Research Article

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Enhanced and sustained pesticidal activity of a graphene-based pesticide delivery system against the diamondback moth *Plutella xylostella*

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Abstract

Background: Traditional abamectin (Abm) formulations have several shortcomings, such as low water solubility, burst release behavior, poor photostability, and short persistence periods, which decrease their pesticidal activity and the risks they pose to the environment. Nanomaterial-based pesticide delivery systems (PDSs) provide new strategies for the efficient and safe application of pesticides. Here, we developed Abm-loaded graphene oxide (Abm/GO) as a PDS for the sustained release of Abm, which shows enhanced control efficacy against *Plutella xylostella*.

Results: The hydrophobic Abm molecule was effectively loaded on GO nanocarrier by a physisorption method, which formed a uniform and stable Abm/GO nanoformulation. GO possesses high adsorption capacity and can effectively load Abm. The Abm/GO nanoformulation shows enhanced water dispersion stability and can remain stable during a 2-year storage period in contrast to the water-insoluble Abm. In addition, the Abm/GO nanoformulation exhibits sustained pesticide release behavior and possesses significantly improved anti-ultraviolet properties. Thus, the Abm/GO nanoformulation shows superior pesticidal activity compared with Abm. Abm/GO showed negligible toxicity to maize seedlings, and its GO nanocarrier can reduce the cytotoxicity of Abm to A549 cells.

Conclusion: GO-based PDSs can effectively overcome the disadvantages of traditional pesticides, such as their insolubility, burst release behavior, instability, and short persistence period. GO shows much future promise in agriculture in light of its industrialization potential.

Supporting information may be found in the online version of this article.

Keywords: graphene oxide; abamectin; pesticide delivery system; sustained release; biosafety assay

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1 INTRODUCTION

Pesticides are critically important agrochemicals for controlling the spread of pests; they have thus greatly contributed to crop yield increase and food safety.[1,2] Most pesticides are insoluble in water and show low stability and burst release behavior, and these properties limit their ability to be widely used. Previous studies have shown that more than 90% of pesticides applied are lost following their application.[3] Such low efficiency encourages the repeated application and abuse of pesticides, which poses major risks to the production of food and the environment.[4–6] There is thus a need to develop agrochemical products that are both efficient and environmentally friendly. The development of nanomaterials-based pesticide delivery systems (PDSs) and nanoformulations in recent years has provided new approaches for overcoming many of the drawbacks associated with traditional pesticide formulations.[7–9] Various materials including porous inorganic materials, hollow mesoporous silica, polymer, carbon nanomaterials, clay, and two-dimensional (2D) nanomaterials are used as vectors for PDSs.[10,11] The development of advanced PDSs can enhance the solubility and stability of pesticides, promote stimuli-responsive and pesticide-release behavior, enhance efficiency, and reduce environmental risks.[12–14]

Abamectin (Abm) is a broad-spectrum and highly efficient biological pesticide that has been widely applied to enhance the production of rice, corn, and wheat. However, Abm has several shortcomings, such as its poor water solubility, burst release in the surrounding environment, and rapid degradation under ultraviolet (UV) light, all of which have substantially limited its practical use. The low water solubility of Abm encourages the overuse of organic solvents and adjuvants, which can lead to the waste of resources and severe pollution.[15] In addition, the burst release of Abm decreases its persistence in the environment; it thus requires several applications for the pesticidal effect to be sustained. Abm can be easily degraded when exposed to sunlight because of its unstable structure, which results in the rapid loss of its pesticidal activity. [16,17]

High-efficiency and environmentally friendly PDSs have been developed to overcome some of the major drawbacks of Abm.[8,15] For example, Feng *et al*. synthesized Abm-loaded mesoporous silica nanoparticles (Abm@MSNs) using a one-pot method and studied its pesticidal activity. [8] They showed that Abm could be effectively loaded on MSNs, and that the nanoformulation exhibits controlled release performance and improved resistance to degradation by UV light. Chun and Feng developed a flash nano-precipitation method for constructing Abm nanoformulations.[15] With this strategy, Abm can be effectively encapsulated in wall materials. This Abm nanoformulation shows high photostability and sustained release performance, which improves the pesticidal activity of Abm. Although some major advances have been made with the use of the aforementioned strategies, some drawbacks require attention, such as the complexity of the preparation process, the low pesticide loading ratio, and the potential for industrial production. There is thus a need to develop carriers with high pesticide loading performance, simple preparation processes, and high industrialization capacity.

Graphene oxide (GO), a novel (2D) nanomaterial with high biosafety, aqueous solubility, and drug loading capacity, has been widely used as a carrier for hydrophobic chemotherapeutic drugs in nanomedicine.[18–21] For example, Zhang *et al*. used a PEGylated GO as a nanocarrier for doxorubicin, and it exhibited excellent drug loading performance.[22] Yaghoubi *et al*. studied the co-delivery of doxorubicin and curcumin by GO, which showed pH-response release performance.[23] GO also shows high loading performance for hydrophobic pesticides. Maliyekkal *et al*. have demonstrated that GO has high adsorption capacity for three hydrophobic pesticides: chlorpyrifos (1200 mg g^{-1}), endosulfan (1100 mg g^{-1}), and malathion (800 mg g^{-1}).[24] Suo *et al*. used cellulose-modified GO as the adsorbent for organophosphorus pesticides (dichlorvos, dimethoate, chlorpyrifos, chlorfenvinphos, methidathion, and profenofos), and they found that these pesticides could be effectively loaded on GO-based nanocarrier.[25] Given the maturity of technology used for the industrial preparation of GO, such nanocarriers could be easily applied in downstream industries such as agriculture.

Here, we studied the use of GO as a nanocarrier for Abm delivery, investigated its pesticidal efficiency against *Plutella xylostella*, and evaluated the biosafety assay of Abm/GO on maize seedling growth and A549 cells. The as-prepared nano-sized formulation contains three components: water, GO, and Abm. In our strategy, Abm is loaded on GO by simple physical adsorption, which results in the formation of a uniform and stable suspension. The good water dispersion stability of Abm/GO nanoformulation enhances its potential in future applications. Abm/GO exhibits improved anti-photolysis performance due to the protection provided by GO. This, coupled with the controlled release performance of Abm, prolongs the period of pesticidal activity of Abm/GO.

2 MATERIALS AND METHODS

2.1 Materials

Graphite powder (5000 mesh) was purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Abm was provided by Jiangsu Yangnong Chemical Co., Ltd (Yangzhou, China). Other reagents were purchased from Sinopharm Chemical Reagent Company (Shanghai, China).

2.2 Preparation of the Abm/GO nanoformulation

GO was prepared by Hummers' method according to our previous study.[2] Briefly, 2 g of graphite powder was dispersed in 50 mL of concentrated sulfuric acid (H_2SO_4) and placed in an ice-water bath, and then 6 g of potassium permanganate ($KMnO_4$) was slowly added. After stirring for 30 min, the reaction system was heated to 35 °C for 2 h. Then 90 mL of water was slowly added and the suspension was heated to 95 °C. After reaction for 1 h, 200 mL of water was added and 5 mL of 30% hydrogen peroxide (H_2O_2) was added to terminate the reaction. The suspension was centrifuged for several times and washed with water until neutral.

Abm ethanol solution (500 mL) was mixed with 100 mL of GO aqueous solution under vigorous stirring at room temperature (RT) for 2 h. Then, ethanol was removed by rotary evaporation at 60 °C. Finally, an appropriate amount of water was added to maintain the total volume of 100 mL.

The scanning electron microscop (SEM) samples of GO and Abm/GO were prepared by dropping the GO or Abm/GO suspension on the silicon wafer with smooth surface and drying by airing.

2.3 Stability of the Abm/GO nanoformulation

All the stability experiments, including storage stability at high/low temperatures at different time points, colloidal stability with different types of water, and photostability, were carried out as described later.

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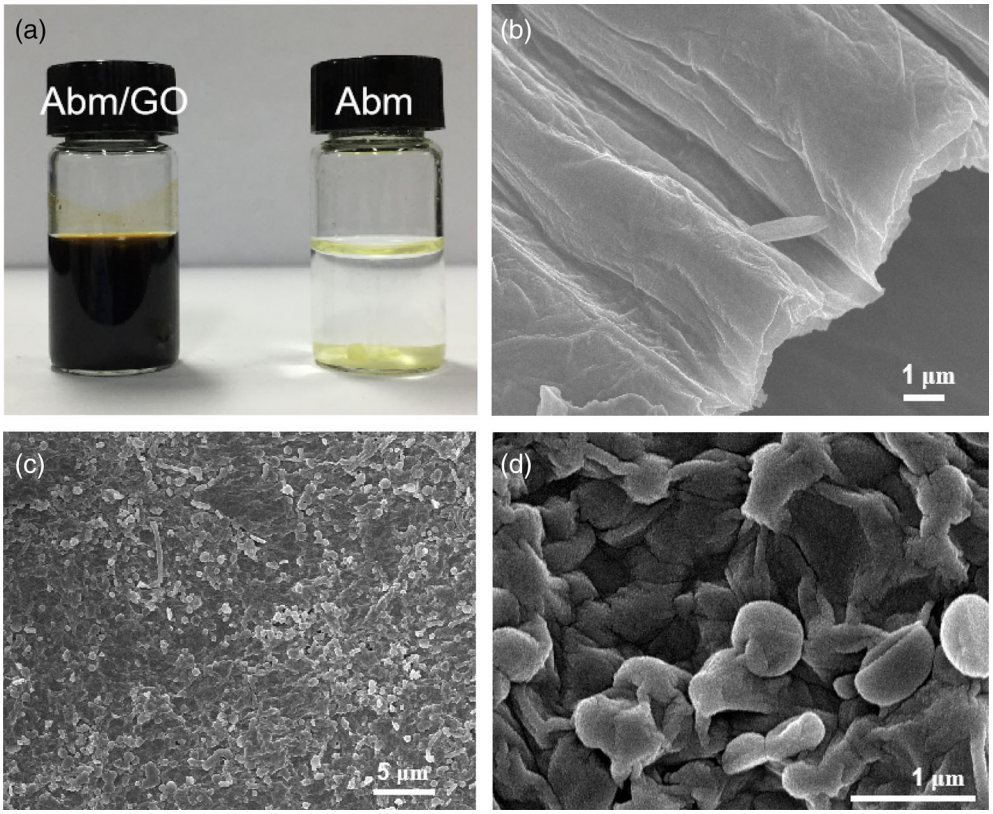

FIGURE 1. (a) Photographs of Abm/GO nanoformulation (10 mg mL^{-1}) and Abm in distilled water; SEM images of (b) GO and (c,d) Abm/GO nanoformulation.

2.3.1 *Low-temperature storage stability*

Abm/GO nanoformulation (0.2 mg mL^{-1}) was placed into 10 mL glass bottles and stored at 0 °C for 7 days. The samples were then placed at RT for 4 h, and the content of Abm was determined.

2.3.2 *High-temperature storage stability*

Abm/GO nanoformulation (0.2 mg mL^{-1}) was placed into 10-mL glass bottles and stored at 54 °C for 14 days. The samples were then placed at RT for 4 h, and the content of Abm was determined.

2.3.3 *Long-term storage stability*

Abm/GO nanoformulation (0.2 mg mL^{-1}) was placed into 10-mL glass bottles and stored in a cool ventilated place for 2 years. The content of Abm was determined every 4 months.

2.3.4 *Colloidal stability with different types of water*

Distilled water, standard hard water (hardness 342 ppm), and water samples from Guiyang (hardness 189 ppm), Guilin (hardness 197 ppm), Suzhou (hardness 108 ppm), and Nanjing (hardness 116 ppm) were used to dilute 0.2 mL of 20 mg mL^{-1} Abm/GO nanoformulation; the samples were then placed into a shaker at 200 rpm for 10 min.

2.3.5 *Photostability*

Abm/GO or free Abm solution was injected into a six-well plate and then dried in a vacuum drying oven at 50 °C. The weight of Abm in each well was 1 mg. The plates containing Abm/GO or free Abm were placed under a UV lamp (36 W, 20 cm height) for 12, 24, 36, 48, 72, 96, and 120 h. Abm in each sample was dissolved by ethanol and measured using high-performance liquid chromatography.

2.4 Sustained release of Abm

To evaluate the sustained release behavior of Abm from nanocarrier, a dialysis membrane containing 10 mL of Abm or Abm/GO solution was placed in a flask with 2 L of 30% ethanol aqueous solution under gentle stirring. The solvent of Abm and Abm/GO was 30% ethanol aqueous solution, and the Abm concentration was 1 mg mL^{-1}. At various time points, 2 mL from the outside solution (2 L) was removed, and the Abm concentration in the solution was determined.

2.5 Pesticidal activity

Plutella xylostella was maintained in the insect room at Guizhou University, Guiyang, China. The leaves of *Ipomoea batatas* were immersed in Abm/GO aqueous solution (Abm concentrations: 0, 0.25, 0.5, 1, 2, 4, 8, and 16 ppm) for 10 s and then placed into plastic cases containing 30 insects. The cases were then stored in the insect room at 25 °C. After 48 h, insect mortality in the different groups was recorded to characterize the pesticidal activity of the Abm/GO nanoformulation. The commercial formulation of Abm was used as the control.

An outdoor pesticidal experiment was conducted to evaluate the persistence of Abm and Abm/GO. *Ipomoea batatas* was planted in flowerpots with a density of 100 plants m^{-2}. The commercial Abm formulation and Abm/GO nanoformulation were then sprayed at a density of 20 mg m^{-2} (calculated by the Abm concentration). All the plants were placed in a standardized experimental glasshouse. The leaves of *I. batatas* in each group were collected at 1, 2, 4, 7, 10, and 14 days after spraying and used to feed *P. xylostella* for 48 h. Insect mortality was then recorded.

2.6 Biosafety assay

The maize seedling growth was tested to evaluate the phytotoxicity of Abm/GO, and the experimental steps were similar to the

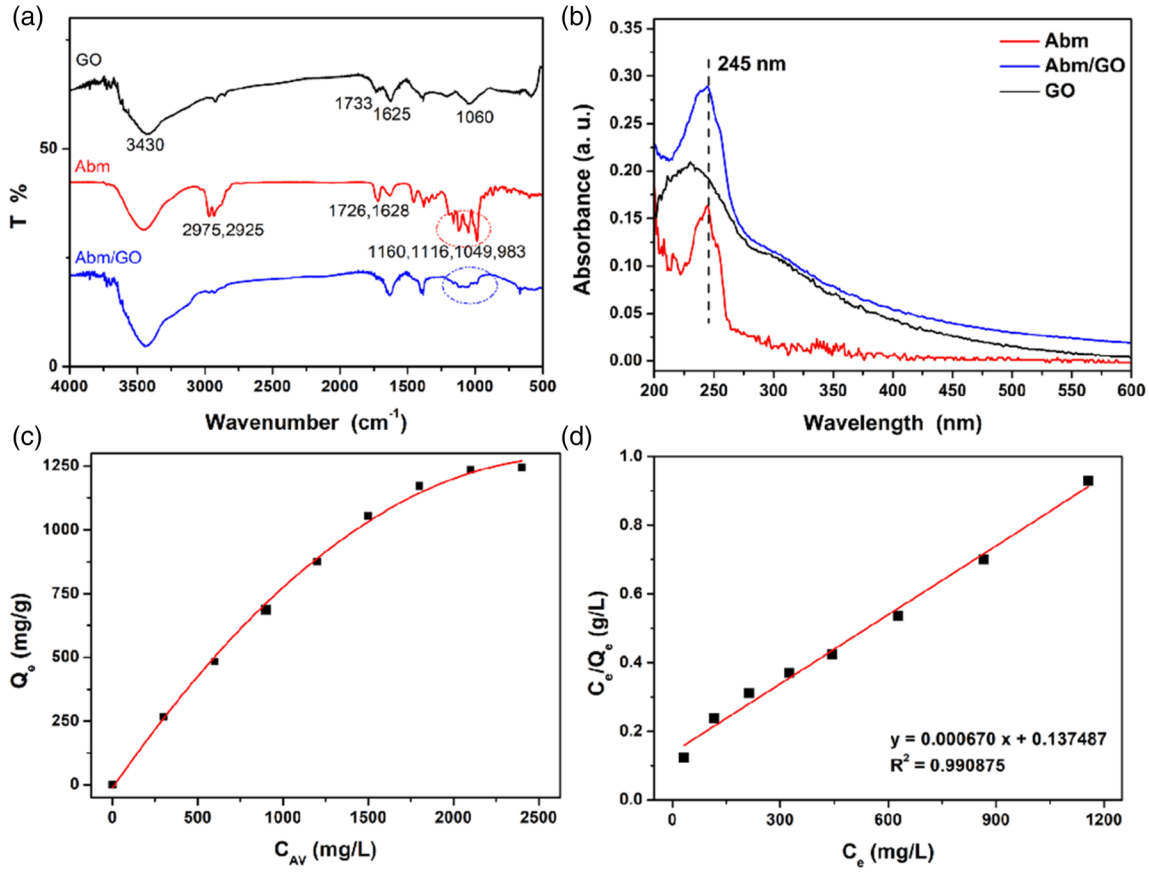

FIGURE 2. (a) FTIR spectra; (b) UV spectra of GO, Abm, and Abm/GO; (c) loading capacity of Abm on GO at different initial Abm concentrations; (D) Langmuir adsorption isotherm of Abm on GO.

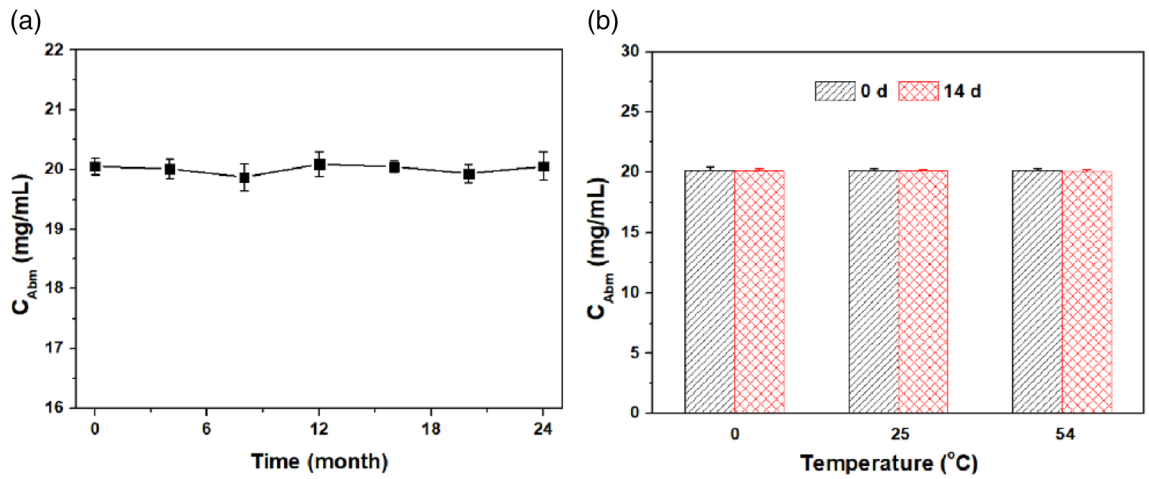

FIGURE 3. Storage stability of Abm/GO. (a) Abm concentrations during the 2-year storage period. (b) Abm concentrations before (0 day) and after (14 days) storage at different temperatures: 0, 25, and 54 °C.

previous literature.[10,12] In short: 70% ethanol was used to soak the maize seeds for 2 min, and then the seeds were rinsed with sterile water and placed in Petri dishes. Then, 5 mL Abm/GO nanoformulation was added into each dish. The maize seed generation was carried out in an artificial climate chest (25 °C, 24 h dark). After 5 days, the germination rate maize seed in each group was collected. After that, the maize seedlings were cultured for another 7 days (condition: 25 °C, 14 h light/10 h dark), and then the fresh/dried weights of aerial/root parts in each group were collected.

The cytotoxicity of Abm/GO was tested according to the method in previous literature.[8] Briefly, A549 cells were seeded into a 96-well plate (100 μL cell culture medium per well). Next, 10 μL of Abm, GO, and Abm/GO were added to the wells separately, and the cell viability of each group was tested after 2 and

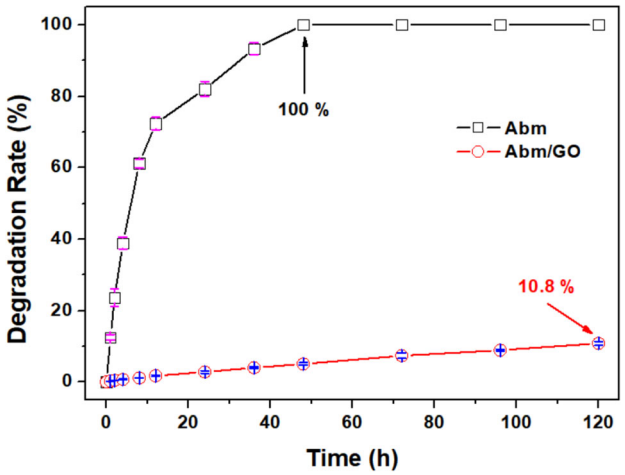

FIGURE 4. Anti-UV performance of Abm and Abm/GO nanoformulation under UV irradiation.

24 h. For the control group, 10 μL phosphate-buffered saline (PBS) was added to the wells and the cell viability was also tested after 2 and 24 h.

3 RESULTS AND DISCUSSION

3.1 Preparation and characterization of Abm/GO

As previous literature reported, GO can effectively improve the water dispersion stability of water-insoluble drugs and pesticides.[2,4,18,22,23] Abm/GO was formed by adsorption of Abm on GO nanocarrier. Compared with water-insoluble Abm, Abm/GO suspension exhibits good dispersion stability in water (Fig. 1(a) and Supporting Information Fig. S1).

SEM images were used to confirm the micromorphology of GO and Abm/GO (Figure 1(b–d)). GO exhibits a clean wrinkled surface without any impurities (Figure 1(b)). After loading with Abm, the Abm/GO nano-dispersion present is about several hundred nanometers in size (Fig. 1(c,d)). Consistent with previous studies, the use of a well-dispersed nanocarrier improved the solubility of poorly dissolved drugs or pesticides.[26,27]

The Fourier-transform infrared (FTIR) spectra of GO, Abm, and Abm/GO are shown in Fig. 2(a). The characteristic peaks at 3430 cm^{-1}, 1733 cm^{-1}, 1625 cm^{-1}, and 1060 cm^{-1} (black curve) were attributed to the stretching vibration of –OH, C = O of the carboxyl on GO, C = C in the aromatic ring skeleton, and C–O–C, respectively.[28] For the red curve in Fig. 2(a) (FTIR spectrum of Abm), the characteristic peaks at 1049–1160 cm^{-1} were attributed to the symmetric absorption of C–O–C–O–C; the characteristic peaks at 2925 and 2975 cm^{-1} were attributed to the stretching vibration of $–CH_3$; and the characteristic peak at 1726 cm^{-1} was attributed to the stretching vibration of C = O.[29] For the blue curve in Fig. 2(a), the characteristic peaks of Abm were observed, indicating that Abm was present in the Abm/GO nanoformulation. The UV spectra indicated that Abm was combined with GO (Fig. 2(b)). The maximum absorption peak at 245 nm (specific peak of Abm) occurred in the Abm/GO nanoformulation. The loading amount of Abm at different initial concentrations is shown in Fig. 2(c). We examined the adsorption isotherm of Abm on GO to further study the pesticide loading process. The experimental data were fitted with Langmuir and Freundlich adsorption isotherm models (Figs 2(d) and S1). The Langmuir model is a better fit (R^2 = 0.990875) for the adsorption of Abm on GO nanocarrier than the Freundlich model (R^2 = 0.973872). Therefore, the adsorption of Abm on GO follows a monolayer adsorption manner.[2] The maximum adsorption capacity of GO was 1492.5 mg g^{-1} according to the Langmuir model.

3.2 Stability of Abm/GO nanoformulation

We studied the stability of Abm/GO nanoformulation under various conditions. Its colloidal stability after preparation, long-term stability during 2 years of storage, stability at high or low temperatures, and stability in different types of water were tested.

3.2.1 *Colloidal stability*

The as-prepared Abm/GO nanoformulation exhibited high colloidal stability. After being left at RT for 48 h, the aqueous solution remained stable, and no flocculation or precipitation was observed (Fig. S3).

3.2.2 *Long-term storage stability*

The freshly prepared Abm/GO nanoformulation was stored in a dry, cool, and ventilated place. During the 2-year storage period, the concentration of Abm in the nanoformulation was determined every 4 months. The concentration of Abm was maintained within a relatively stable range at each time point (Fig. 3(a)). During the storage period, the Abm/GO nanoformulation was

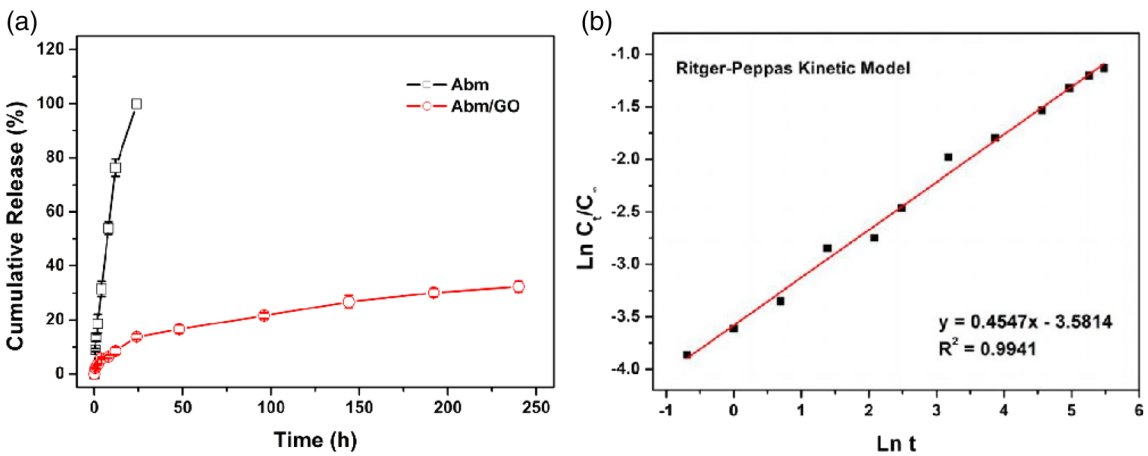

FIGURE 5. (a) The release of Abm from Abm/GO nanoformulation during the 240 h release period. (b) The kinetics of Abm release from Abm/GO nanoformulation.

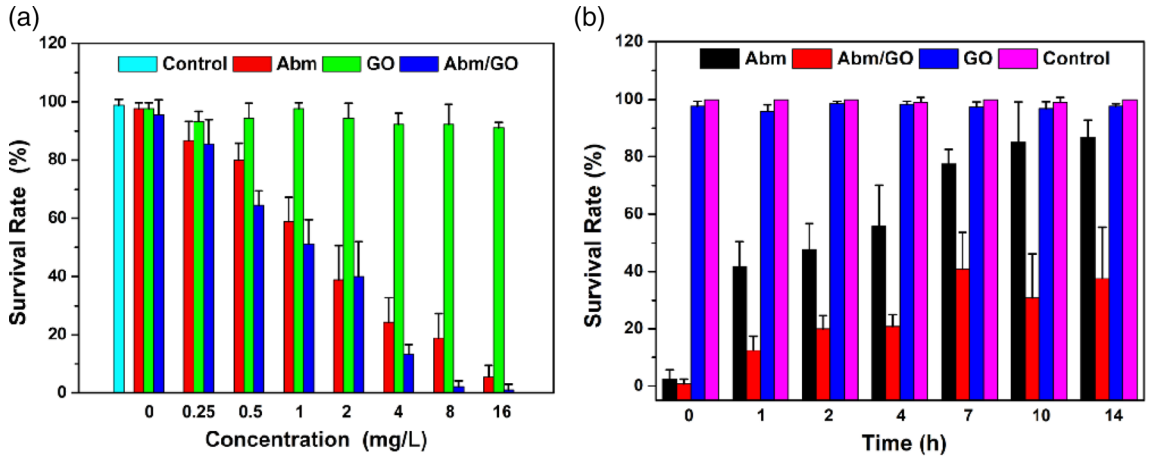

FIGURE 6. (a) The toxicity of Abm and Abm/GO nanoformulation to *Plutella xylostella* at different concentrations. (b) The pesticidal efficacy of Abm and Abm/GO nanoformulation at 0, 1, 2, 4, 7, 10, and 14 days after spraying.

TABLE 1. Results of toxicity analysis for abamectin (Abm) and abamectin-loaded graphene oxide (Abm/GO)

Sample	Toxicity regression equation	LC_{50} (mg L^{-1})	95% Confidence limit	χ^2
Abm	$y = -0.261 + 1.472x$	1.503	1.253–1.791	19.134
Abm/GO	$y = 0.003 + 1.781x$	0.996	0.844–1.164	20.709

Note: LC_{50}, median lethal concentration.

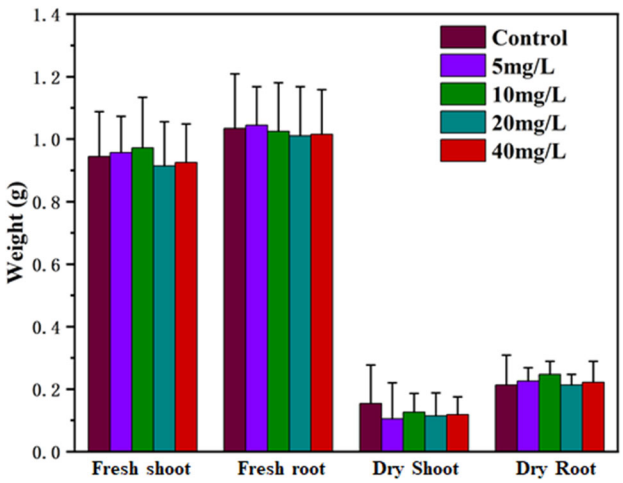

FIGURE 7. Effect of Abm/GO on the growth of maize seedlings.

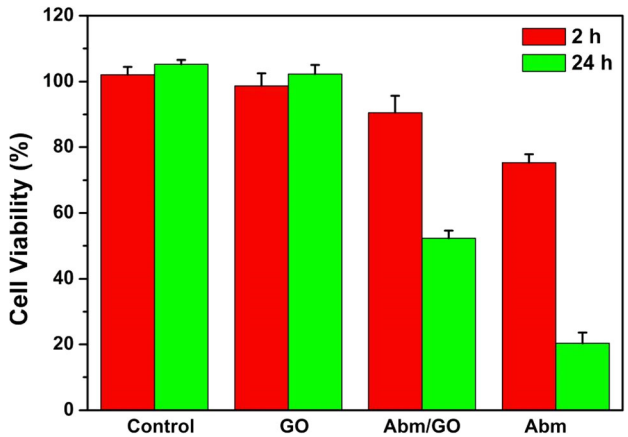

FIGURE 8. Cytotoxicity of GO, Abm/GO, and Abm against A549 cells after incubation for 2 and 24 h.

uniform and stable in terms of its visual appearance (Fig. S4**)**. The earlier findings indicate that Abm/GO nanoformulation shows high long-term storage stability.

3.2.3 Storage stability at low/high temperature

The pesticide formulation may crystallize and precipitate at low temperature, and thermolysis, caking, and volatilization can occur at high temperature; such changes can affect its pesticidal activity. Samples were stored at different temperatures for 14 days to evaluate the stability of Abm/GO nanoformulation under low/high temperatures. No precipitation or stratification occurred (Fig. S5). In addition, no significant changes in the Abm content were observed after the storage period (Fig. 3(b)).

3.2.4 Stability of Abm/GO nanoformulation in different types of water

The species and content of trace elements in water can vary, and this might have implications for the stability of pesticide formulations. For example, the local water in South China (e.g. Guangxi, Yunnan, and Guizhou), which features karst topography, often contains high concentrations of calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}). Previous studies have indicated that the presence of bivalent cations (including

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Ca^{2+} and Mg^{2+}) can deteriorate the colloidal stability of GO and result in precipitation.[30] Thus, we compared the stability of Abm/GO nanoformulation in three different types of water, including distilled water, standard hard water, and tap water from Suzhou, Nanjing, Guilin, and Guiyang. The Abm/GO nanoformulation remained stable when it was dispersed in distilled water and tap water from Suzhou and Nanjing; however, flocculation and precipitation occurred immediately following dilution of the Abm/GO nanoformulation by standard hard water and tap water from Guiyang and Guilin (Fig. S6(a)). The earlier findings indicate that the Abm/GO nanoformulation shows high stability in soft water and low stability in hard water. In light of the excellent chelation effect of EDTA-2Na on Ca^{2+} and Mg^{2+}, we added EDTA-2Na as the metal-chelator in Abm/GO nanoformulation (Figure S6(b)). After dilution with different samples, the Abm/GO nanoformulation containing EDTA-2Na remained stable in both soft water and hard water.

3.3 Anti-UV light performance

High-energy UV light can destroy the chemical structure of pesticides and reduce pesticidal activity. Abm is unstable under UV light irradiation, and its half-life is only several hours after spraying. The low photostability of Abm necessitates increased spraying frequencies and dosages, which limits its practical use.

More than 70% of Abm was lost after 12 h of UV irradiation in the free Abm group (Fig. 4). By contrast, the Abm/GO nanoformulation showed high stability, and only 10.82% of Abm was lost following 120 h of irradiation. Previous studies have indicated that nanomaterials can prevent the rapid decomposition of unstable pesticides by absorbing and reflecting high-energy UV light.[31,32] The improved stability of Abm/GO under UV light might allow spraying frequencies and dosages to be reduced.

3.4 Controlled release behavior

The initial burst release of active components is a major challenge for conventional pesticide formulations. This rapid release of active components has several disadvantages, with the most salient being a sharp reduction in activity and pesticidal efficacy. This can lead to the repeated and excessive spraying of pesticides and serious environmental pollution. The controlled release of active components is thus necessary for ensuring that pesticides can produce their intended effect without harming the environment. In our experiment, the long-term release performance of Abm was surveyed in a 30% ethanol–water system (Fig. 5(a)). The rapid release of Abm occurred during the first 2 h, and then the release rate decreased. Approximately 32.3% of Abm was released to the surrounding ethanol–water system during 240 h.

The release kinetics of Abm/GO were studied to further clarify the sustained release process of Abm from GO nanocarrier (Figure 5(b)). The release process of Abm from GO fit the Korsmeyer–Peppas model and followed a Fickian diffusion mechanism ($n < 0.43$).

3.5 Pesticidal activity assay

Figure 6(a) shows the toxicity of Abm, GO, and Abm/GO to *P. xylostella*. GO (0–16 mg mL^{-1}) exhibited negligible toxicity to *P. xylostella*; this indicates that it is a safe carrier for Abm, which shows high toxicity to lepidopteran pests, suggesting that it can have a control effect on *P. xylostella* at low concentrations. The survival rate of *P. xylostella* was below 20% when the Abm concentration was 8 mg L^{-1} (Fig. 6(a)). After loading on GO nanocarrier, the pesticidal activity of the Abm/GO nanoformulation slightly improved, which is caused by the aggregation effect of the pesticide.[2,33] The toxicity results (LC_{50} and toxicity regression equation) are listed in Table 1. The LC_{50} value of Abm/GO (0.996 mg L^{-1}) only accounts for 65% of the LC_{50} value of Abm (1.503 mg L^{-1}).

Figure 6B shows the sustained pesticidal activity of Abm and Abm/GO. The toxicity of Abm to *P. xylostella* decreased rapidly, which is caused by its burst release and poor anti-UV properties. By contrast, the Abm/GO nanoformulation exhibited significantly stronger pesticidal activity than Abm during the 14 day period. The increase in the sustained toxicity to *P. xylostella* is likely caused by the high photostability and controlled release performance of Abm/GO.

3.6 Biosafety assay

According to previous literature, the seedling growth can be used to evaluate the biosafety of nanopesticides.[10,12] As Figure 7 shows, after treating with Abm/GO nanopesticide (5–40 mg L^{-1}), the fresh/dry weights of shoot and root parts shows no significant difference to control group. The results indicates that Abm/GO has negligible toxicity to maize seedlings.

The cytotoxicity of GO, Abm/GO, and Abm against A549 cells were further studied to confirm the biosafety of the nanocarrier and nanopesticide (Fig. 8). It is obvious that GO nanocarrier possesses excellent biosafety, with no significant damage to A549 cells. Abm significantly damages A549 cells (cell viability 20.4% at 24 h). After loading on GO, the cytotoxicity of Abm/GO is lower than that of Abm, indicating that GO nanocarrier can reduce the cytotoxicity of Abm to A549 cells. This phenomenon was also found in the previous literature that nanocarriers can reduce the toxicity of pesticides to cells.[8]

4 CONCLUSIONS

We studied a GO-based nanopesticide formulation and its application in pest control. The hydrophobic pesticide Abm can be effectively loaded on GO and form nanoformulations with stable water dispersion, slow-release, and anti-UV properties. The high toxicity of Abm to *P. xylostella* is sustained in the Abm/GO nanoformulation, which showed negligible toxicity to maize seedlings and reduced the cytotoxicity of Abm to A549 cells. The future potential of GO-based applications is high in light of the industrialization potential of GO.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT

Research data are not shared.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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