dropped quickly onto the central area of sample, and the temperature and time were recorded by using an infrared camera.

The heat released by zeolite into the environment can be calculated from the temperature change of water. During the initial 2 min of exothermic period, the water temperature was constant. Therefore, the temperature change of water ($\Delta\mathbf{T}$) could be easily obtained by using **Eq.(S1)**:

$$\Delta\mathbf{T}\ (\mathrm{K}) = \mathbf{T}_w - \mathbf{T}_{w0} \tag{S1}$$

Where $\mathbf{T}_w$ is the water temperature during the initial 2 min of exothermic period, and the $\mathbf{T}_{w0}$ is the original water temperature before experiment, which is 24.7℃. The total heat of water ($\mathbf{Q}_w$) could be estimated by **Eq.(S2)** ~ **Eq.(S5)**:

$$\mathbf{Q}_w = \mathbf{Q}_t + \mathbf{Q}_h \tag{S2}$$

$$\mathbf{Q}_t = \Delta\mathbf{T} \times \mathbf{m}_w \times \mathbf{C}_w \tag{S3}$$

$$\mathbf{Q}_h = \Delta\mathbf{T}_e \times \mathbf{h} \times \mathbf{A} \times \mathbf{t} \tag{S4}$$

$$\Delta\mathbf{T}_e\ (\mathrm{K}) = \mathbf{T}_w - \mathbf{T}_e \tag{S5}$$

Where $\mathbf{Q}_t$ is the heat absorbed by the water for temperature rise, $\mathbf{Q}_h$ is the heat released from water to environment during 2 min; the mass of water $\mathbf{m}_w$ = 1.5 mL, the specific heat capacity of water $\mathbf{C}_w$ = 4.2 J/(g·K), the heat transfer coefficient $\mathbf{h}$ = 5.5 W/(m²·K) for the 25℃ static air, the heat transfer surface area $\mathbf{A}$ = 3.14 × 10^{-4} m^2 for the approximately circular area with a diameter of 1 cm, the heat transfer time $\mathbf{t}$ = 120 s, the temperature of air environment $\mathbf{T}_e$ = 25.1℃. Thus, the heat absorbed by microcapsules ($\mathbf{Q}_{en}$) could be calculated via **Eq.(S6)**:

$$\mathbf{Q}_{en} = \mathbf{Q}_{w,0} - \mathbf{Q}_{w,m} \tag{S6}$$

Where $\mathbf{Q}_{w,0}$ is the total heat of water for original zeolite sample, $\mathbf{Q}_{w,m}$ is the total heat of water for modified zeolite sample. Finally, the specific power of microcapsules ($\mathbf{P}_s$) could be calculated by using **Eq.(S7)**:

$$\mathbf{P}_s = \mathbf{Q}_{en} / (\mathbf{m}_c \times \mathbf{t}) \tag{S7}$$

Where $\mathbf{m}_c$ is the dosage of microcapsules in modified zeolite sample, $\mathbf{t}$ is the heat transfer time and the value was 120 s.

S1.2 Antibacterial examination

Escherichia coli (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) were selected as model strains to evaluate the antibacterial performances of original zeolite and modified zeolite samples through the colony counting method. All the experiments were designed according to the standard method (GB/T 21510–2008) and related literature. 100 μL bacterial dilutions (105 ~ 106 CFU/ mL) were added to 5 mL Luria-Bertani broth (LB). Then, 100 mg samples was added into the above solution and incubated under constant shaking at 37℃, pH = 7.2, and 150 rpm for 4 h. 100 μL diluted mixture solution were spread onto LB agar plates and cultivated at 37℃ for 12 h to observe colony growth. Following incubation, bacterial colonies were counted, and the antibacterial rates (η) were calculated with the help of ImageJ and according to **Eq.(S8)**:

$$\boldsymbol{\eta} = (1 - \mathbf{C}/\mathbf{C}_0) \times 100\% \tag{S8}$$

Where $\mathbf{C}_0$ is the initial bacterial concentration and **C** is the remaining bacterial concentration after treatment.

S1.3 Thermal management test for burn injury

First, a red area was drawn on the hand by a marker pen to simulate the burn wound. Then, a liquid burn plaster was covered on the injured area. After this, the P1-30 microcapsules were sprinkled onto the area and spread evenly. Subsequently, the treated hand was moved under an infrared camera and recording was started immediately. The first data point from the injured area was recorded, and data were collected once every minute until the temperature stabilized. After the measurement, the powder on the hand was carefully collected and weighed. The ambient temperature during the test was approximately 27°C.

Figures

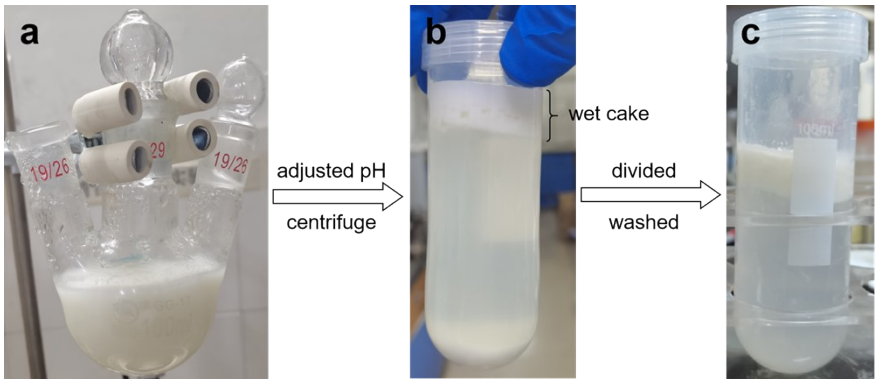

Figure S1 The photos to illustrate the separation of as-prepared microcapsules from the solution after polymerization. (a) The solution was cooled to room temperature naturally. (b) The stratification of solution after centrifuge, and the wet cake was formed on top area. (c) The wet cake after washing and centrifuging for 3 times.

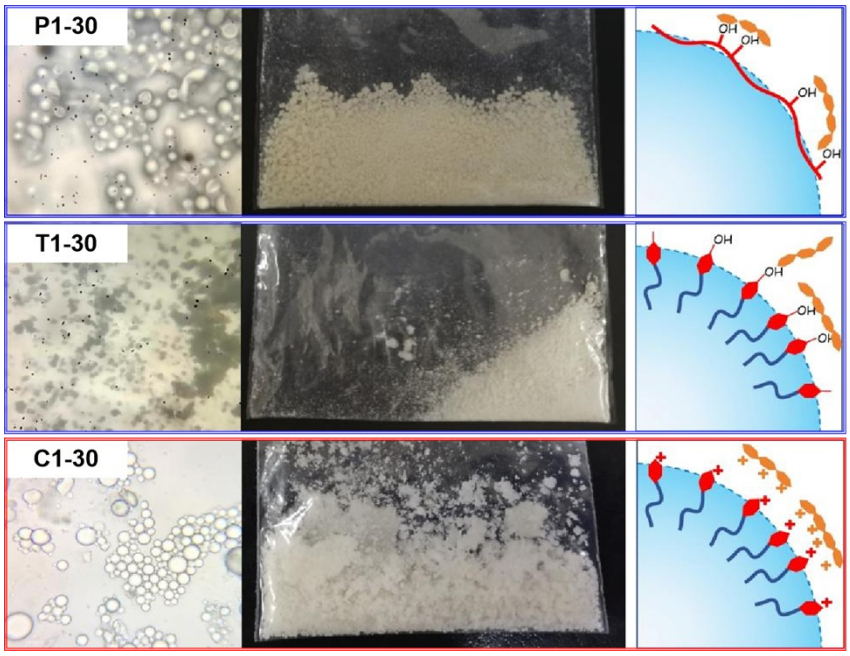

Figure S2 The as-prepared microcapsules by three different types of emulsifiers. The left images are the optical pictures of microcapsules; the photos at middle position are the appearances of samples; the schematic diagrams located on the right are the mechanism of the differences made by emulsifiers.

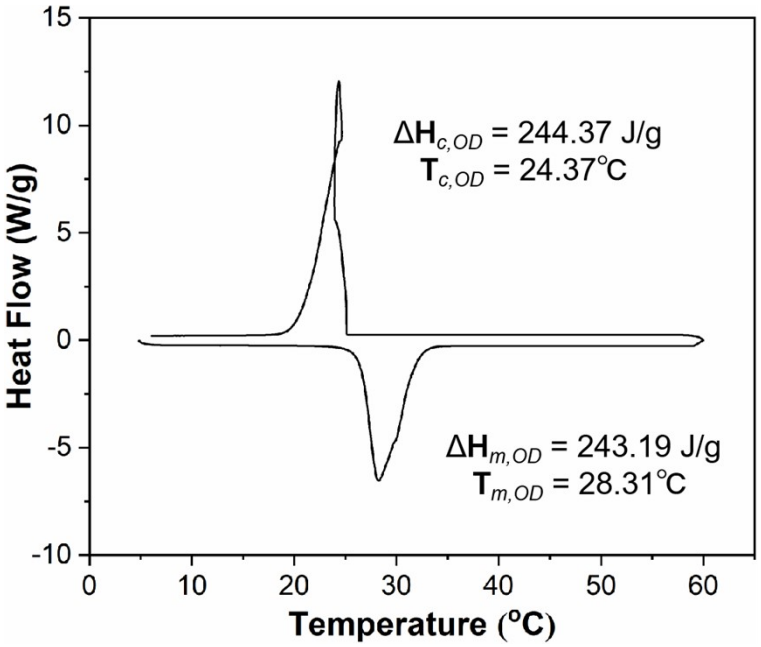

Figure S3 The DSC result of *n*-octadecane.

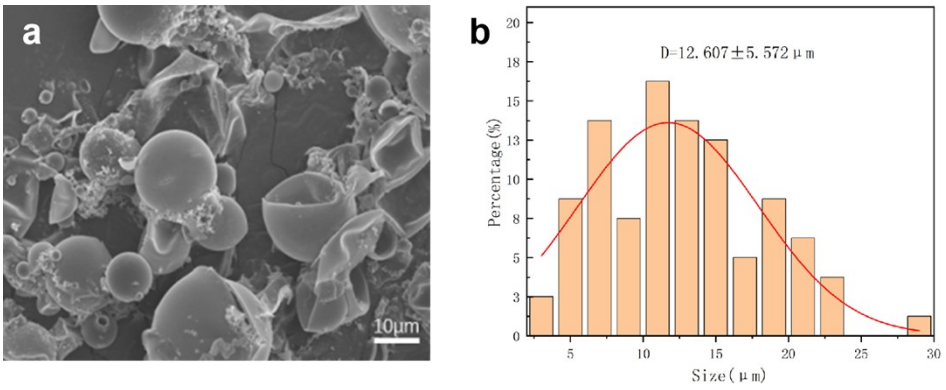

Figure S4 The morphology and size of the P1-0 sample. (a) The SEM image. (b) The size distribution.

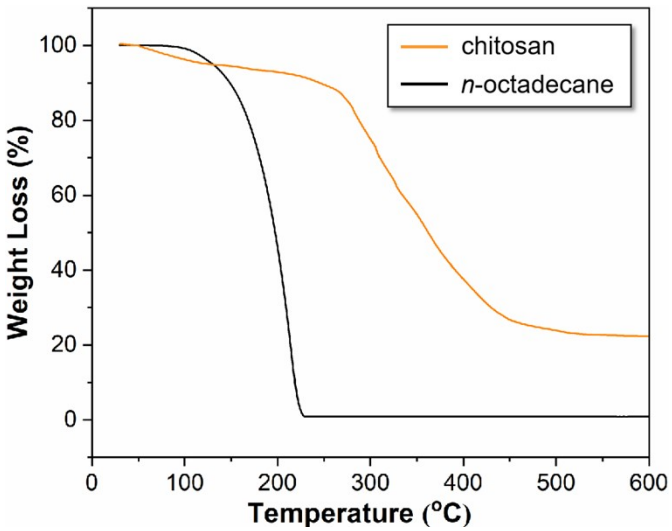

Figure S5 The TGA curves of chitosan and *n*-octadecane.

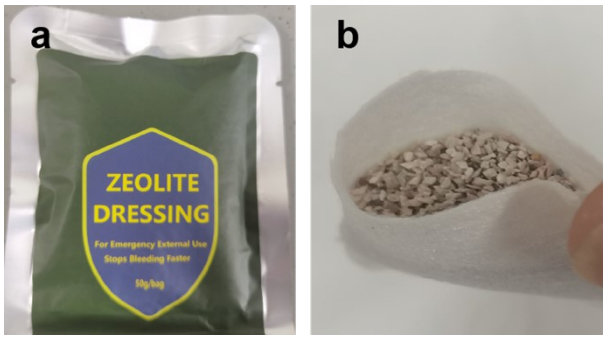

Figure S6 (a) The original package of QuikClot zeolite dressing. (b) The modified zeolite sample.

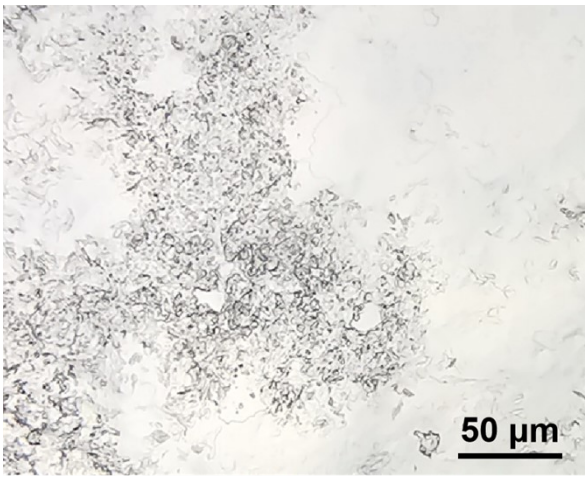

Figure S7 The optical photo of broken microcapsules made with $\mathbf{R}_{c\text{-}s}$ = 2:1 after drying naturally.

Tables

Table S1 The thermal properties of microcapsules made by different emulsifiers and *n*-octadecane.

Sample	ΔH_m (J/g)	ΔH_c (J/g)	T_m (℃)	T_c (℃)	ΔT_{sc} (℃)	$T_{m,i}$ (℃)	$T_{m,f}$ (℃)	$T_{c,i}$ (℃)	$T_{c,f}$ (℃)	E_{en} (%)	E_{es} (%)
P1-30	195.69	197.90	29.23	23.02	6.21	23.16	34.82	24.95	9.97	80.4	80.7
T1-30	154.31	154.56	28.41	23.54	4.87	26.65	35.45	24.86	16.70	63.5	63.4
OD	243.19	244.37	28.31	24.37	3.94	23.54	33.88	25.15	17.37	--	--

$T_{m,i}$ and $T_{c,i}$ are the initial melting temperature and initial crystallization temperature.

$T_{m,f}$ and $T_{c,f}$ are the final melting temperature and final crystallization temperature.

Table S2 Main wavenumber values (in cm^{-1}) of FTIR measurement.

-NH-CH_2-		Chitosan		PMMA		*n*-Octadecane	
Value	Assignment	Value	Assignment	Value	Assignment	Value	Assignment
1470	υ(NH)	3490	υ(OH)	1730	υ(C=O)	2960	$\upsilon_s(CH_2)$
1150	υ_s(C-N)	2929	υ(CH_2)	1268	υ_s(C-C-O)	2930	
988	δ(C-N)	2850		811	υ(CC4)	1402	δ(CH_3)
		1350	υ(C-N)				
		1080	υ(C-O-C)				

Table S3 The thermal properties of microcapsules made by different C_{cs}.

Sample	ΔH_m (J/g)	ΔH_c (J/g)	T_m (℃)	T_c (℃)	ΔT_{sc} (℃)	$T_{m,i}$ (℃)	$T_{m,f}$ (℃)	$T_{c,i}$ (℃)	$T_{c,f}$ (℃)	E_{en} (%)	E_{es} (%)
P1-0	195.36	196.90	28.11	24.54	3.57	22.66	32.31	24.81	13.21	80.3	80.5
P1-30	195.69	197.90	29.23	23.02	6.21	23.16	34.82	24.95	9.97	80.4	80.7
P1-50	108.22	103.79	32.05	22.69	9.36	21.67	38.17	26.50	14.03	44.5	43.5

Table S4 The thermal properties of samples made by different $R_{c\text{-}s}$.

Sample	ΔH_m (J/g)	ΔH_c (J/g)	T_m (℃)	T_c (℃)	ΔT_{sc} (℃)	$T_{m,i}$ (℃)	$T_{m,f}$ (℃)	$T_{c,i}$ (℃)	$T_{c,f}$ (℃)	E_{en} (%)	E_{es} (%)
P1-30	195.69	197.90	29.23	23.02	6.21	23.16	34.82	24.95	9.97	80.4	80.7
P2-30	213.10	215.11	29.49	23.89	5.60	22.74	34.30	24.98	11.05	87.6	87.8
P3-30	227.16	228.18	29.59	23.87	5.72	22.49	34.15	25.11	10.10	93.4	93.4

Table S5 The pressure resistance test of microcapsules made by using different $R_{c\text{-}s}$.

Sample	1st Test (MPa)	2nd Test (MPa)	3rd Test (MPa)	4th Test (MPa)	5th test (MPa)	Average Value (MPa)
P1-30	3.2	3.2	3.1	3.3	3.3	3.22
P2-30	2.6	2.5	2.5	2.5	2.4	2.50
P3-30	1.7	1.6	1.7	1.8	1.5	1.66
P1-0	2.2	2.1	2.1	2.3	2.1	2.16

Table S6 The thermal management test of zeolite materials with different F_m.

F_m (g/g)	T_w (℃)	ΔT (K)	Q_t (J)	Q_h (J)	Q_w (J)	Q_{en} (J)	P_s (W/g)
0	27.0	2.3	14.49	0.42	14.91	--	--
0.033	26.9	2.2	13.86	0.39	14.25	0.66	0.055
0.1	25.7	1.0	6.30	0.14	6.44	8.47	0.235

Table S7 The antibacterial examination of zeolite materials with different F_m.

E. coli		***S. aureus***	
F_m	η	F_m	η
0	98.49%	0	94.12%
0.033	99.35%	0.033	95.15%
0.1	100%	0.1	95.74%

Table S8 Comparison of P1-30 to other recent reports about the synthesis of phase change microcapsules

Name	$\mathbf{E}_{en}$ (%)	**Y** (%)	Core material	Shell material	Method	Origin
P1-30	80.4	46.6	*n*-octadecane	CS-*g*-PMMA	Microemulsion polymerization	Our work
PDA@SiO_2@n-HD	54.1	81.5	*n*-hexadecane	SiO_2	Interfacial condensation	Ref. (S1)
PMMA/RT27	94	67	Rubitherms®27	PMMA	Miniemulsion polymerization	Ref. (S2)
Eicosane@$CaCO_3$	55	33	*n*-eicosane	$CaCO_3$	Microemulsion polymerization	Ref. (S3)
RT21@PMMA	87.8	61.6	Rubitherms®21	PMMA	Photo-induced polymerization	Ref. (S4)
RT21@PEAA	84.7	56.2	Rubitherms®21	PEAA	Photo-induced polymerization	Ref. (S4)
RT21@PBAA	49.2	33.4	Rubitherms®21	PBAA	Photo-induced polymerization	Ref. (S4)
RT21@PTBMA	29.1	27.1	Rubitherms®21	PTBMA	Photo-induced polymerization	Ref. (S4)
HD-MC5	65.4	100	Hexadecane	NOA	Microfluidic encapsulation	Ref. (S5)
hyb-ACLSCs	57.2	40.8	Stearic acid	Acetylated lignin	Anti-solvent approach	Ref. (S6)
0.84 kg/h flow rate*	35	60	Methyl palmitate	SiO_2	Spray drying process	Ref. (S7)
MePCM-2	47.3	98	*n*-octadecane	PMMA	Microemulsion polymerization	Ref. (S8)
MMA:PETA =7:3*	63.2	81.4	Capric acid & stearic acid	PMMA	*In-situ* polymerization	Ref. (S9)

* The samples marked by the key parameters in the name column because they are not named specifically in the references.

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