Supporting Information

A pH-responsive copper doped ZIF-8 MOF nanoparticle for enhancing pesticide delivery and translocation in wheat plants

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Pesticide extraction and purification

1.0 g of leaf (1 g of root) or 1 mL of solution samples were weighed into 10 mL polytetrafluoroethylene (PTFE) centrifuge tubes. Then, 1 ml water, 2.5 mL of ACN and 0.1 mL H_3PO_4 were added and vortexed for 10 min with an oscillation frequency of 2500 min^{-1}. For nutrient solutions samples, only 2.5 mL of ACN and 0.1 mL H_3PO_4 were added for further pesticide extraction. Afterward, 1 g of NaCl was added to the tubes and vortexed for another 5 min. Subsequently, the tubes were centrifuged at 4000 rpm for 5 min. For nutrient solutions, the upper layer was directly transferred into an autosampler vial by passing through a 0.22-µm PTFE membrane filter. For shoot and root samples, 1.2 mL of the upper layer was transferred into a 2 mL centrifuge tube containing 150 mg anhydrous $MgSO_4$ and sorbents (50 mg C18 + 25 mg GCB for leaf and 50 mg C18 for root). The tubes were then vortexed for 1 min and centrifuged at 5000 rpm for 5 min. The upper layer was also filtered through a 0.22-µm PTFE membrane filter. The samples were stored at −20 °C before analysis.

UPLC–MS/MS Analysis

AB 5500+ LC-MS/MS system (AB SCIEX, United States) was applied for quantitative analysis of fludioxonil. The system was equipped with an Phenomenex Kinetex Biphenyl column (2.6 × 100 mm, 2.6 µm particle size). The solvent system consisted of ACN (phase A) and 0.2 % FA in pure water (phase B). A gradient elution program was used with a flow rate of 0.4 mL/min: 0.5 min, 30% solvent A, 1.5 min, 90% solvent A, 4.0 min, 90% solvent A, 4.1 min, 30% solvent A, 5.0 min, 30% solvent A. The injection volume was 1 µL, and the column temperature and temperature of the sample vial holder were 40°C and 4°C, respectively. The MS conditions were as

follows: ion spray voltages, 4500 V (Negative mode); *m/z* range, 50−1200 Da; accumulation time, 0.25 s; gas source 1 and gas source 2, 55 psi; curtain gas, 30 psi; source temperature, 500 °C; declustering potential (DP), -50 V. Multiple reaction monitoring (MRM) parameters for MS/MS analysis of fludioxonil are listed in Table S1.

Quality Assurance and Quality Control (QA and QC)

Quality control was performed by regular analyses of procedural blanks, and solvent blanks were injected after each batch of 20 samples to monitor the background and instrumental contamination. A recovery test was conducted to verify the extraction efficiency, and the precision was represented by RSD within replicated samples. The test contained three spiked levels (1, 100, and 1000 μg/kg for wheat leaf; 1, 10, and 1000 μg/kg for wheat roots; 10, 100, and 1000 μg/L for hydroponic solution). The mean recoveries and relative standard deviations (RSD) of the test were 87.3−106.3% and 1.1−16.2% in all samples, respectively (Table S2). The matrix-matched calibration standards were applied to quantify fludioxonil in different matrices, which were calculated based on the peak areas of the quantitative ion of fludioxonil. The correlation coefficients (R^2) of the standard curves were all ≥0.9916 (Table S3). No fludioxonil was detected in the matrices and solvent blanks.

Table S1. Experimental parameters for fludioxonil in Multiple Reaction Monitoring (MRM) mode

| Pesticides	Ion source	DP(V)	Qualitative ion /(m/z)	Collision Energy (V)	Dwell Time (s)
fludioxonil	ESI-	-50	246.9/126.1	-39.1	0.080
		-50	246.9/180.1	-39.11	0.080

Table S2. Mean extraction efficiency (%) of fludioxonil in wheat and hydroponic solution with the relative standard deviation (%).

Samples	Spike level	Mean recovery ± RSD (%)
	(μg/kg or μg/L)	Roots
root	1	87.3 ± 12.2
	10	106.1 ± 3.5
	1000	98.8 ± 7.7
leaf	1	84.7 ± 16.2
	100	86.3 ± 1.6
	1000	106.3 ± 3.2
Hydroponic solution	10	91.5 ± 8.7
	100	105.8 ± 1.6
	1000	103.8 ± 1.1

Table S3. Matrix-matched calibrations and LOQ for fludioxonil

Samples	Regression equation	R^2	LOQ[a] (μg/kg or μg/L)
Shoot	y = 48713x + 335460	0.9979	1
root	y = 42415x + 678984	0.9916	1
Hydroponic solution	y= 45756x + 459537	0.9969	1

[a] LOQ represents the lowest spiked level of the validation meeting the method performance acceptability criteria.
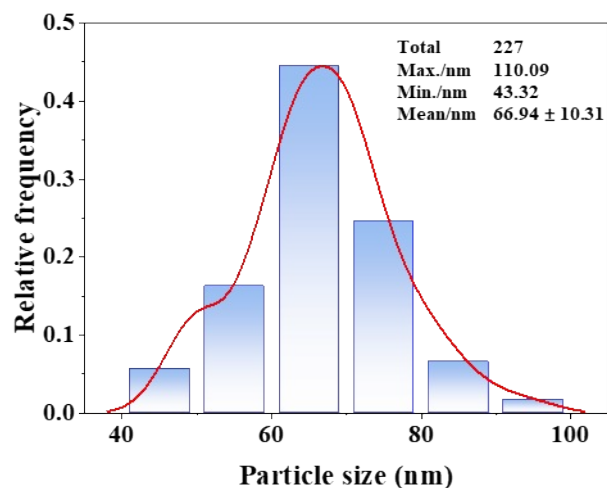
Figure S1. Size distributions determined by SEM for Cu@ZIF-8 crystal.

To further explore the pH-responsive behaviors of copper doped ZIF-8 nanoparticles, the morphology change of the nanoparticles was studied by putting them in the solutions with the pH values ranging from 3 to 9, respectively. The SEM images of Cu@ZIF-8 and ZIF-8 nanoparticles (Fig. S2) showed that the nanoparticles were regular and monodispersed. After 24 h of incubation, the morphologies of Cu@ZIF-8 nanoparticles remained almost unchanged in solution at pH 9, which was similar to those of ZIF-8. When incubated at pH 3-7, the Cu@ZIF-8 nanoparticles significantly changed and became amorphous or smaller. These results clearly demonstrated that Cu@ZIF-8 nanoparticles have acid sensitive characteristic, which endowed the cargo molecules with pH-responsive release behavior. Compared with Cu@ZIF-8, the morphology of ZIF-8 nanoparticles at pH 7 showed lighter collapse and deformation, suggesting that Cu@ZIF-8 nanoparticles are more pH-sensitive than ZIF-8 MOF nanoparticles.
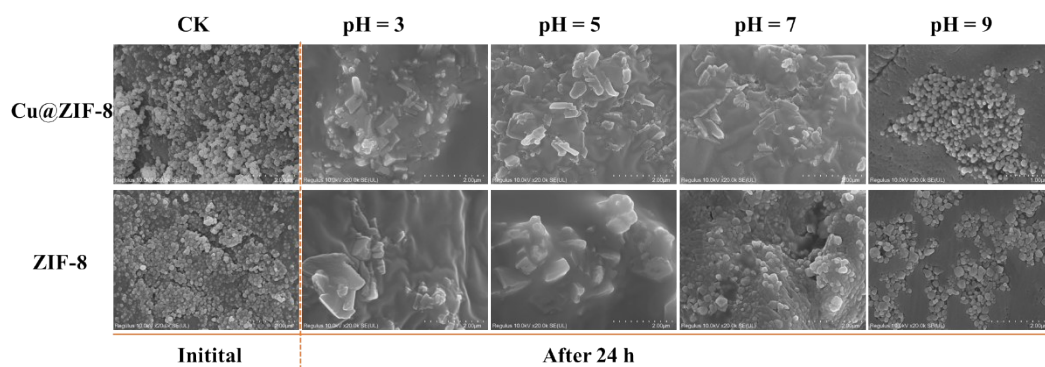
Figure S2. SEM images of Cu@ZIF-8 and ZIF-8 nanoparticles after incubation in aqueous solutions at different pH values for 24 h.
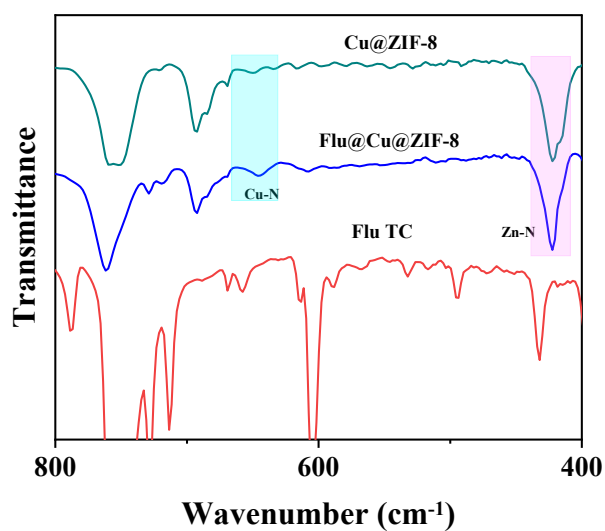

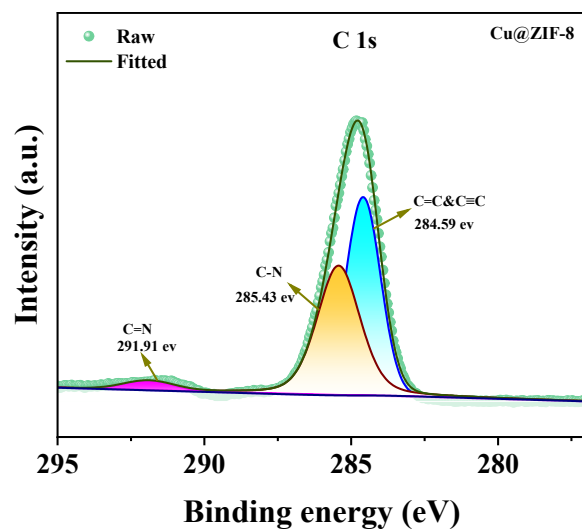**Figure S3.** FTIR characterizations of samples.
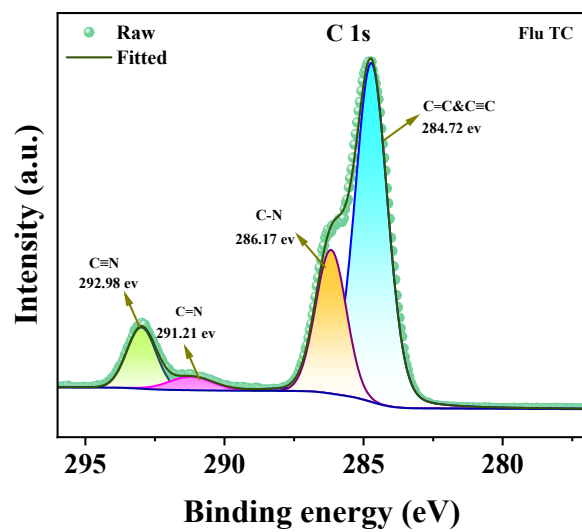
Figure S4. C 1s spectra of Cu@ZIF-8 NPs.
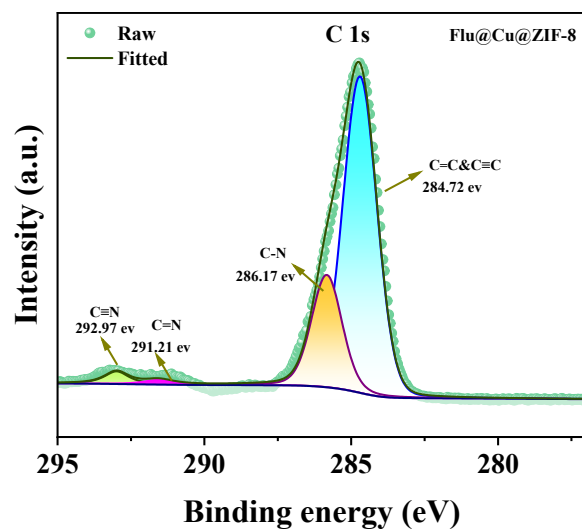

Figure S5. C 1s spectra of Flu TC.

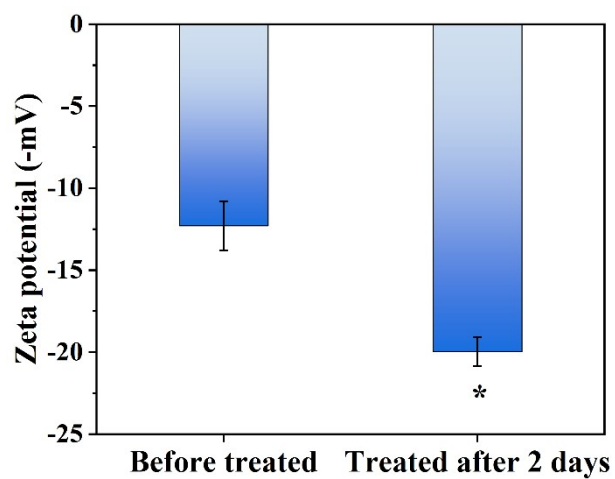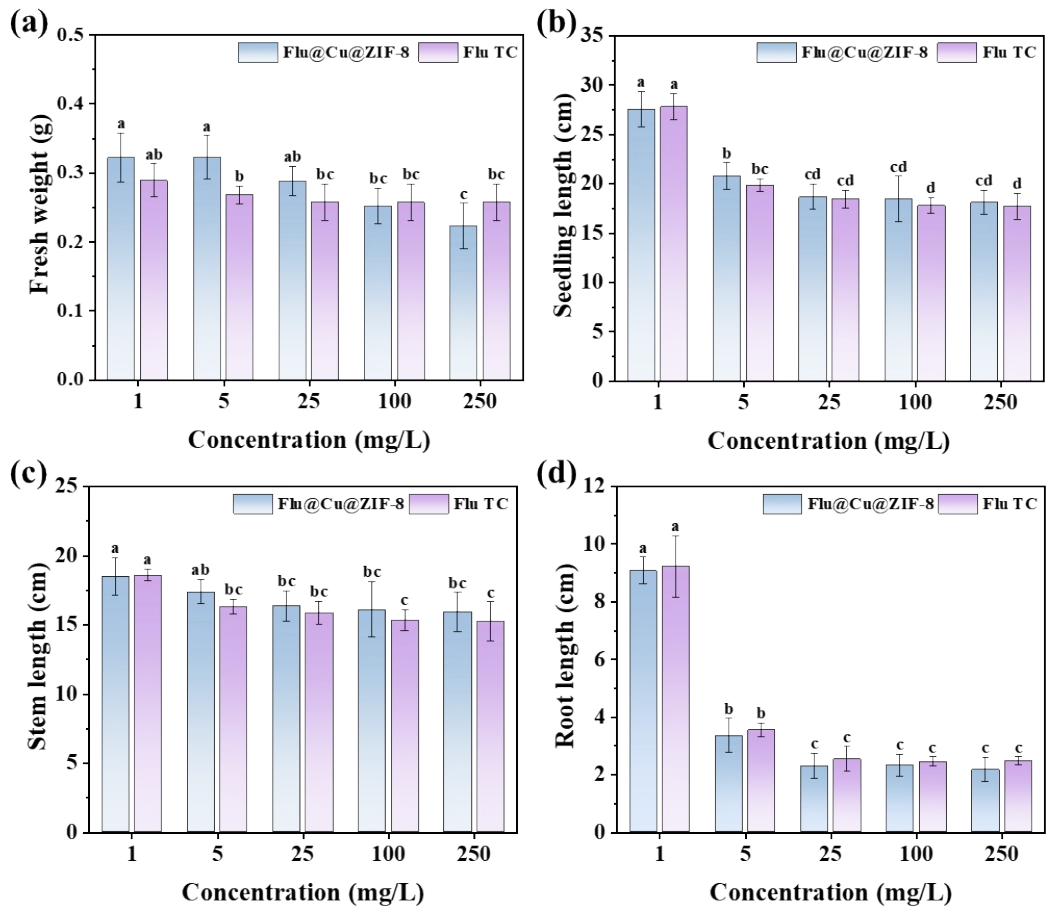**Figure S6.** C 1s spectra of Flu@Cu@ZIF-8 NPs.

Figure S7. Zeta potential of FITC labeled Cu@ZIF-8 NPs.

Figure S8. Effects of root treatment of Flu@Cu@ZIF-8 and Flu TC on fresh weight (a), and seedling length (b), root length (c), and stem length (d) of wheat plant. Different letters indicate a statistically significant difference by ANOVA ($P < 0.05$).