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Research Article

Halloysite Nanotube-Based Pesticide Formulations with Enhanced Rain Erosion Resistance, Foliar Adhesion, and Insecticidal Effect

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Cite This: *ACS Appl. Mater. Interfaces* 2022, 14, 41605−41617

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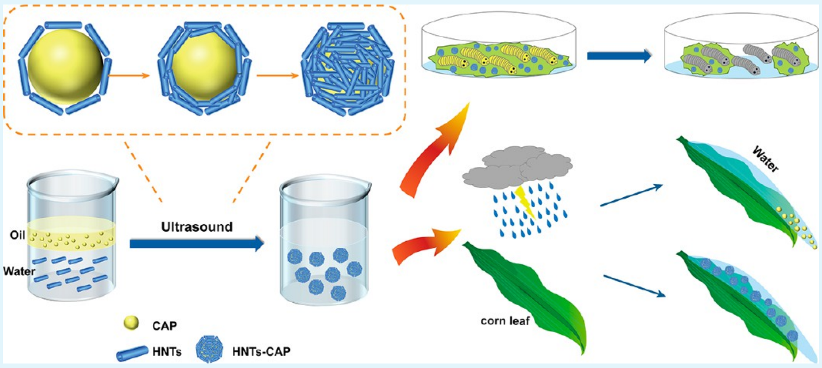


ABSTRACT: The incorporation of green and sustainable nanomaterials in pesticide formation is an effective method to lower the use of conventional pesticides without adverse effects on productivity. Here pesticide Pickering emulsions stabilized by halloysite nanotubes (HNTs) were developed for low cost, less environmental pollution, low toxic effects, and better emulsion stability. HNTs were added to chlorantraniliprole (CAP) emulsions, and good stability was exhibited due to the adsorption and aggregation of HNTs at the interface of CAP oil droplets, forming a three-dimensional network structure that prevented the emulsion from aggregation. In addition, *Spodoptera frugiperda* was used as a pest model and corn was used as a plant model to explore the washout resistance, insecticidal effect, and biological safety of HNTs−CAP emulsion. After spraying emulsion on corn leaves and washing for 10 min, the HNTs−CAP emulsion (5 wt % HNTs) pesticide residue rate was 2.7 times that of pristine CAP emulsion. When the HNT dispersion concentration was 2 wt %, the larva mortality was 83%, which was 1.5 times that of the CAP emulsion group. These results demonstrated that HNTs−CAP emulsion showed good foliar adhesion, rainfall resistance, and insecticidal effect. The tubular clay-based nanopesticide formulations show potential applications in the control of crop pests with modern agriculture technology.

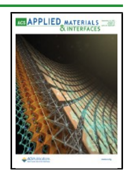
KEYWORDS: *halloysite, chlorantraniliprole, Spodoptera frugiperda, emulsion stability, washout resistance*

1. INTRODUCTION

Population growth and climate change will lead to increased production and use of pesticides globally.[1] The long-term widespread and inefficient use of traditional pesticide formulations has caused serious harm to both the environment and humans. It is necessary for us to control pesticide pollution to mitigate its negative impact on the environment and other non-target organisms.[2,3] Improving pesticide utilization efficiency, reducing pesticide losses, reducing the negative impact of pesticides on the environment, and reducing costs are important goals in the application of pesticides.[4−6] Among them, reducing leaching losses and improving plant adhesion of pesticides are the most effective methods to improve the utilization efficiency of pesticides.

In recent years, Pickering emulsions stabilized by rod-like nanoparticles have attracted significant attention due to the advantages of low cost, few environmental pollution and toxic effects, and high emulsion stability.[7] Halloysite nanotubes (HNTs) have a large length:diameter ratio and a tubular structure, while their surfaces possess active hydroxyl groups. Therefore, HNTs can be used as an anchor point for molecular adsorption and grafting reactions.[8−10] Moreover, HNTs are environmentally friendly and biocompatible materials, which can be used in essentially all applications. For example, Yang et al. designed a green, environmentally friendly multifunctional detergent by utilizing the properties of HNTs with stabilizing O/W emulsions.[11] In other words, the unique properties of HNTs, including large surface area, tunable size, high loading capacity, biocompatibility, low cost, and the ability for

Received: June 24, 2022
Accepted: August 15, 2022
Published: August 30, 2022



controlled release, make them good candidates for stabilizing pesticide Pickering emulsions for pest control in agriculture.[12−14] Additionally, HNTs in combination with functional polymers show promise for targeted delivery of active compounds and potential for encapsulation of both hydrophobic and hydrophilic chemical pesticides or biopesticides.[15,16]

The fall armyworm, *Spodoptera frugiperda* (J. E. Smith) (Lepidoptera: Noctuidae), is a highly destructive global agricultural pest that is noted for its wide host range, strong long-distance flight capability, and potential to inflict high yield losses.[17,18] Originally, native to the Americas, fall armyworm has long been a major agricultural problem in the Western Hemisphere. Since 2016, it has rapidly spread to and throughout the vast region of Africa, the Indian subcontinent, Southeast Asia and East Asia, and Oceania. It has caused huge economic losses in crop production and posed a real threat to global food security.[19]

Chlorantraniliprole (CAP) is a broad-spectrum pesticide with long residual activity, low toxicity, and no cross-resistance to other pesticides, which has been widely used to control pests.[20] Due to its poor solubility, CAP is often prepared as a suspension or emulsified dispersion, requiring large amounts of organic solvents or emulsifiers to ensure its stability. In contrast, oil-in-water (O/W) emulsion formulations of CAP are a good choice. However, emulsions are thermodynamically unstable systems and are prone to agglomeration, flocculation, or settling during storage.[21] Therefore, it is also important to improve long-term stability in the design of pesticide O/W emulsion formulations. Li et al. found that amphiphilic sodium alginate derivatives/alkyl glycosides can be used as emulsifiers in pesticide O/W emulsion formulations to improve emulsion stability and foliar wettability.[22] Liu et al. used an O/W double emulsion method that involved a premixed film emulsion in preparing a CAP microcapsule formula with good light and thermal stability.[23] Feng et al. prepared O/W emulsions loaded with λ-cypermethrin (a biologically active ingredient) using a low-energy-consumption method to improve the stability of pesticide emulsions.[21] Improving the stability of pesticide emulsions, reducing leaching loss, and improving the foliar adhesion of pesticides are beneficial to the development of pesticide O/W emulsion formulations. Wu et al. developed a λ-cyhalothrin microcapsule suspension using viscous polydopamine microcapsules as a carrier, which exhibited good suspension properties, flow behavior, storage stability, and high retention on the plant leaves.[24]

In this work, the effect of HNTs on improving the stability of O/W emulsions using xylene as the organic phase was first investigated. The water−xylene emulsion tended to be stable with the increase in HNT concentration. Then HNTs−CAP O/W emulsions were prepared by mixing the CAP xylene solution and HNT aqueous dispersions. The HNTs−CAP emulsions exhibited good stability due to the adsorption and aggregation of HNTs at the interface of CAP oil droplets, forming a three-dimensional network structure that prevented aggregation of the emulsion. The global invasive agricultural pest *S. frugiperda* was used as the pest model, and corn was used as the plant model to explore washout resistance, insecticidal effect, and biological safety of HNTs−CAP emulsion. All the results demonstrated that HNTs−CAP emulsion showed good foliar adhesion, rainfall resistance, and insecticidal effect. *Escherichia coli* and wheat were used as toxicity models for assessing the biosafety of the pesticide carriers. This work provides a new option for the development of stable storage and rain resistance of water-insoluble pesticide emulsions in controlling crop pests of modern agriculture technology.

2. EXPERIMENTAL SECTION

2.1. Materials. Halloysite nanotubes (HNTs) were obtained from Guangzhou Runwo Materials Technology Co., Ltd., China. *S. frugiperda*, chlorantraniliprole (CAP), corn, and mulberry leaves were obtained from Guangdong Academy of Agricultural Sciences, China. Wheat seeds were acquired from Sunong Seed Industry Co., Ltd. (Jiangsu, China). Xylene was provided by Aladdin Biochemical Technology Ltd., China. Deionized water was used in all the experiments.

2.2. Preparation of HNTs−Xylene Emulsion. Pickering emulsions were prepared by sonicating an aqueous solution of xylene and HNTs for 20 min with an oil/water volume ratio of 1:9. Pickering emulsions were stabilized with aqueous solutions of different concentrations (0, 0.5, 1, 2, 5 wt %) of HNTs. The xylene droplet was warped by the halloysite in the emulsion system, and no free oil phase existed. Ten microliter drops of the emulsion were placed on a glass slide with a cover glass, and the morphology of the emulsion was photographed using a polarizing microscope (BX51, Olympus, Japan). ImageJ was used to measure the droplet size.

2.3. Preparation of HNTs−CAP−Xylene Emulsion. A Pickering emulsion of pesticide was prepared by adding 0.5 g of CAP to 1 mL of xylene and adding 9 mL of aqueous solutions at different concentrations (0, 0.5, 1, 2, and 5 wt %) of HNTs and sonicating for 20 min.

2.4. Characterization. Transmission electron microscopy (TEM) (JEM-2100F, JEOL Ltd., Japan) and a particle analyzer (NanoBrook Omni, Brookhaven Instruments Ltd., Holtsville, NY) were used to test the diluted HNT aqueous dispersion. After diluting the O/W emulsion to 0.05%, the particle size distribution was measured and recorded using a zeta potential particle size analyzer (Zetasizer Nano ZS, U.K.). Rheological behavior of HNTs−CAP emulsion was measured by a rotational rheometer (Kinexus pro+, Austria) with a 20 mm diameter parallel plate model and a 400 μm thickness of the emulsion sample. Frequency scans were performed at 0.01−100 Hz at 0.5% fixed strain. Shear viscosity was performed from 0.01 to 100 s^{-1}. The CAP emulsion and HNTs−CAP emulsion were lyophilized, the samples were coated with gold on the surface of the lyophilized samples, and the morphology of the samples was observed with a scanning electron microscope (SEM) (Ultra 55 SEM instrument, Zeiss, Germany). A Fourier transform infrared spectroscopy (FTIR) instrument (Nicolet iS50, Thermo Fisher Scientific Ltd., Waltham, MA) was used to measure the infrared spectra of the HNTs, lyophilized CAP emulsion, and lyophilized HNTs−CAP emulsion in the range of 4000 to 400 cm^{-1}. The X-ray powder diffraction (XRD) patterns of HNT powder, CAP emulsion lyophilized powder, and HNTs−CAP emulsion freeze-dried powder were measured with an XRD instrument (MiniFlex-600, Rigaku Corporation, Japan) at a scan rate of 5°min^{-1} ranging from 5° to 70°. The stability of HNTs, CAP emulsion lyophilized powder, and HNTs−CAP emulsion lyophilized powder was tested with a TGA instrument (Mettler Toledo, Switzerland) from 30 to 800 °C under nitrogen atmosphere at a temperature increase rate of 10 °C min^{-1}.

2.5. Contact Angle of HNTs−CAP Emulsion on the Leaf Surface. To determine the wetting property of the emulsions on the crop leaves, 8 μL of CAP emulsion containing 0, 0.5, 1, 2, and 5 wt % HNTs in water was dropped on the surface of maize leaves and mulberry leaves, and the contact angle analyzer (DSA 100, DataPhysics, OCA-25, Germany) was used to test the size of the droplet contact angle on the leaf surface.

2.6. Surface Tension of HNTs−CAP Emulsion. Ten microliters of CAP emulsion containing 0, 0.5, 1, 2, and 5 wt % HNT aqueous solutions was placed into a 0.5 mm syringe and slowly squeezed out to produce droplets. The surface tension was obtained from suspension droplet analysis, pictures of the droplets were taken, and the surface

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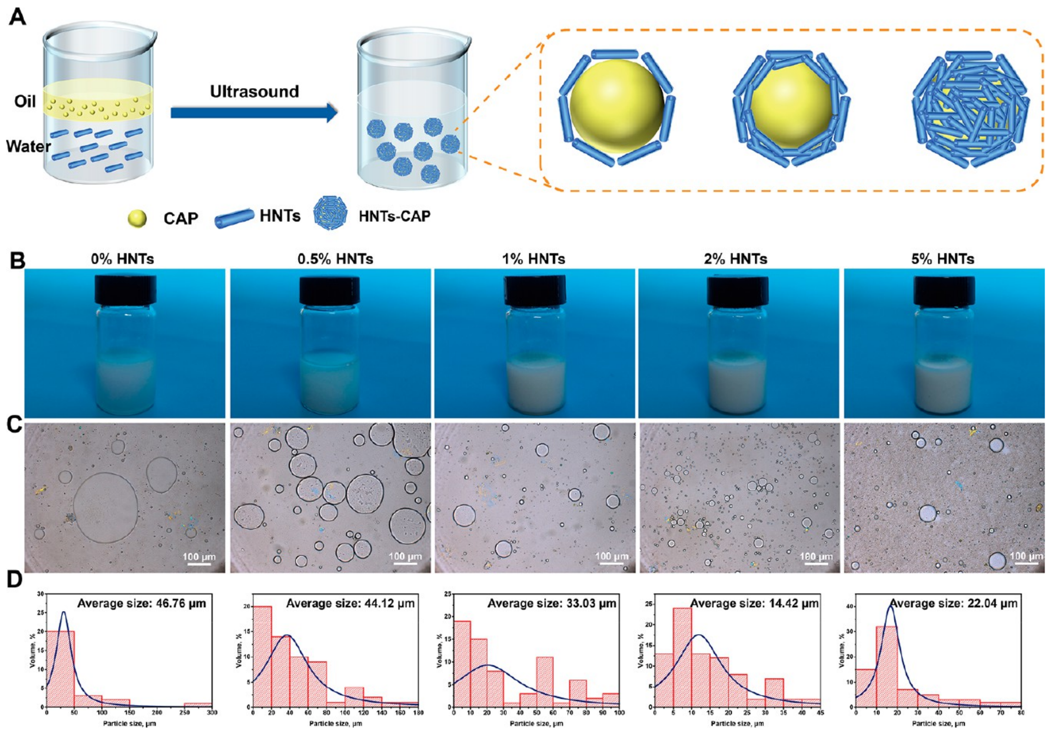

Figure 1. Schematic diagram of the synthesis of HNTs−CAP emulsion (A). Appearances (B), polarizing microscope images (C), and droplet size statistics (D) of emulsions composed of HNT dispersions with different concentrations (0, 0.5, 1, 2, and 5 wt %) and xylene.

tension values were calculated, observed, and recorded using built-in software of the instrument (DSA 100, DataPhysics, OCA-25, Germany). Measurements were taken at 60 s intervals to obtain a relationship between time and surface tension.

2.7. Washout Resistance of HNTs−CAP Emulsion. The concentration of HNTs−CAP emulsion was too large for practical application in controlling pests. Diluting to a low concentration is a common way to spray a pesticide formulation on crop leaves for subsequent analysis.[4] HNTs−CAP emulsion was diluted to 200 mg L^{-1}, and 0.5 mL of the sample diluent was sprayed on corn leaves having an area of 4 × 4 cm and then dried naturally. To simulate rainwater flushing, each leaf was tilted 30°, and deionized water was dripped on the leaves at a rate of 20 mL min^{-1} and washed for 2, 4, 6, 8, and 10 min.[4] After washing, the leaves were minced and collected into centrifuge tubes, 5 mL of acetonitrile was added, the mixture was sonicated and centrifuged, and the supernatant was aspirated. Finally, the supernatant was vacuum-dried and dissolved in 1 mL of acetonitrile. The amount of CAP was determined using high performance liquid chromatography (Agilent 1260 Infinity II; Agilent Technologies; Santa Clara, CA) equipped with a UV detector according to the literature.[25] Analytes were separated using an Agilent Diamonsil C18 column (250 mm × 4.6 mm id, 5 μm). An acetonitrile/water mixture (70:30, v/v) was used as the mobile phase at a flow rate of 0.8 mL min, injection volume of 5 μL, column temperature of 30 °C, retention time of approximately 12.5 min, and UV detector detection wavelength set to 260 nm.

2.8. Pharmacodynamic Test of HNTs−CAP Emulsion. For the insecticidal effect experiment, the emulsion was diluted to 30 mg/L (30 ppm was the LC_{50} value for the CAP toward *Spodoptera frugiperda*) because a high concentration leads to potential environmental risk and high cost. The insecticidal experiment was conducted on diluted CAP emulsion containing 5 wt % CAP, HNTs−CAP emulsion (0.5, 1, 2, and 5 wt % HNTs in water), and HNTs emulsion (2 wt % HNTs) to 30 mg L^{-1}. Moist filter paper was put into the culture container, and 120 second instar larvae of *S. frugiperda* were taken. They were divided into 6 groups of 20 worms stochastically and starved for 4 h. The same volume of corn leaves was soaked in the same diluents and water for 10 s, and then they were allowed to dry naturally. The leaves were placed in the culture vessels for different times of 4, 8, 12, 24, and 36 h. Mortality of the pest for every group was recorded. The experiment was repeated four times.

2.9. Safety Evaluation of HNTs−CAP Emulsion. *E. coli* was cultured in Luria−Bertani medium at different concentrations (0, 31.25, 125, and 500 μg mL^{-1}) at 37 °C for 24 h, and the absorbance of *E. coli* was determined by UV−vis spectroscopy at 600 nm. Wheat seeds were soaked in distilled water for 12 h and then transferred to Petri dishes containing 6 mL of aqueous solutions of CAP emulsion and HNTs−CAP emulsion at concentrations of 31.25, 125, and 500 μg mL^{-1} for 7 days. During this period, the wheat was treated with different concentrations of the samples and the Petri dishes were kept moist. After 7 days, the germination rate, root length, and shoot length of the different groups were counted.

2.10. Statistical Analysis. The data were statistically analyzed using SPSS software and displayed as the means and the standard error (SE) by Tukey's multiple range test ($p < 0.05$).

3. RESULTS AND DISCUSSION

3.1. Stability of HNTs−Xylene Emulsion. The basic characterization of HNTs used is shown in Figure S1. HNTs show a rod-like morphology with an empty lumen and high aspect ratio, the adsorbed water on HNTs can be removed by heating, and the structure of the tubes is stable. HNT surfaces contain hydroxyl groups which can be employed for surface modification. The purity of the HNTs is high as shown by XRD, and the particle size distribution is narrow. Due to their high aspect ratio, natural availability, and low toxicity, HNTs have been widely investigated for the design of Pickering emulsions. The anisotropic HNT particles can considerably improve the stabilization of Pickering systems by irreversibly anchoring at the oil−water interface and creating a physical barrier which provides steric hindrance and inhibits Ostwald ripening and coalescence.[13] The preparation process of an O/W emulsion of aqueous HNTs and xylene is illustrated in Figure 1A. The appearance and morphology of HNTs−xylene

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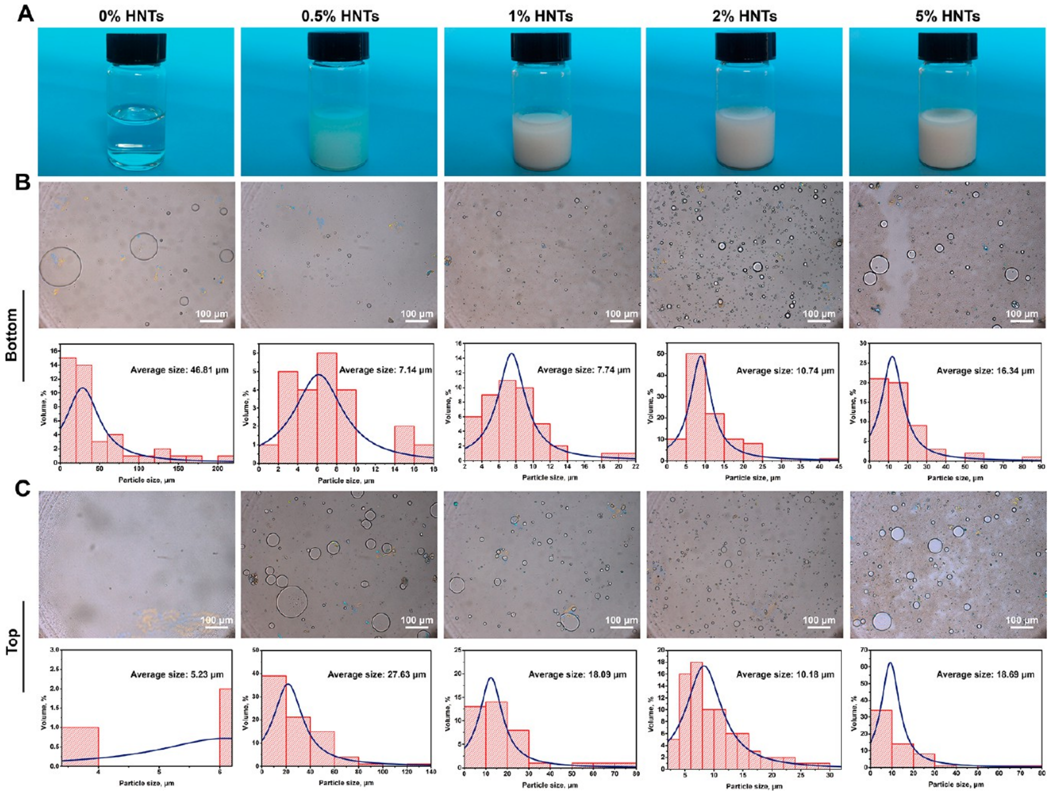

Figure 2. Appearances of emulsions composed of HNT dispersions (0, 0.5, 1, 2, and 5 wt %) and xylene after standing for 7 days (A). Polarizing microscope images and droplet size statistics of the upper (B) and bottom (C) layer of the emulsion.

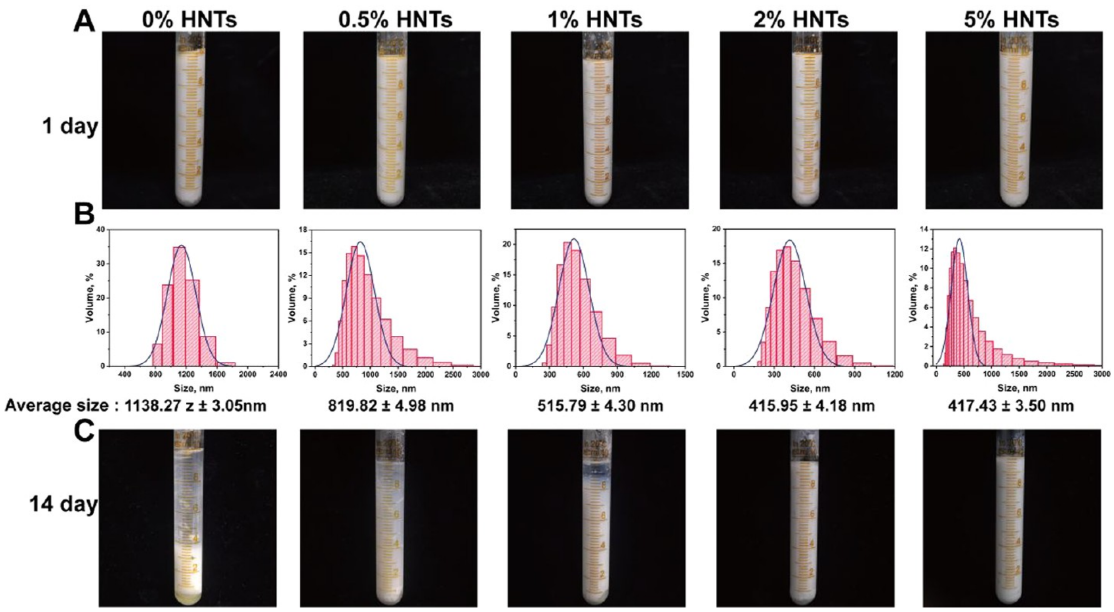

Figure 3. Appearances of HNTs−CAP (0, 0.5, 1, 2, and 5 wt % HNTs) (A). Particle size distribution diagram (B) and the images of these emulsions after standing for 14 days (C).

emulsion with different HNT concentrations (0, 0.5, 1, 2, and 5 wt %) were then observed (Figure 1B and 1C). Due to the presence of capillary force, HNTs gathered into bundles in the oil−water system, laterally attached to the oil/water interface, and covered the oil droplets, preventing them from coalescing. Thus, HNTs would be used as the solid stabilizers in a Pickering emulsion. It can be seen from Figure 1C,D that the emulsion droplets in the emulsion tended to become smaller as the concentration of HNTs increases. When the HNT dispersion concentration was 2 wt %, the emulsion droplets were the smallest. The emulsion droplets were homogenized, and the oil droplet size decreased, which indicated that the addition of HNTs could make the water−xylene emulsion more stable. When the concentration of HNT dispersion was 2 wt %, the stabilizing effect of HNTs on the emulsion was the best. As the hydrophilic HNTs were added, the water−xylene

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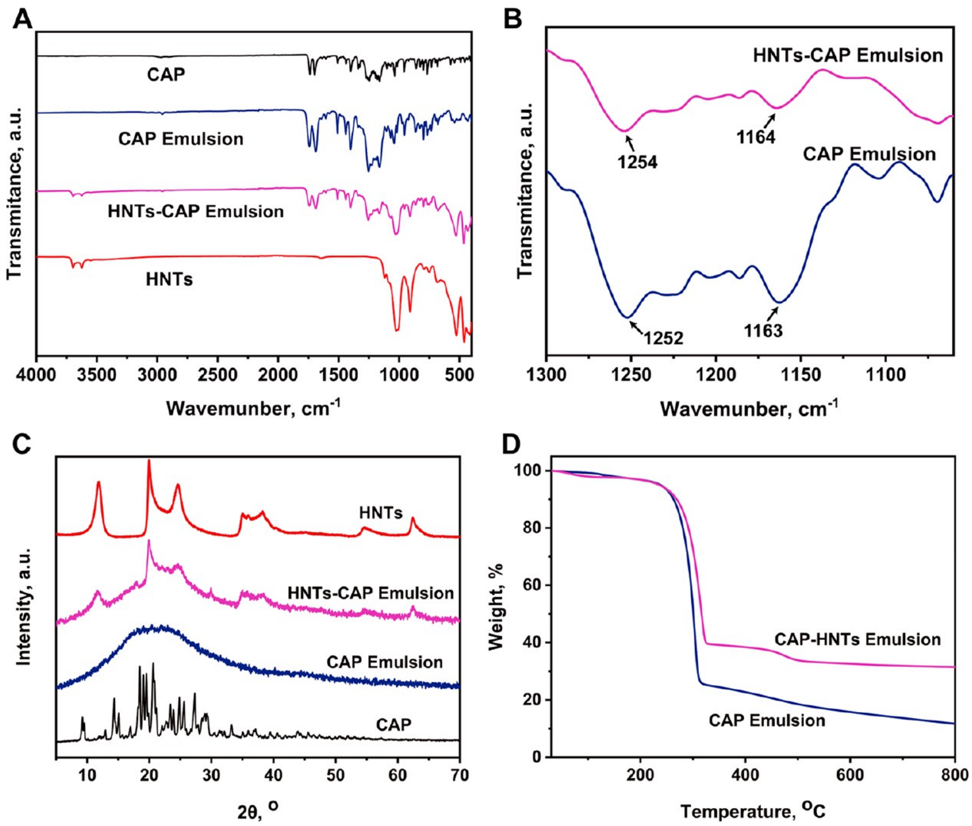

Figure 4. FTIR (A), magnified FTIR in the range of 1300−1000 cm^{-1} (B), XRD (C), and TGA (D) of HNTs−CAP emulsion freeze-dried powder.

system is in the state of an O/W emulsion, and HNTs are aggregated at the water−oil interface. Therefore, the high concentration of hydrophilic HNTs stabilize the interfaces of the oil-in-water emulsion. Inorganic particles (including silica, clay, hydroxyapatite) and some organic particles can effectively serve as Pickering emulsifiers. It has been proposed that compared to spherical silica emulsifiers, rod-shaped particles can restrict the coalescence and deformation of droplets to a larger extent at the water−oil interface, resulting in relatively more stable emulsions.[26]

Emulsion destabilization refers to the separation of the water−oil phase, which is the main phenomenon of emulsion denaturation.[27] Thus, the emulsion stability can be judged by allowing it to stand. HNTs−xylene emulsions with different HNT concentrations (0, 0.5, 1, 2, and 5 wt %) were allowed to stand at room temperature for 7 days, as shown in Figure 2. The xylene−water emulsions without HNTs were delaminated and became transparent after standing for 7 days while the HNT-treated emulsion appeared milky white, although delamination also occurred. As the concentration of HNT dispersion increased, the delamination phenomenon was weakened. The upper and lower layers of the emulsion after delamination were observed using a polarizing microscope (Figure 2B,C). In the xylene−water system without HNTs, the water−oil phase was completely separated, and the droplet sizes of the upper and lower layers differed by 40 μm. With the increase of HNT concentration, the droplet sizes of the upper and lower layers were similar. When the concentrations of HNT dispersion were 2−5 wt %, the droplet sizes were similar to that of the emulsion before standing. It is suggested that raw HNTs without any surfactants could act as effective stabilizers for Pickering emulsions. HNTs have a large specific surface area and special tubular structure, which limits the rotation of its particles. Therefore, HNTs are easily adsorbed on the water−oil surface and aggregate at the oil−water interface, which can reduce the interfacial tension and energy between the oil and water phases, resulting in a better emulsification effect.[11,28]

3.2. Stability of HNTs−CAP Emulsions. Because HNTs play a key role as stabilizers in Pickering emulsions, HNTs could be used as an additive to form HNTs−CAP formulations to improve the stability of CAP pesticide emulsions. The pesticide emulsion formulation was composed of an aqueous dispersion of HNTs and an oil phase of CAP dissolved in xylene (Figure 3A). The droplet size distribution was measured using dynamic laser scattering (Figure 3B). As the HNT dispersion concentration increased, the emulsion droplet size decreased. When the concentration of the HNT dispersion was 2 wt %, the smallest droplet had a particle size of 415.9 nm, which was 0.36 times that of the CAP emulsion. Further increasing the HNT concentration (5 wt %) led to increased droplet size, because the nanotubes aggregated and decreased the emulsifying efficiency. It is suggested that HNTs can significantly reduce droplet size. Observing the appearance of the emulsion when stored at room temperature was a simple and intuitive way to investigate the stability of CAP emulsions. From Figure 3C, the raw CAP emulsion showed distinct delamination after 14 days compared to other emulsion samples, and it was difficult to determine the polydispersity index of the emulsion. It is generally known that an excellent pesticide formulation should have good long-term stability. With the concentration of HNT dispersion increased, the

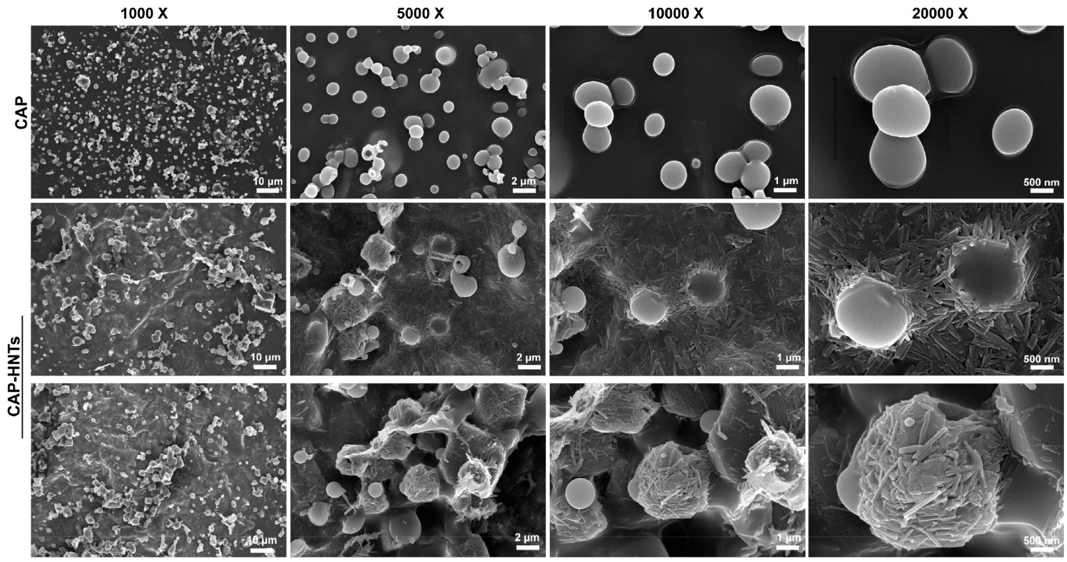

Figure 5. SEM images of CAP and HNTs−CAP emulsions after lyophilization.

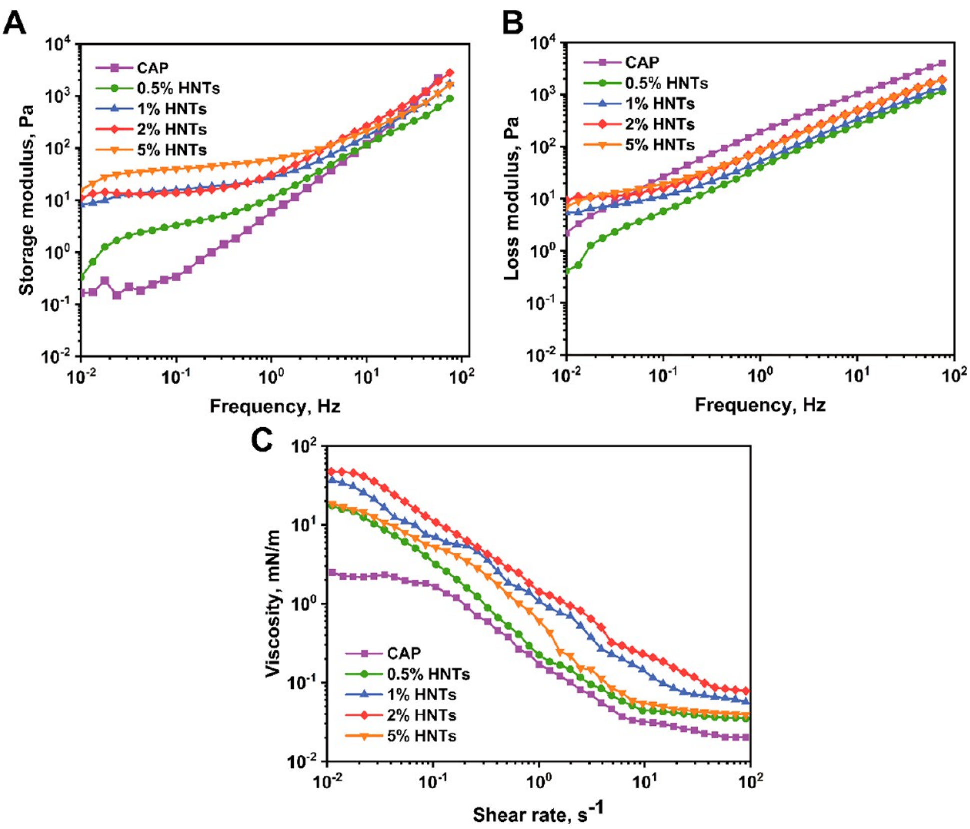

Figure 6. Rheological properties of HNTs−CAP emulsion with different HNT contents. Storage moduli (A) and loss moduli (B) at angular frequencies from 0.01 to 100 Hz. Shear rate−dynamic viscosity diagram of HNTs−CAP emulsions with different HNT contents (C).

apparent phase separation degree of HNTs−CAP emulsion tended to decrease. These results indicate that the addition of HNTs could effectively improve the long-term storage stability of pesticide emulsions.

3.3. Characterization of HNTs−CAP Emulsion Lyophilizate. To investigate the interactions between HNTs and CAP, the emulsion was freeze-dried and examined with FTIR (Figure 4A and 4B). The characteristic absorption peaks of the HNTs were located at 3695 and 3623 cm^{-1}, which were attributed to the stretching vibrations of the internal surface hydroxyl groups and internal hydroxyl groups, respectively.[29] The absorption peaks at 1744, 1690 cm^{-1} and 1252, 1164 cm^{-1} correspond to the C═O stretching vibration and amide C−N stretching vibration absorption, which are the characteristic absorption peaks of CAP.[30] The characteristic absorption peaks of HNTs and CAP coexist in the infrared spectrum of HNTs−CAP emulsion freeze-dried powder, but the stretching vibration peaks of C−N shift slightly from 1252 and 1163 cm^{-1} to 1254 and 1164 cm^{-1}. This suggests that the binding interactions between HNTs and CAP are weak, and the

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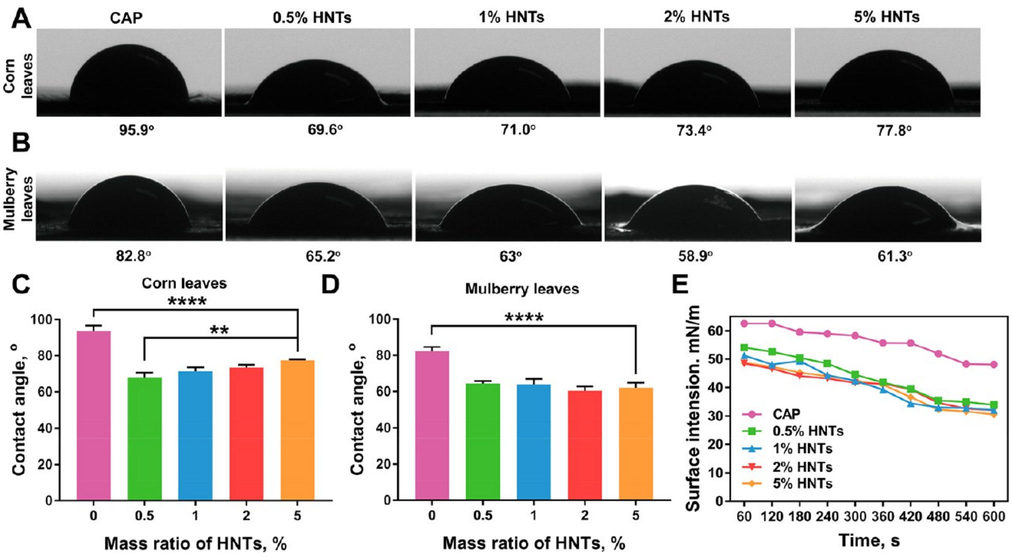

Figure 7. Contact angle image (A) and average contact angle statistics (C) of HNTs−CAP emulsion with different HNT contents on corn leaves. Contact angle images (B) and average contact angle statistics (D) of HNTs−CAP emulsion with different HNT contents on mulberry leaves. Surface tension of HNTs−CAP emulsion with different HNT contents (E). Data values correspond to mean ± SD. Error bars represent SD ****$p < 0.0001$, **$p < 0.01$, one-way analysis of variance (ANOVA).

stabilizing effect of HNTs for CAP emulsion can be attributed to the changed rheology properties. Figure 4C shows the XRD patterns of CAP, HNTs−CAP emulsion lyophilized powder, CAP, and HNTs. The diffraction peaks of the HNTs appeared at 12°, 20°, and 25°, corresponding to the (001), (020, 110), and (002) planes, respectively.[31] The structure of CAP emulsion became amorphous after lyophilization. The diffraction peaks of the HNTs could be clearly seen in the spectrum of the lyophilized powder of HNTs−CAP emulsion, and no obvious new peaks or peak shifts were found in the pattern. Therefore, no intercalation occurs in the preparation of HNTs−CAP emulsion. The thermal degradation curve of CAP and HNTs−CAP emulsion freeze-dried powder are compared in Figure 4D. After introduction of the HNTs, the decomposition temperature of CAP increased. Therefore, HNTs can significantly protect pesticides from heat decomposition, and HNTs−CAP shows better thermal stability. These results suggest that the interactions between HNTs and CAP improve the thermal stability of CAP.

The three-dimensional structure of the freeze-dried emulsion droplet was investigated by SEM (Figure 5). It can be seen that the solidified emulsion particles are spherical in the images. After the HNTs were added, the tubes gathered around the spherical particles, and some tubes wrapped the emulsion into a spherical shape. The oil/water interface was laterally attached to hydrophilic HNTs such that the HNTs aggregated into bundles due to capillary forces, covering the oil droplets and preventing them from coalescing. HNTs solid particles were compactly distributed at the oil−water interface until the pesticide in the oil phase was completely wrapped, which made the size of all the Pickering emulsion droplets gradually smaller and evenly dispersed. It can also be seen from the images that the Pickering emulsion became stable due to the coalescence of the HNTs at the oil/water interface and wrapping the oil droplets.

3.4. Rheological Properties of HNTs−CAP Emulsions.

The oil−water interface might adsorb solid particles to form a particle monolayer that acts as a rigid network and provide a physical barrier to coalescence, which controls the stability of the Pickering emulsion. It is also possible that particle−particle interactions form a 3D particle network in the continuous phase and then increase the viscosity to improve the stability of the emulsion, which is especially evident in clay-based systems.[32,33] The changes in viscosity and modulus of CAP emulsion and HNTs−CAP emulsion were tested (Figure 6). As the shear rate increased, the storage and loss moduli also increased, and both the CAP and HNTs−CAP systems presented similar fluid-like behaviors.[34] The introduction of HNTs increased the storage modulus of the emulsion. This indicated that HNTs had a certain enhancement ability toward CAP emulsions. From the shear rate−dynamic viscosity changes of CAP emulsions and HNTs−CAP emulsions (Figure 6C), it was found that with the increase of shear rate, all the emulsions showed obvious shear thinning behavior. The addition of HNTs increased the viscosity of the emulsion, and with the concentration of HNT dispersion increased, the shear viscosity increased except for the 5 wt % HNTs sample. The slightly decreased viscosity of the 5 wt % sample was attributed to aggregation of the nanotubes and the decreased emulsifying ability as illustrated above. Furthermore, due to the electroviscosity effects of the charged droplets, the increase of the surface charge density on the droplets leads to the increase in viscosity.[35] The increase in viscosity helps to inhibit the movement of oil droplets, reducing the migration rate and collision probability of the oil droplets, thereby enhancing the stability of the emulsion. These results suggest that HNTs can improve the viscosity and strength of CAP emulsion and then enhance the stability of the emulsion.

3.5. Foliar Adhesion and Washout Resistance of HNTs−CAP Emulsions.

The contact angle and surface tension of pesticide formulations are important parameters affecting their spreading, wetting, and adhesion behavior on plant leaves.[36] The droplet wettability of a leaf surface is largely affected by the contact angle, which ranges from good wettability ($\theta < 60°$), moderate wettability ($60° \leq \theta < 80°$), poor wettability ($80° \leq \theta < 100°$), to very poor wettability ($\theta \geq 100°$).[37] The larger the contact angle of the droplet on the leaf surface, the less wet the liquid will be on that surface.

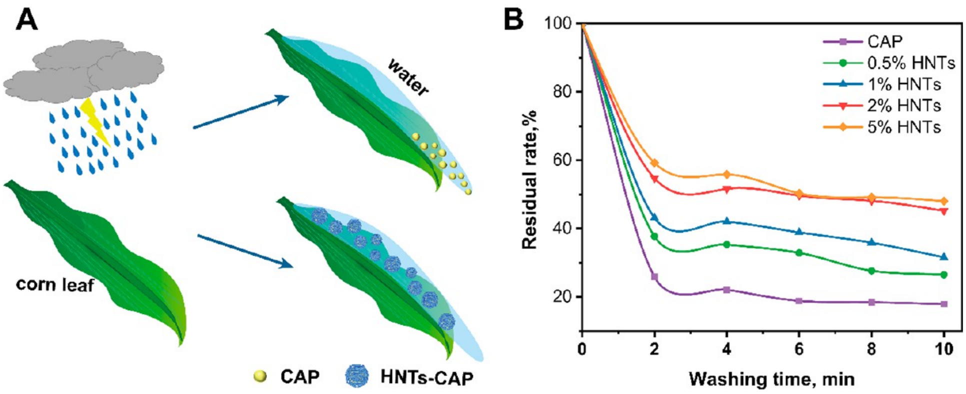

Figure 8. Schematic diagram of HNTs−CAP emulsion on corn leaves washed by rainwater (A) and the residue rate of CAP on corn leaves after washing at different times (B).

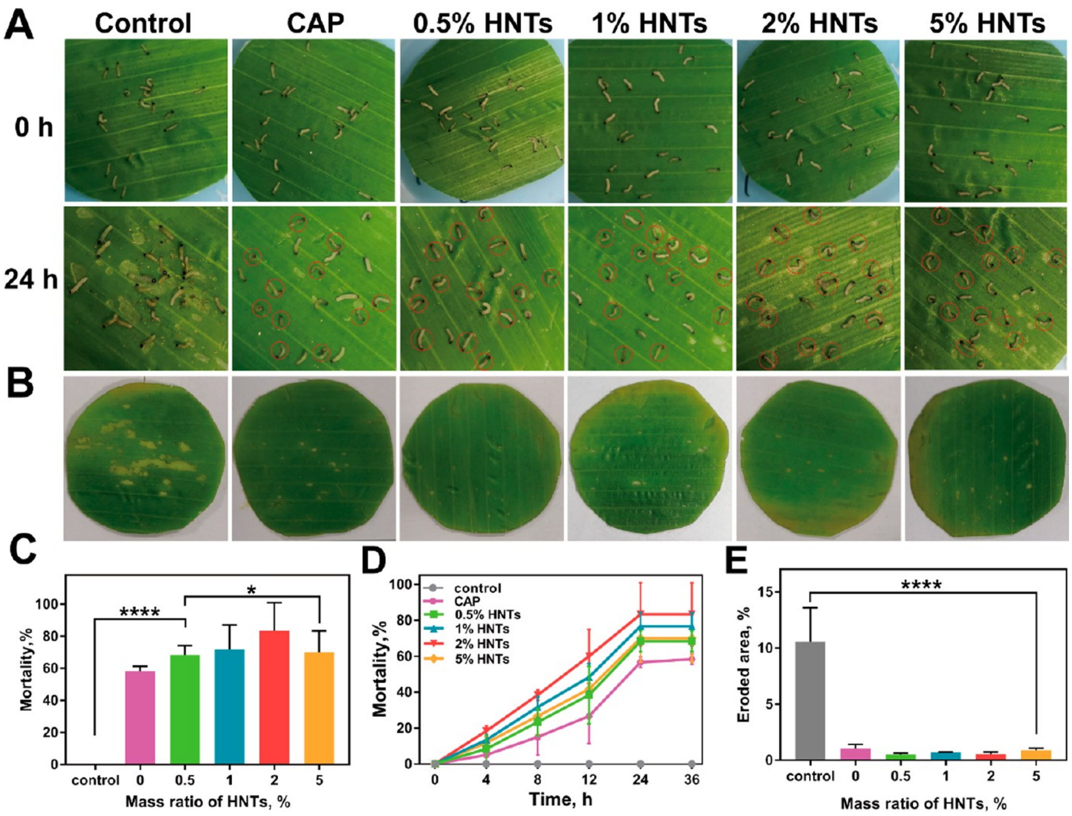

Figure 9. Insecticidal efficacy of HNTs−CAP emulsion toward *S. frugiperda*: Pest state on corn leaves by soaking in 30 ppm of HNTs−CAP emulsion (A), 24 h mortality (C), and mortality statistics at different times (D) (red circle indicates dead larvae). Images of the leaf by removing the pest (B) and residue area statistics (E) after feeding for 36 h. Data values correspond to mean ± SD. Error bars represent SD ****$p < 0.0001$, *$p < 0.05$, one-way analysis of variance (ANOVA).

Foliar contact angles of HNTs−CAP emulsions were measured on corn leaves and mulberry leaves, and the contact angle results are shown in Figure 7A−D. With the introduction of HNTs, the contact angle of CAP emulsion on corn leaves decreased from 95.9° to 69.6−77.8°, from poor wettability to moderate wettability, while the contact angle of CAP emulsion on mulberry leaves decreased from 82.8° to 58.8−65.2°. Therefore, HNTs can improve the wettability of CAP emulsion formulations on leaves. Figure 7E shows that the surface tension of HNTs−CAP emulsion is lower than that of CAP emulsion. The lower the surface tension of the pesticide preparation, the greater the retention on the same leaves. The bouncing of pesticide droplets on the surface of cabbage leaves, which have lower surface tension, can be reduced.[38] The lower surface tension can indirectly prevent droplets from flowing away from plant leaves. As decreased surface tension and static contact angle of the droplet on the blade surface occur, the droplet retention rate is improved.[39] Thus, HNTs can reduce the surface tension and contact angle of CAP emulsion on leaves, improving the adhesion and retention of CAP on the leaf surface.

Pesticides are deposited on plant leaves by spraying and then exert their effects when pests eat the leaves. The potency of pesticides can be prolonged by improving the adhesion of pesticide liquid to leaves and resistance to scour.[4] Owing to the nanoscale size effect and changed wetting property, the

https://doi.org/10.1021/acsami.2c11234
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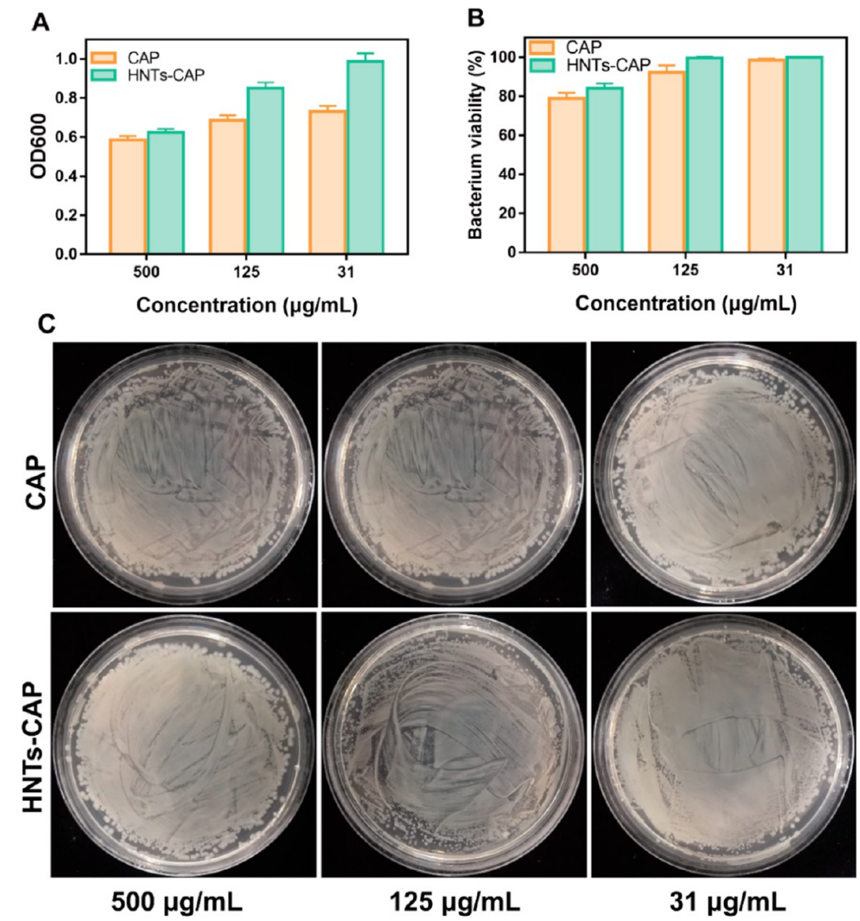

Figure 10. Effect of CAP and HNTs−CAP emulsions on *Escherichia coli* activity. OD value at 600 nm of *E. coli* (A), bacterial activity (B), and digital photo of *E. coli* colonies (C) cultured after 24 h.

HNTs−CAP emulsions widely cover the leaf surfaces before washing and form a scattered distribution state based on the textures of the leaf surfaces[4] (Figure 8A). Figure 8B shows the residual amount of CAP on corn leaves after HNTs−CAP emulsions at different concentrations of HNTs (0, 0.5, 1, 2, and 5 wt %) were continuously applied. The washout resistance was improved with the increase in HNT concentration. With the increase in washing time, HNTs increased the pesticide residue on the leaf surface compared with that of the control group. After washing for 2 min, the pesticide residue rates from CAP emulsion and HNTs−CAP emulsion formulation were 25% and 40−60%, respectively. When the HNT concentration was 5 wt %, the residue rate of pesticide emulsion was 60%, which is 2.4 times that of CAP emulsion. Another research study using nanocapsule-loaded λ-cyhalothrin (NCS@LC) showed that the residue rate of the NCS@LC group was still approximately 60%, after washing for 2 min.[40] After 10 min of washing, the pesticide residue rates of CAP emulsion and HNTs−CAP emulsion were 18% and 26%−48%, respectively. When the concentration of HNT dispersion was 5 wt %, the residue rate of pesticide emulsion was 2.7 times higher than that of CAP emulsion. Compared with the raw CAP emulsion, the washout resistance of the pesticide emulsion was significantly enhanced after the addition of HNTs. These results demonstrate that HNTs can enhance the foliar adhesion of CAP and reduce the loss of effective components of CAP. Nanopesticide fate including stability, release kinetics, leaching, and elemental analysis of plants and soil, needs to be evaluated in detail. Halloysite clay, as a soil component and Chinese mineral medicine, can be eaten and is safe for humans.[41] However, to avoid risk, precise guiding of the clay at targeting sites inside plants needs to be explored, and the understanding of enhancing the efficacy and preventing nanotube release into the environment should be improved.[42] Previous findings indicate that HNTs are safe for plant growth at a commonly used dose.[43]

3.6. Insecticidal Efficacy of HNTs−CAP Emulsion. Fall armyworm, *S. frugiperda*, a highly destructive agricultural pest, has spread with remarkable speed, and caused high losses to maize production globally.[19] CAP is one of the effective pesticides against *S. frugiperda*. Therefore, *S. frugiperda* was used to evaluate the insecticidal effects of HNTs−CAP and CAP emulsion, and the results are shown in Figure 9. The mortality rate of insects on corn leaves soaked in water was 0. After *S. frugiperda* gnawed on corn leaves soaked with CAP reagent for 4 h, the insects began to die, and the mortality of all HNTs−CAP groups was significantly higher than that of the CAP emulsion group (0 wt % HNTs). The experimental results showed that the mortality rates of all experimental treatment groups tended to balance in 24 h, and that the CAP emulsion group had the lowest mortality rate of 56%. At this time, the larval mortality increased with the increase in HNT dispersion concentration except for the 5 wt % HNTs sample. When the concentration of HNT dispersion was 2 wt %, the mortality of larvae was 83%, which is 1.5 times that of the CAP emulsion group. This indicated that HNTs have a controlled

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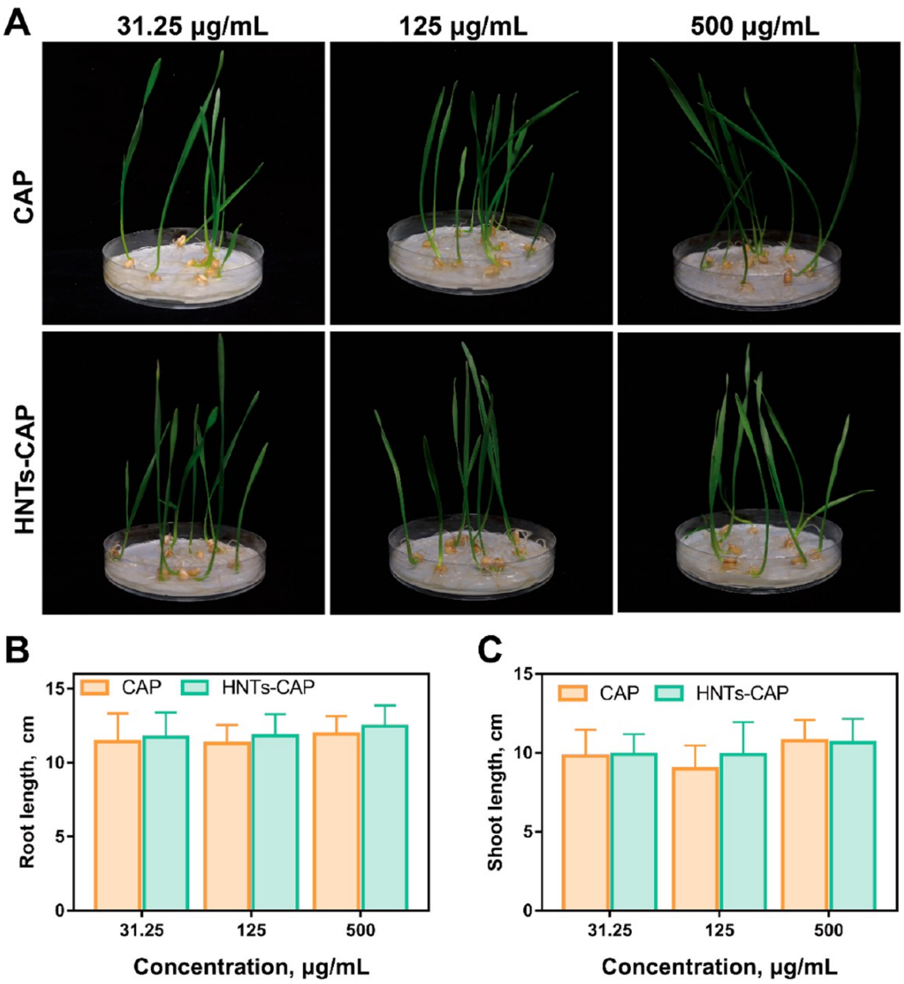

Figure 11. Effects of CAP and HNTs−CAP emulsions on wheat growth. Appearance (A), root length (B), and wheat stem length (C) of wheat cultured for 7 d.

release effect toward CAP on foliar surfaces. A previous study showed mortality of about 40% of larvae after 10 days of feeding on baby corn dipped in ZnO nanoparticle solution.[44] In contrast, HNTs are inexpensive nanomaterials and significantly increase larval mortality. HNTs demonstrate a promising potential to be used as an alternative to the more lethal insecticides in controlling *S. frugiperda* and other species. Figure 9B,E shows the statistics of the state of corn leaves and the gnawed area. The corn leaves soaked in water were significantly eaten by *S. frugiperda*. In the four experimental groups treated with HNTs−CAP emulsion dilution, most of the larvae died, and the leaves were gnawed on a small area. The gnawed area of the corn leaves soaked in the CAP emulsion dilution was 3 times that of the HNTs−CAP emulsion treatment group. These results indicated that HNTs−CAP emulsions can provide better insecticidal activity and leaf protection. As expected, pure HNTs did not show any insecticidal effects toward *S. frugiperda* (Figure S2). HNTs−CAP can improve foliar adhesion, washout resistance, and insecticidal effect of the emulsion, thereby protecting plants, and HNTs have a great potential in the field of pesticide carriers.

3.7. Biosafety of HNTs−CAP Emulsions. Pesticides might enter the soil environment during application due to migration, rain wash, and runoff. When a pesticide is applied in fields, plants, insects, and soil microbes are supposed to be exposed to the same concentration of pesticide. CAP is significantly toxic to aquatic organisms; thus, a biosafety evaluation toward model organisms should be performed. To evaluate the biosafety of HNTs−CAP emulsions, the effects of different concentrations of HNTs−CAP emulsions on bacteria (*Escherichia coli*) and plants (wheat) were investigated (Figure 10). Because the absorbance at 600 nm was proportional to the concentration of *E. coli* strains, the growth status of *E. coli* can be determined by UV−vis spectroscopy. In Figure 10A, *E. coli* was treated with different concentrations of CAP emulsion and HNTs−CAP emulsion (31, 125, and 250 μg/mL), and the absorbance of *E. coli* decreased as the emulsion concentration increased. At the same concentration, the absorbance of *E. coli* treated with HNTs−CAP emulsion was higher than that of CAP emulsion. The biological activity of *E. coli* is shown in Figure 10B after culturing for 24 h. The activity of *E. coli* cultured with HNTs−CAP was comparable to that of the CAP emulsion at low concentrations. The activity of *E. coli* cultured in HNTs−CAP emulsion was higher than that in CAP emulsion at higher concentrations. From these results, the effects of CAP emulsions on *E. coli* growth and metabolism were not altered by introduction of HNTs, and HNTs were even more beneficial to *E. coli* growth and metabolism. This was further demonstrated by digital photographs of *E. coli* (Figure 10C). Similarly, Xiang et al. cultured the bacteria (*E.*

https://doi.org/10.1021/acsami.2c11234
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coli) with different concentrations of nano pesticide carrier to evaluate the biosafety of the carrier.[45]

Pesticides may reach nontarget areas and humans via wind drift, surface runoff, leaching, and bystander exposure. Specifically, pesticide residues reaching wheat grains may lead to risks for humans from consumption of wheat-based food products.[46] So, wheat seeds were used as models to study the effects of CAP emulsion and HNTs−CAP emulsion on wheat germination and growth (Figure 11). At the same concentration, the germination rates of wheat seeds cultured with CAP emulsion and HNTs−CAP emulsion were the same, and both were 100%. The root/stem length of wheat cultured in HNTs−CAP emulsion was similar to that of wheat cultured in CAP emulsion. This indicated that HNTs−CAP have no significant effect on wheat seed germination rate and wheat growth, which demonstrates that HNTs as a pesticide carrier have good biological safety.

4. CONCLUSIONS

HNTs, a tubular natural clay, can significantly improve the stability of water−xylene emulsion. HNTs were then introduced to the pesticide formulation by dissolving the CAP in xylene as the oil phase and HNT dispersions as the water phase. HNTs adsorbed and aggregated at the interface of CAP oil droplets, forming a three-dimensional network structure and preventing coalescence of the emulsion. HNTs−CAP emulsion showed increased leaf adhesion, rain erosion resistance, and insecticidal effect. The residue rate of pesticide emulsion in HNTs−CAP emulsion was 2.7 times higher than that in CAP emulsion. *S. frugiperda* was selected as a pest model, and the mortality of all HNT−CAP emulsion groups was significantly higher than that of CAP emulsion group. When the HNT dispersion concentration was 2 wt %, the larva mortality was 83%, which was 1.5 times that of the CAP emulsion group. Moreover, HNTs have good biosafety toward *E. coli* and wheat models. This work provides a new natural nanomaterial for the development of stable storage and rain resistance of water-insoluble pesticide emulsions to control crop pests with modern agriculture technology.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c11234.

> TEM, SEM, thermogravimetric analysis, FTIR, XRD, particle size distribution, and zeta potential of HNTs. Insecticidal efficacy of HNTs emulsion toward *S. frugiperda*: pest state on corn leaves by soaking in 30 ppm of HNTs emulsion and mortality statistics at different times (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (52073121), Natural Science Foundation of Guangdong Province, China (2019A1515011509), the Fundamental Research Funds for the Central Universities (21622406), the Key-Area Research and Development Program of Guangdong Province (2020B020223004), the Project of Collaborative Innovation Center of GDAAS(XTXM202202), and the Innovation Team of Modern Agricultural Industry Generic Key Technology R&D of Guangdong Province (2021KJ134).

■ REFERENCES

(1) Ur Rahim, H.; Qaswar, M.; Uddin, M.; Giannini, C.; Herrera, M. L.; Rea, G. Nano-Enable Materials Promoting Sustainability and Resilience in Modern Agriculture. *Nanomaterials* **2021**, *11* (8), 2068.

(2) Sharma, A.; Shukla, A.; Attri, K.; Kumar, M.; Kumar, P.; Suttee, A.; Singh, G.; Barnwal, R. P.; Singla, N. Global Trends in Pesticides: A Looming Threat and Viable Alternatives. *Ecotoxicol. Environ. Saf.* **2020**, *201*, 110812.

(3) Tudi, M.; Daniel Ruan, H.; Wang, L.; Lyu, J.; Sadler, R.; Connell, D.; Chu, C.; Phung, D. T. Agriculture Development, Pesticide Application and Its Impact on the Environment. *Int. J. Environ. Res. Public Health* **2021**, *18* (3), 1112.

(4) Luo, J.; Gao, Y.; Liu, Y.; Huang, X.; Zhang, D.-x.; Cao, H.; Jing, T.; Liu, F.; Li, B. Self-Assembled Degradable Nanogels Provide Foliar Affinity and Pinning for Pesticide Delivery by Flexibility and Adhesiveness Adjustment. *ACS Nano* **2021**, *15* (9), 14598−14609.

(5) Wang, X.; Zheng, K.; Cheng, W.; Li, J.; Liang, X.; Shen, J.; Dou, D.; Yin, M.; Yan, S. Field Application of Star Polymer-Delivered

Chitosan to Amplify Plant Defense against Potato Late Blight. *Chem. Eng. J.* **2021**, *417*, 129327.
(6) Sun, D.-W.; Huang, L.; Pu, H.; Ma, J. Introducing Reticular Chemistry into Agrochemistry. *Chem. Soc. Rev.* **2021**, *50* (2), 1070−1110.
(7) Cavallaro, G.; Milioto, S.; Nigamatzyanova, L.; Akhatova, F.; Fakhrullin, R.; Lazzara, G. Pickering Emulsion Gels Based on Halloysite Nanotubes and Ionic Biopolymers: Properties and Cleaning Action on Marble Surface. *ACS Appl. Nano Mater.* **2019**, *2* (5), 3169−3176.
(8) Yuan, P.; Tan, D.; Annabi-Bergaya, F. Properties and Applications of Halloysite Nanotubes: Recent Research Advances and Future Prospects. *Appl. Clay Sci.* **2015**, *112*, 75−93.
(9) Lisuzzo, L.; Cavallaro, G.; Milioto, S.; Lazzara, G. Pickering Emulsions Stabilized by Halloysite Nanotubes: From General Aspects to Technological Applications. *Adv. Mater. Interfaces* **2022**, *9*, 2102346.
(10) Cui, Y.; Threlfall, M.; van Duijneveldt, J. S. Optimizing Organoclay Stabilized Pickering Emulsions. *J. Colloid Interface Sci.* **2011**, *356* (2), 665−671.
(11) Yang, X.; Cai, J.; Chen, L.; Cao, X.; Liu, H.; Liu, M. Green Detergent Made of Halloysite Nanotubes. *Chem. Eng. J.* **2021**, *425*, 130623.
(12) Massaro, M.; Noto, R.; Riela, S. Past, Present and Future Perspectives on Halloysite Clay Minerals. *Molecules* **2020**, *25* (20), 4863.
(13) Rahman, N.; Scott, F. H.; Lvov, Y.; Stavitskaya, A.; Akhatova, F.; Konnova, S.; Fakhrullina, G.; Fakhrullin, R. Clay Nanotube Immobilization on Animal Hair for Sustained Anti-Lice Protection. *Pharmaceutics* **2021**, *13* (9), 1477.
(14) Rahman, N.; Karan, A.; Lvov, Y.; Liao, Z.; Parekh, A.; Rughani, R.; Muthukrishnan, S. Lawsone and Indigo-Loaded Sepiolite Nanofibers for Hair Coloring with Sustained Release. *ACS Appl. Nano Mater.* **2022**, *5* (2), 1855−1863.
(15) Massaro, M.; Campofelice, A.; Colletti, C. G.; Lazzara, G.; Noto, R.; Riela, S. Functionalized Halloysite Nanotubes: Efficient Carrier Systems for Antifungine Drugs. *Appl. Clay Sci.* **2018**, *160*, 186−192.
(16) Panchal, A.; Fakhrullina, G.; Fakhrullin, R.; Lvov, Y. Self-Assembly of Clay Nanotubes on Hair Surface for Medical and Cosmetic Formulations. *Nanoscale* **2018**, *10* (38), 18205−18216.
(17) Stokstad, E. New Crop Pest Takes Africa at Lightning Speed. *Science* **2017**, *356* (6337), 473−474.
(18) Goergen, G.; Kumar, P. L.; Sankung, S. B.; Togola, A.; Tamò, M. First Report of Outbreaks of the Fall Armyworm *Spodoptera* frugiperda (JE Smith)(Lepidoptera, Noctuidae), a New Alien Invasive Pest in West and Central Africa. *PLoS One* **2016**, *11* (10), e0165632.
(19) Early, R.; González-Moreno, P.; Murphy, S. T.; Day, R. Forecasting the Global Extent of Invasion of the Cereal Pest *Spodoptera* frugiperda, the Fall Armyworm. *NeoNeoBiota* **2018**, *40*, 25391847−50.
(20) Rodrigues, A. C.; Gravato, C.; Quintaneiro, C.; Golovko, O.; Žlábek, V.; Barata, C.; Soares, A. M.; Pestana, J. L. Life History and Biochemical Effects of Chlorantraniliprole on Chironomus Riparius. *Sci. Total Environ.* **2015**, *508*, 506−513.
(21) Feng, J.; Chen, Q.; Wu, X.; Jafari, S. M.; McClements, D. J. Formulation of Oil-in-Water Emulsions for Pesticide Applications: Impact of Surfactant Type and Concentration on Physical Stability. *Environ. Sci. Pollut. Res.* **2018**, *25* (22), 21742−21751.
(22) Li, Y.; Feng, Y.; Yu, G.; Li, J.; Zhou, Y.; Liu, Y. Preparation and Characterization of Oil-in-Water Emulsion Based on Eco-Friendly Emulsifiers. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *602*, 125024.
(23) Liu, B.; Wang, Y.; Yang, F.; Cui, H.; Wu, D. Development of a Chlorantraniliprole Microcapsule Formulation with a High Loading Content and Controlled-Release Property. *J. Agric. Food Chem.* **2018**, *66* (26), 6561−6568.
(24) Wu, T.; Fang, X.; Yang, Y.; Meng, W.; Yao, P.; Liu, Q.; Zhang, B.; Liu, F.; Zou, A.; Cheng, J. Eco-Friendly Water-Based Λ-Cyhalothrin Polydopamine Microcapsule Suspension with High Adhesion on Leaf for Reducing Pesticides Loss. *J. Agric. Food Chem.* **2020**, *68* (45), 12549−12557.
(25) Badawy, M. E. Development and Validation of Hplc Methods for Analysis of Chlorantraniliprole Insecticide in Technical and Commercial Formulations. *J. Environ. Sci. Health, Part B* **2018**, *53* (7), 411−422.
(26) Yang, Y.; Fang, Z.; Chen, X.; Zhang, W.; Xie, Y.; Chen, Y.; Liu, Z.; Yuan, W. An Overview of Pickering Emulsions: Solid-Particle Materials, Classification, Morphology, and Applications. *Front. Pharmacol.* **2017**, *8*, 287.
(27) Cai, X.; Li, C.; Tang, Q.; Zhen, B.; Xie, X.; Zhu, W.; Zhou, C.; Wang, L. Assembling Kaolinite Nanotube at Water/Oil Interface for Enhancing Pickering Emulsion Stability. *Appl. Clay Sci.* **2019**, *172*, 115−122.
(28) Kpogbemabou, D.; Lecomte-Nana, G.; Aimable, A.; Bienia, M.; Niknam, V.; Carrion, C. Oil-in-Water Pickering Emulsions Stabilized by Phyllosilicates at High Solid Content. *Colloids Surf. A Physicochem. Eng. Asp.* **2014**, *463*, 85−92.
(29) Madejová, J. Ftir Techniques in Clay Mineral Studies. *Vib. Spectrosc.* **2003**, *31* (1), 1−10.
(30) Suraphan, N.; Fan, L.; Liu, B.; Wu, D. Co-Delivery of Chlorantraniliprole and Avermectin with a Polylactide Microcapsule Formulation. *RSC Adv.* **2020**, *10* (43), 25418−25425.
(31) Brindley, G.; Robinson, K.; MacEwan, D. The Clay Minerals Halloysite and Meta-Halloysite. *Nature* **1946**, *157* (3982), 225−226.
(32) Van Hooghten, R.; Blair, V. E.; Vananroye, A.; Schofield, A. B.; Vermant, J.; Thijssen, J. H. Interfacial Rheology of Sterically Stabilized Colloids at Liquid Interfaces and Its Effect on the Stability of Pickering Emulsions. *Langmuir* **2017**, *33* (17), 4107−4118.
(33) Abend, S.; Lagaly, G. Bentonite and Double Hydroxides as Emulsifying Agents. *Clay Miner.* **2001**, *36* (4), 557−570.
(34) Lai, Y.; Wu, Y.; Sheng, P.; Zhang, Z.-Q. Hybrid Elastic Solids. *Nat. Mater.* **2011**, *10* (8), 620−624.
(35) Zhang, X.; Liu, J.; Fan, Z. Stability of Etofenprox in Water Emulsion Induced by Block Copolymer and Surfactant. *Colloids Surf. A Physicochem. Eng. Asp.* **2013**, *422*, 191−198.
(36) Zhang, X.-p.; Jing, T.-f.; Zhang, D.-x.; Luo, J.; Li, B.-x.; Liu, F. Assessment of Ethylene Glycol Diacetate as an Alternative Carrier for Use in Agrochemical Emulsifiable Concentrate Formulation. *Ecotoxicol. Environ. Saf.* **2018**, *163*, 349−355.
(37) Gaskin, R.; Steele, K.; Forster, W. Characterising Plant Surfaces for Spray Adhesion and Retention. *N. Z. J. Crop Hortic. Sci.* **2005**, *58*, 179−183.
(38) Guan, W.; Zhang, W.; Tang, L.; Wang, Y.; Cui, H. Fabrication of Novel Avermectin Nanoemulsion Using a Polyurethane Emulsifier with Cleavable Disulfide Bonds. *J. Agric. Food Chem.* **2018**, *66* (26), 6569−6577.
(39) Gao, Y.; Lu, J.; Zhang, P.; Shi, G.; Li, Y.; Zhao, J.; Liu, Z.; Yang, J.; Du, F.; Fan, R. Wetting and Adhesion Behavior on Apple Tree Leaf Surface by Adding Different Surfactants. *Colloids Surf., B* **2020**, *187*, 110602.
(40) Luo, J.; Gao, Y.; Liu, Y.; Du, J.; Zhang, D.-x.; Cao, H.; Jing, T.; Li, B.-x.; Liu, F. Using a Reactive Emulsifier to Construct Simple and Convenient Nanocapsules Loaded with Lambda-Cyhalothrin to Achieve Efficient Foliar Delivery and Insecticidal Synergies. *Nanoscale* **2021**, *13* (37), 15647−15658.
(41) Qihua, L.; Jin, W.; Zhiping, P.; Fenglin, L.; Xiaolin, T. Review of the Powder and Decoction Formulae in Traditional Chinese Medicine Based on Pharmacologically Active Substances and Clinical Evidence. *J. Tradit. Chin. Med.* **2015**, *35* (3), 355−360.
(42) Sharma, S.; Sahu, B. K.; Cao, L.; Bindra, P.; Kaur, K.; Chandel, M.; Koratkar, N.; Huang, Q.; Shanmugam, V. Porous Nanomaterials: Main Vein of Agricultural Nanotechnology. *Prog. Mater. Sci.* **2021**, *121*, 100812.
(43) Chen, L.; Guo, Z.; Lao, B.; Li, C.; Zhu, J.; Yu, R.; Liu, M. Phytotoxicity of Halloysite Nanotubes Using Wheat as a Model: Seed Germination and Growth. *Environ. Sci. Nano* **2021**, *8* (10), 3015−3027.

(44) Pittarate, S.; Rajula, J.; Rahman, A.; Vivekanandhan, P.; Thungrabeab, M.; Mekchay, S.; Krutmuang, P. Insecticidal Effect of Zinc Oxide Nanoparticles against Spodoptera Frugiperda under Laboratory Conditions. *Insects* **2021**, *12* (11), 1017.
(45) Xiang, Y.; Zhang, G.; Chen, C.; Liu, B.; Cai, D.; Wu, Z. Fabrication of a pH-Responsively Controlled-Release Pesticide Using an Attapulgite-Based Hydrogel. *ACS Sustain. Chem. Eng.* **2018**, *6* (1), 1192−1201.
(46) Fantke, P.; Charles, R.; de Alencastro, L. F.; Friedrich, R.; Jolliet, O. Plant Uptake of Pesticides and Human Health: Dynamic Modeling of Residues in Wheat and Ingestion Intake. *Chemosphere* **2011**, *85* (10), 1639−1647.

https://doi.org/10.1021/acsami.2c11234
ACS Appl. Mater. Interfaces 2022, 14, 41605−41617

Supporting information

Halloysite nanotubes-based pesticide formulations with enhanced rain erosion resistance, foliar adhesion and insecticidal effect

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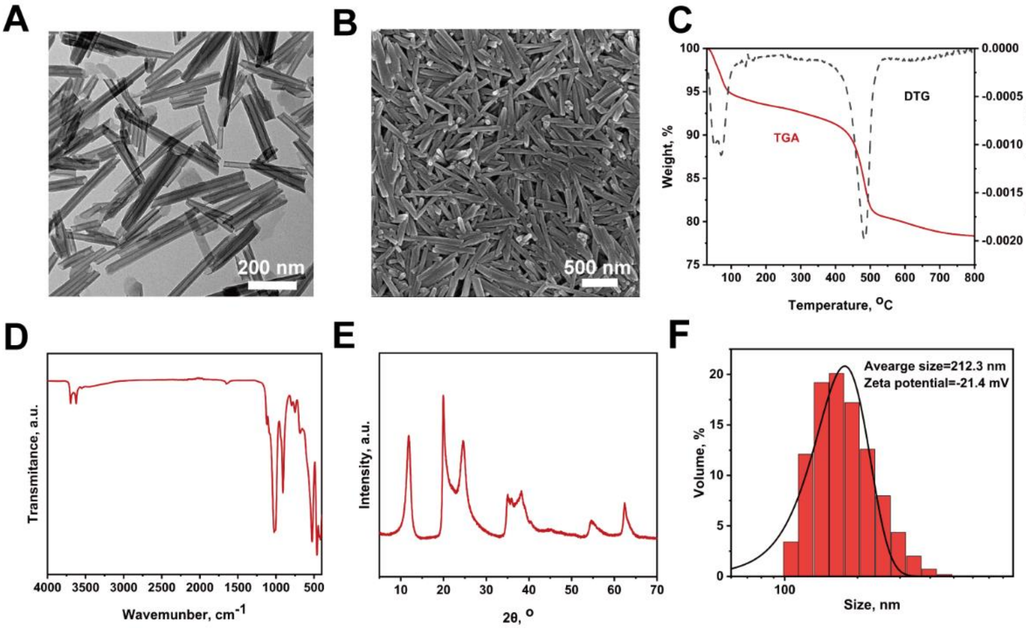

Figure. S1. TEM (A), SEM (B), thermogravimetric analysis (C), FTIR (D), XRD (E), particle size distribution and zeta potential (F) of HNTs.

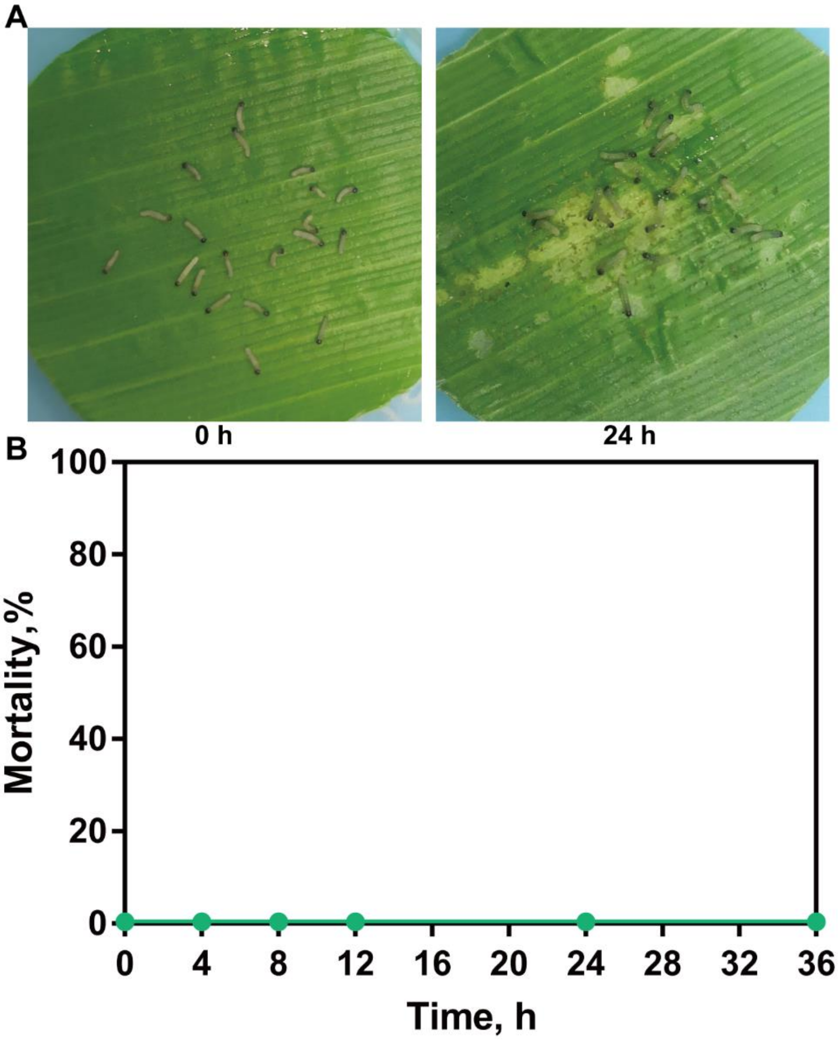

Figure. S2. Insecticidal efficacy of HNTs emulsion towards *S. frugiperda*: Pest state on corn leaves by soaking in 30 ppm HNTs emulsion (A), and mortality statistics at different times (B) (red circle indicates dead larvae).