Supporting Information

Cellulose nanocrystals for crop protection: leaf adhesion and controlled delivery of bioactive molecules

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Table S1 Formulation of all tested samples.

Samples	Composition			
	XCM	CNC-COOH	β-CD	TA
CNCs				
CNC-COOH		√		
βCNC		√	√	
XCM@βCNC	√	√	√	
TA/Cu@βCNC		√	√	√
TA/Cu-XCM@CNC	√	√		√
TA/Cu-XCM@βCNC	√	√	√	√

Table S2 Pesticide loading efficiency (LE) of XCM@βCNC, TA/Cu-XCM@βCNC.

	XCM@βCNC	TA/Cu-XCM@βCNC
LE (%)	4.77±0.03	9.04±0.02

Table S3 The hydrodynamic diameter of CNC, βCNC, XCM@βCNC, and TA/Cu-XCM@βCNC.

Sample	Hydrodynamic diameter (nm)
CNCs	156
βCNC	181
XCM@βCNC	322
TA/Cu-XCM@βCNC	**242**

The release kinetics of TA/Cu-XCM@βCNC was analyzed using Zero-order, First-order, Higuchi, Bhaskar, and Ritger Peppas models in Eq. (1), (2), (3), (4), (5):

Zero-order model: $M_t/M_\infty = a + kt.$ (1)

First-order model: $M_t/M_\infty = a(1 - e^{-kt}).$ (2)

Higuchi model: $M_t/M_\infty = kt^{1/2}.$ (3)

Bhaskar model: $M_t/M_\infty = a(1 - e^{-kt0.65}).$ (4)

Ritger-Peppas model: $M_t/M_\infty = kt^n.$ (5)

where M_t/M_∞ is the accumulative release ratio (%) of XCM at time t, a is the initial concentration, k is the kinetic constant and n is the diffusion exponent.

n is an index which reflects release mechanism: Fickian diffusion (n < 0.43), non-Fickian or anomalous diffusion (0.43 < n < 0.85), and case II transport (n > 0.85)[1].

Table S4 Fitting results for XCM release curves of TA/Cu-XCM@βCNC at different pH values.

Fitting model	pH 6		pH 7		pH 8	
	kinetic equation	R^2	kinetic equation	R^2	kinetic equation	R^2
Zero-order	$y = 32.82+1.50x$	0.6089	$y = 17.17+1.36x$	0.8168	$y = 15.44+1.56x$	0.8726
First-order	$y = 59.23(1 - e^{-0.91x})$	0.9003	$y = 45.36(1 - e^{-0.24x})$	0.8602	$y = 50.48(1 - e^{-0.16x})$	0.9010
Higuchi	$y = 15.31\ x^{1/2}$	0.4966	$y = 10.49\ x^{1/2}$	0.8750	$y = 10.88\ x^{1/2}$	0.9502
Bhaskar	$y = 62.45(1-e^{-0.73x\wedge 0.65})$	0.9468	$y = 50.90(1-e^{-0.32x\wedge 0.65})$	0.9506	$y = 60.70(1-e^{-0.22x\wedge 0.65})$	0.9688
Ritger-Peppas	$y = 37.51\ x^{0.18}$	0.9960	$y = 18.37\ x^{0.30}$	0.9918	$y = 15.98\ x^{0.36}$	0.9937

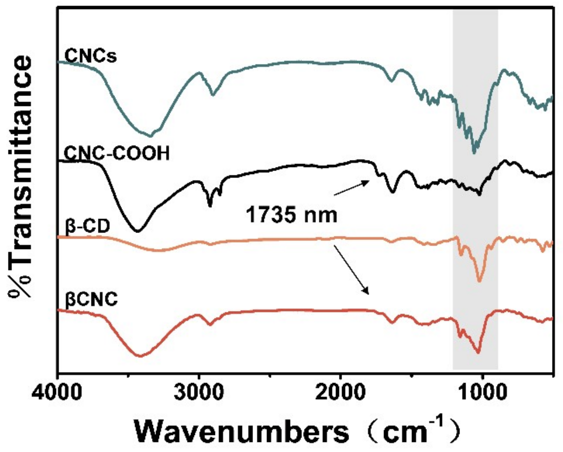

Figure S1 FTIR spectra of CNCs, CNC-COOH, β-CD and βCNC.

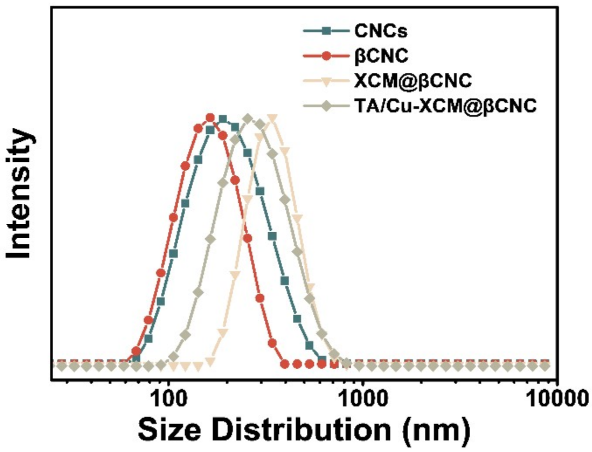

Figure S2 Size distribution of CNCs, βCNC, XCM@βCNC and TA/Cu-XCM@βCNC.

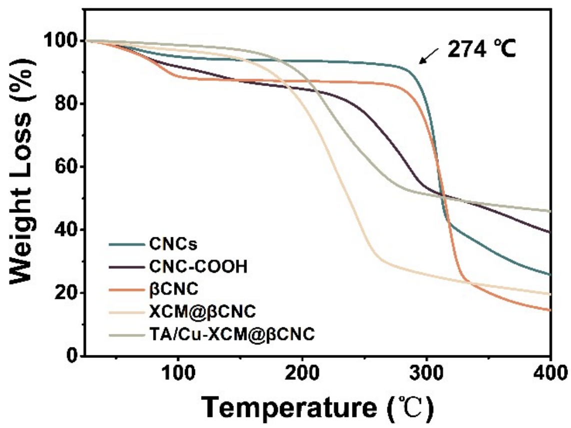

Figure S3 TGA curves of dried CNCs, CNC-COOH, βCNC, XCM@βCNC and TA/Cu-XCM@βCNC.

For the deposition properties of pesticide carriers on superhydrophobic surfaces, silanized glass slides were selected to simulate the leaves. One slide was placed horizontally and the other slide was fixed at a slope of 45°[2]. Then, the formulations were sprayed on the siliconized glass slides with identical volumes. The deposition ratio (DR, %) was calculated using Eq. (6):

$$DR\ (\%) = \frac{w_i}{w_h} \times 100\% \quad (6)$$

where w_i was the additional weight of the inclined slide; w_h was the additional weight of the horizontal slide. Each test was measured in six replicates.

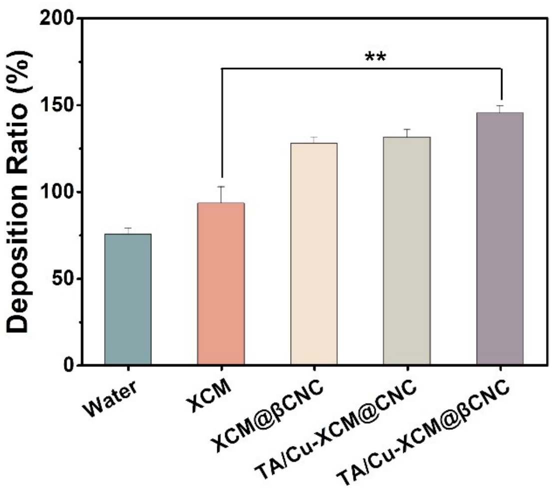

Figure S4 Deposition profile of water, XCM, XCM@βCNC, TA/Cu-XCM@CNC and TA/Cu-XCM@βCNC on glass.

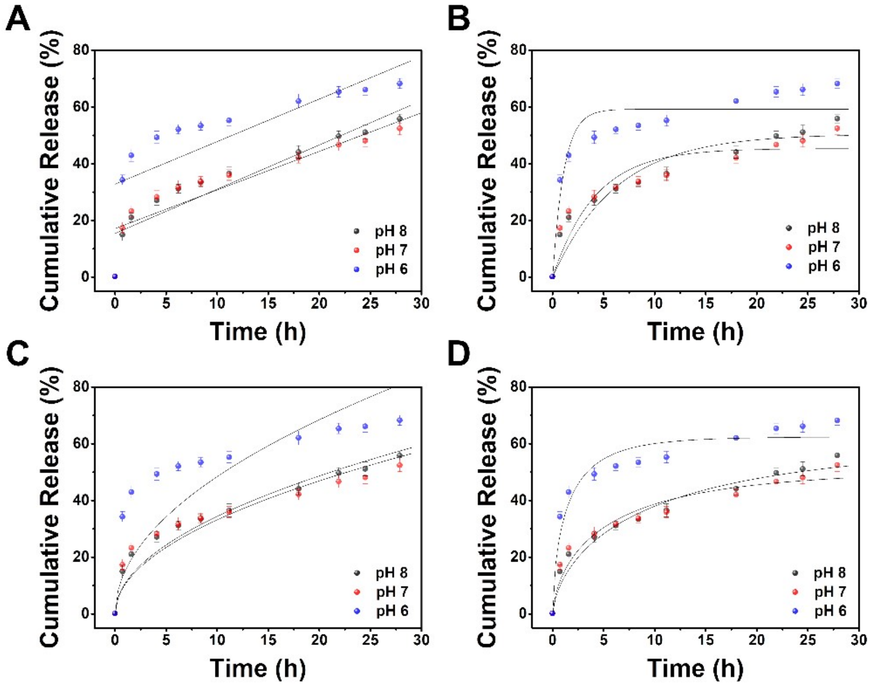

Figure S5 Fitting profiles of the XCM time-dependent release from TA/Cu-XCM@βCNC using the Zero-order, First-order, Higuchi, and Bhaskar models, respectively.

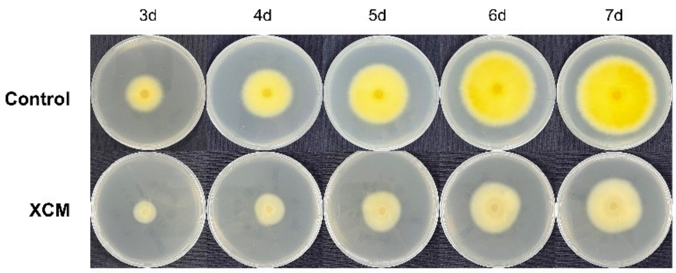

Figure S6 Digital photos of *R. solani* that incubated with XCM solution.

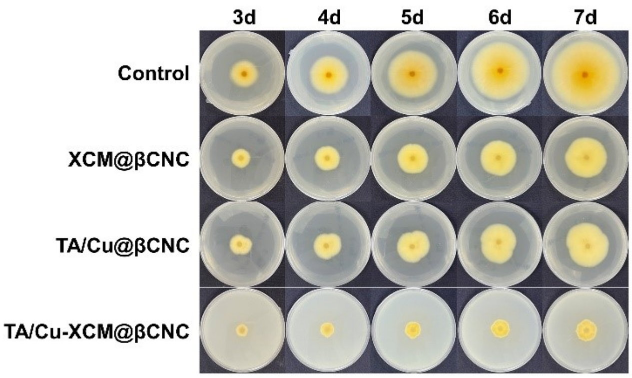

Figure S7 Digital photos of *C. capsica* that incubated with XCM@βCNC, TA/Cu@βCNC and TA/Cu-XCM@βCNC.

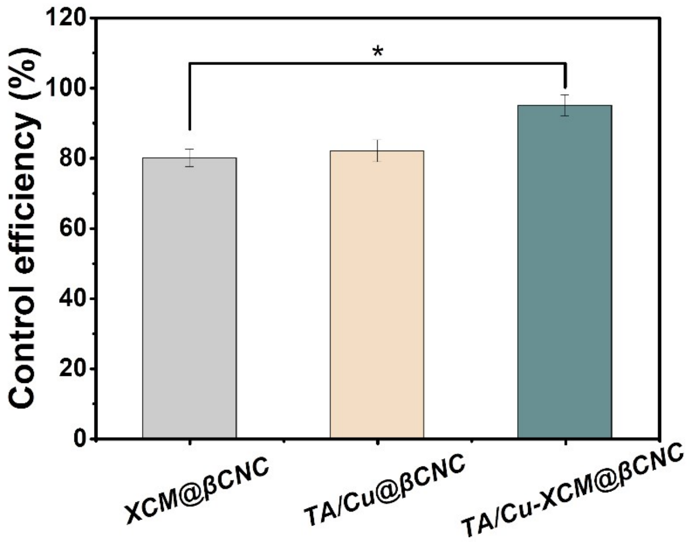

Figure S8 Control efficiency of different suspensions against *R. solani* on pepper plants.

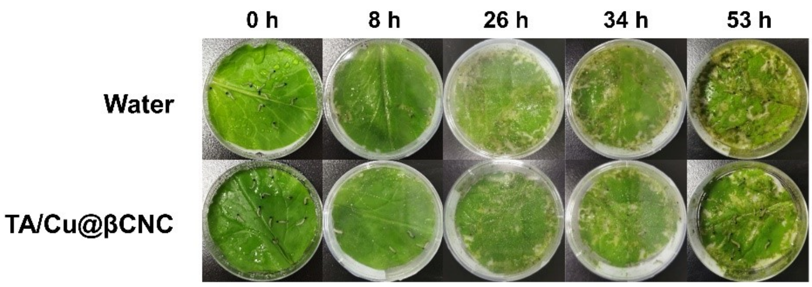

Figure S9 Digital photos to assess the insecticidal activity of water and TA/Cu@βCNC.

REFERENCES

1 G. Teng, C. Chen, N. Jing, C. Chen, Y. Duan, L. Zhang, Z. Wu and J. Zhang, *Chem. Eng. J.*, 2023, **451**, 139052.

2 Y. Zhang, B. Y. Liu, K. X. Huang, S. Y. Wang, R. L. Quirino, Z. X. Zhang and C. Q. Zhang, *ACS Appl. Mater. Inter.*, 2020, **12**, 37607-37618.