Supplementary Information

Dual-responsive microcapsules with tailorable shells from oppositely charged biopolymers for pesticide precise release

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Experimental section

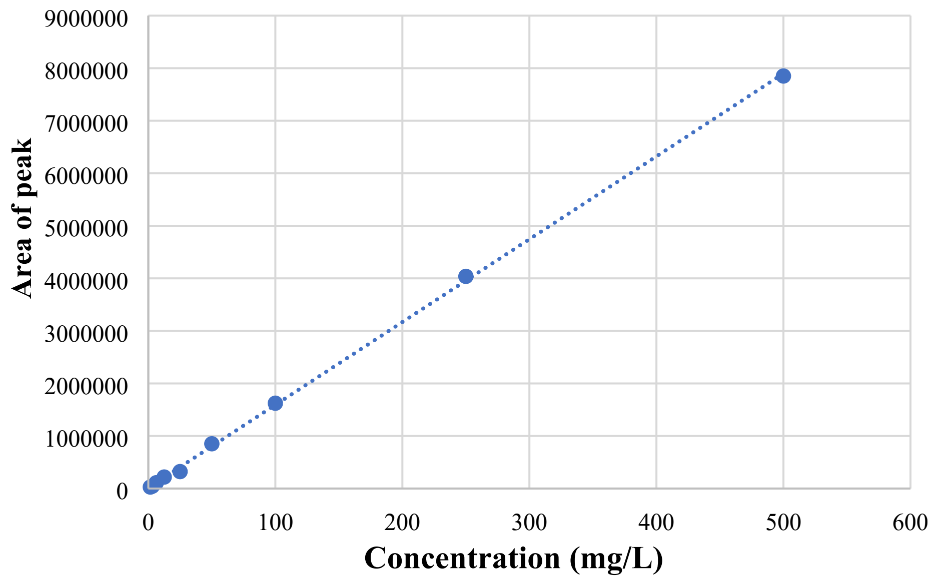

Fig. S1 The standard curves for determining AVM content.

Sustained-release behavior of AVM@(CH+SL)n

20 mg AVM@(CH+SL)n and laccase (50 U/g, 100 U/g, 500 U/g) were suspended in 20 mL of water and then transferred into a dialysis bag (MwCO = 1000 Da). The dialysis bag was submerged into 170 mL of ethanol/water (80/20, v/v) in a glass bottle and then placed in a shaking incubator with an oscillation rate of 200 rpm at a constant 35°C. In order to study the stimulus response to pH, the pH value of the release medium was adjusted to 5, 7, 9, and 11 by sodium hydroxide/hydrochloric acid. At certain intervals, 1 mL medium was taken out to test the AVM concentration by HPLC, and meanwhile, the same volume of fresh ethanol/water solution was added to ensure the same volume of medium.

Mathematical modelling of *in vitro* release: AVM release kinetics

Table S1. Kinetic models used for the analysis of AVM release from

AVM@(CH+SL)n.

Math. model	Equation	Characteristics
Zero-order	$M_t = M_0 + K_0 t$	The release rate of active ingredient is constant and independent of time and drug concentration.
First-order	$M_t = M_\infty (1 - e^{-K_{1st} t})$	The release rate of the active ingredient is proportional to the concentration of active ingredient in the controlled release system.
Higuchi	$M_t = M_\infty (K_{HG} t^{1/2})$	The release of active ingredient is proportional to the square root of time, which follows the Fickian diffusion mechanism.
Peppas	$M_t = M_\infty (K_{KP} t^n)$	It is an extension of the Higuchi model and only suitable for release data fitting within 60% of cumulative drug release.

Results

Table S2. Four models used for explaining kinetics of AVM release from AVM@(CH+SL)n and commercial AVM.

	Zero-order Release Model		First-order Release Model		Higuchi Model		Peppas Model	
	Kinetic equation	R^2	**Kinetic equation**	R^2	**Kinetic equation**	R^2	**Kinetic equation**	R^2
AVM	y=0.0029t+0.3787	0.4790	$y=0.9493(1-e^{-0.0374t})$	0.9919	$y=0.0620\times t^{1/2}+0.1548$	0.7410	$y=0.1810\times t^{0.3242}$	0.8236
AVM@(CH+SL)1	y=0.0035t+0.2019	0.7297	$y=0.9684(1-e^{-0.0167t})$	0.9956	$y=0.0688\times t^{1/2}-0.0269$	0.9150	$y=0.0754\times t^{0.4733}$	0.9188
AVM@(CH+SL)3	y=0.0036t+0.1178	0.8519	$y=1.0416(1-e^{-0.0096t})$	0.9940	$y=0.0677\times t^{1/2}-0.0950$	0.9640	$y=0.0374\times t^{0.3244}$	0.9506
AVM@(CH+SL)5	y=0.0034t+0.0719	0.9018	$y=1.1072(1-e^{-0.0065t})$	0.9847	$y=0.0631\times t^{1/2}-0.1196$	0.9592	$y=0.0210\times t^{0.6808}$	0.9551
Commercial AVM	y=0.0035t+0.2155	0.7089	$y=0.9950(1-e^{-0.0173t})$	0.9948	$y=0.0705\times t^{1/2}-0.0200$	0.9059	$y=0.0819\times t^{0.4638}$	0.9085

Table S3. Toxicity of pure AVM, AVM@(CH+SL)n, and commercial AVM against *P. xylostella* larvae at 0, 3, 7, and 15 days after spraying.

Sample	Time after spraying	LC_{50} (95% Confidence interval) (mg/L)
AVM	***Day 0***	0.188 (0.146-0.236)
	Day 3	0.617 (0.404-0.925)
	Day 7	8.506 (4.781-17.775)
	Day 15	122.600 (58.173-313.232)
AVM@(CH+SL)1	***Day 0***	0.329 (0.265-0.403)
	Day 3	0.370 (0.231-0.564)
	Day 7	0.284 (0.159-0.465)
	Day 15	6.136 (4.130-9.823)
AVM@(CH+SL)3	***Day 0***	0.419 (0.341-0.511)
	Day 3	0.249 (0.149-0.392)
	Day 7	0.166 (0.086-0.283)
	Day 15	1.490 (1.076-2.101)
AVM@(CH+SL)5	***Day 0***	0.414 (0.337-0.504)
	Day 3	0.321 (0.198-0.492)
	Day 7	0.082 (0.038-0.150)
	Day 15	0.492 (0.344-0.686)
Commercial AVM	***Day 0***	0.149 (0.114-0.190)
	Day 3	1.394 (0.878-8.277)
	Day 7	4.705 (2.755-9.144)
	Day 15	15.245 (9.427-27.544)
(CH+SL)	***Day 0***	-
	Day 3	-
	Day 7	-
	Day 15	-