Article

β-Cyclodextrin-Modified Mesoporous Silica Nanoparticles with Photo-Responsive Gatekeepers for Controlled Release of Hexaconazole

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Abstract: In the present research, photo-responsive controlled-release hexaconazole (Hex) nanoparticles (Nps) were successfully prepared with azobenzene (Azo)-modified bimodal mesoporous silica (BMMs), in which β-cyclodextrin (β-CD) was capped onto the BMMs-Azo surface via host-guest interactions (Hex@BMMs/Azo/β-CD). Scanning electron microscopy (SEM) confirmed that the nanoparticles had a spherical structure, and their average diameter determined by dynamic light scattering (DLS) was found to be 387.2 ± 3.8 nm. X-ray powder-diffraction analysis and N₂-adsorption measurements indicated that Hex was loaded into the pores of the mesoporous structure, but the structure of the mesoporous composite was not destroyed. The loading capacity of Hex@BMMs/Azo/β-CD nanoparticles for Hex was approximately 27.3%. Elemental components of the nanoparticles were characterized by X-ray photoelectron spectroscopy (XPS) and electron dispersive spectroscopy (EDS). Ultraviolet–visible-light (UV–Vis) absorption spectroscopy tests showed that the azophenyl group in BMMs-Azo undergoes effective and reversible *cis-trans* isomerization under UV–Vis irradiation. Hex@BMMs/Azo/β-CD Nps exhibited excellent light-sensitive controlled-release performance. The release of Hex was much higher under UV irradiation than that in the dark, which could be demonstrated by the bioactivity test. The nanoparticles also displayed excellent pH-responsive properties, and the sustained-release curves were described by the Ritger–Peppas release kinetic model. BMMs nanocarriers had good biological safety and provided a basis for the development of sustainable agriculture in the future.

Keywords: nanoparticle; hexaconazole; photo-responsibility; mesoporous silicas; controlled-release

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1. Introduction

Pesticides are considered the most effective way to control pests and diseases in farmland, and improve agricultural productivity [1]. Currently, traditionally formulated pesticides are dominant in China. However, more than 90% of the pesticides cannot accurately act on specific targets, and their effective utilization rate is low due to poor water dispersibility, dust drift, volatilization, evaporation, and degradation, which has led to serious environmental pollution [2–4]. With the rise of nanotechnology in the agricultural field, slow- and controlled-release pesticides have been rapidly developed [5–7]. Environmental stimulus-responsive systems, such as pH- [8–10], redox- [11,12], temperature- [13,14], enzyme- [15,16], and ultraviolet (UV)-light-responsive [17,18] materials have been developed for triggered pesticide release, which can improve the utilization rate of pesticides and reduce environmental pollution.

Among the various stimulative-responsive systems, light-responsive materials are particularly attractive and more achievable in practical applications [19,20]. UV light, as an external stimulative factor, is widely used in intelligent nano slow/controlled-release

systems, due to its good controllability, remote control, and clean energy. Unlike the traditional “gatekeeper” system, a light-response system is reversible [21]. Pesticides can be accurately released under the illumination of a specific light source at the specified location.

Azobenzene (Azo) is a novel UV-light-responsive molecule, and shows *trans/cis*-isomers. It has been reported that *trans*- and *cis*-isomers of azobenzene (Azo) can be reversibly converted between each other. *Trans-to-cis* isomerization can occur under UV-light (300–400 nm) irradiation, while *cis-to-trans* isomerization can be induced by visible light (435 nm) or heating [22,23]. The host–guest interaction of *trans*-Azo and β -cyclodextrin (β -CD) was well recognized by hydrophobic and van der Waals forces, while *cis*-Azo cannot be, which is fully reversible. No side reaction or decomposition after long-term irradiation occurs, which is one of the ideal photochemical reactions in the materials application field [12,24].

Bimodal mesoporous silica (BMMs) with a double-channel structure was synthesized by the sol–gel method [25,26]. Compared with traditional silicon mesoporous materials, the large pore volume of BMMs can significantly improve the loading capacity of pesticides. BMMs are widely used as drug carriers due to their adjustable structure, good stability, excellent biocompatibility, and low toxicity [27,28]. Hexaconazole (Hex) is a triazole fungicide with broad-spectrum protection and is used as a treatment for plant diseases caused by fungi [29,30]. However, the usage of Hex is limited due to its poor water solubility and low utilization efficiency. In addition, Hex has a long residual life in the environment and is very difficult to degrade in the agricultural soil and water environment. The residual Hex reduces soil and water quality, and causes irreversible harm and toxicity to soil microorganisms and animals and plants in water [31,32]. Therefore, it is desirable to design and prepare an intelligent, controlled-release system to improve the utilization rate and biological safety of Hex.

Herein, aminoazobenzene modified with a silane coupling agent was grafted onto the surface of BMMs, and Hex was encapsulated in the mesopore surface through physical adsorption. A host–guest supramolecular valve was formed after *trans*-Azo was recognized by β -cyclodextrin (β -CD), which was further wrapped on a BMMs carrier to prepare the light-responsive pesticide-release system (Hex@BMMs/Azo/ β -CD). The procedure is shown in Figure 1. The physico-chemical characteristics, release behavior, and biological activity of nanoparticles (Nps) were investigated. This study provides a new method of improving the utilization efficiency of pesticides and reducing environmental pollution.

Figure 1. Schematic diagram for the preparation of Hex@BMMs/Azo/ β -CD and its light-responsive release mechanism.

2. Materials and Methods

2.1. Materials

Hexaconazole (95%) was purchased from Beijing Jinyue Biotechnology Co., Ltd. (Beijing, China). P-aminoazobenzene, 3-isocyanatopropyltriethoxysilane, and β -cyclodextrin (β -CD) were supplied by Sigma Aldrich (Saint Louis, MO, USA). Cetyltrimethyl-ammonium

bromide (CTAB), tetraethyl orthosilicate (TEOS), and ammonia (25%, analytical reagent grade) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Anhydrous tetrahydrofuran (THF) was purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). N-hexane was purchased from the Beijing Chemical Plant (Beijing, China). Deionized water was obtained with a Milli-Q water purification system (Millipore Co., Burlington, MA, USA) and used for all reactions and treatment processes in the laboratory.

2.2. Preparation of BMMs

CTAB (1.0448 g) was dissolved in 41.6 mL of distilled water in a flask and TEOS (3.2 mL) was slowly added dropwise to the solution. Subsequently, 0.96 mL of ammonia was quickly added into the flask with continued stirring until the solution turned into a white gel. The white gel was then suction-filtered, washed with distilled water, and dried at 100 °C for 8 h. The obtained product was heated to 550 °C at 5 °C/min for 5 h to remove CTAB to attain BMMs.

2.3. Modification of Azo-Si

Isocyanate propyltriethoxysilane (1.0255 g), p-aminoazobenzene (0.794 g), and anhydrous tetrahydrofuran (THF, 7.5 mL) were added to a three-necked flask. The reaction mixture was stirred at 70 °C for 10 h under a nitrogen atmosphere. To obtain Azo-Si, 40 mL of nhexane was used as a precipitator. After THF was removed by rotary evaporation, the solid precipitate was frozen overnight at −20 °C and collected by vacuum filtration. The product was washed with n-hexane and dried at 35 °C for 8 h to yield orange needle-like crystals.

2.4. Preparation of BMMs/Azo Nps

After drying at 110 °C for 2 h, 300 mg of BMMs were dispersed in 30 mL of anhydrous methanol and sonicated for 10 min. Next, 30 mg of Azo was added into the BMMs solution with nitrogen protection. The final reaction mixture was stirred at 65 °C for 12 h, and then filtered. The resulting yellow solid precipitate was washed with THF and methanol, and dried in a vacuum at 35 °C for 10 h to provide the product (BMMs/Azo).

2.5. Preparation of Hex@BMMs/Azo Nps

BMMs/Azo (100 mg) and hexaconazole (20 mg/mL) were added to a flask, and the resulting solution was stirred at 35 °C for 24 h, centrifuged at a speed of 5000 rpm, washed with methanol three times, and dried at 35 °C for 8 h. The obtained products were denoted Hex@BMMs/Azo Nps.

2.6. Preparation of Hex@BMMs/Azo/β-CD Nps

Hex@BMMs/Azo (100 mg) was immersed in phosphate buffer solution (PBS, pH = 7.4), and then 50 mg of β-CD was added. The mixture was placed in the magnetic stirrer for 24 h. Next, the solution was centrifuged for 8 min at 5000 rpm, rinsed with PBS three times, and dried at 35 °C for 8 h to obtain H@BMMs/Azo/β-CD Nps.

2.7. Azo Loading Capacity

Nps were collected by centrifugation, and the concentrations of Azo were detected by high-performance liquid chromatography (HPLC, 1200 Series, Agilent Corp., Wilmington, DE, USA) with a C18 bonded reverse-phase column. The mobile phase of the methanol–water mix (70:30, *v/v*) was programmed with a flow rate of 1.0 mL/min at 210 nm with a UV detector. The injection volume was 10 µL and the retention time was 12 min at 30 °C. The loading capacities (LC) were calculated as follows:

$$LC(\%) = \frac{C_{\text{loading}} \times V_{\text{loading}} - C_{\text{residual}} V_{\text{residual}} - C_1 V_1 - C_2 V_2 - C_3 V_3}{m}$$

where LC is the Hex loading capacity (%), m is the total amount of Nps (mg), $C_{loading}$, $C_{residual}$, and C_1 , C_2 , C_3 are the Hex concentrations of the original loading, residual, and eluted solutions for the first, second, and third time respectively (mg/mL) and $V_{loading}$, $V_{residual}$, V_1 , V_2 , and V_3 are the volumes of the original loading, residual, and eluted solutions for the first, second, and third time, respectively (mL).

2.8. Characterization of Hex@BMMs/Azo/ β -CD Nps

The morphologies and the electron dispersive spectroscopy (EDS) maps of nanoparticles were observed by scanning electron microscopy (SEM) (Zeiss, Oberkochen, Germany). Particle size, polydispersity index (PDI), and zeta potential were analyzed by a dynamic light scattering (DLS) detector (Malvern Instruments Ltd., Malvern, UK). The obtained nanoparticles were suspended in deionized water at pH 7.0 ± 0.1 .

The structure and interaction analyses of samples were conducted using X-ray powder diffraction (XRPD, D8 ADVANCE X, Bruker/AXS, Inc., Karlsruhe, Germany) and Fourier-transform infrared spectroscopy (FTIR, Nicolet Nexus 470, Nicolet Instrument Corp., Concord, CA, USA). The nitrogen adsorption–desorption isotherms were determined using an Autosorb-iQ pore analyzer (Quantachrome, Boynton Beach, FL, USA). The surface areas, pore-size distributions, and pore volumes were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda methods. Thermogravimetric analyses (TGA) were carried out by a thermal analyzer (PerkinElmer, Waltham, MA, USA). Elements were analyzed by using X-ray photoelectron spectroscopy (ESCALAB 250Xi, Thermo Fisher Scientific, Waltham, MA, USA). Photoisomerization of azophenyl groups was measured using a UV–Vis spectrophotometer (UV-2600 Shimadzu Co., Ltd., Tokyo, Japan) at wavelength of 250–600 nm.

2.9. Adhesion Test

The contact angles of Hex@BMMs/Azo/ β -CD Nps on leaves were measured using a contact-angle apparatus (JC2000D2M, Powereach Ltd., Shanghai, China). Technical Hex, Hex@BMMs/Azo, and deionized water were used as controls. Two-week-old tomato leaves were selected as model plants, and carefully washed with deionized water. After the leaves were air-dried, Hex@BMMs/Azo/ β -CD dispersion, Hex@BMMs/Azo dispersion, technical Hex solution, and water were dropped onto the leaves on a glass slide, respectively. Images of the droplet on the leaf surface were taken, and the corresponding contact angles were detected using a contact-angle meter (Dataphysics-TP50, DataPhysics Instruments, Filderstadt, Germany).

2.10. Release Behavior of Hex@BMMs/Azo/ β -CD Nps

Hex@BMMs/Azo/ β -CD Nps (15 mg) were suspended in 3 mL of methanol–water solvents (50:50, v/v). The suspension was transferred to a dialysis bag (molecular cutoff capacity 3500 kDa) and then put into flasks with 60 mL of methanol/ H_2O (1:1, v/v) solution. The release medium was then shaken at a speed of 100 rpm at 37 °C and irradiated continuously with 150, 300, and 500 W UV lamps (365 nm). Five milliliters of the sample were collected at fixed time intervals, and the same amount of fresh medium was replenished in the system. Hex contents were measured by HPLC, and the release ratio of Hex from the nano-delivery sample was calculated.

To investigate the pH sensitivity of Hex, the release of Hex from Nps at different pH levels (4.0, 7.0, and 9.0) under 300 W, 365 nm UV light was measured using the same method as described above. The cumulative release rate of Hex in Nps was then calculated using the following equation:

$$Q(\%) = \frac{V_0 \times C_T + V \times \sum_{N=1}^{T-1} C}{W} \times 100\%$$

where W is the total mass concentration of Hex in the Pickering emulsion, V_0 is the volume of the sustained-release solution, and V is the volume of the slow-release solution taken at

a specific interval time. C_T and C are the concentrations of T and N samples, respectively. The release kinetics of Hex from Hex@BMMs/Azo/ β -CD Nps was separately investigated using four mathematical models, namely the pseudo-zero-order equation, pseudo-first-order equation, Higuchi model, and Ritger–Peppas model.

2.11. Bioactivity Test

Hex@BMMs/Azo/ β -CD Nps (40 mg) were dispersed in 8 mL of sterile distilled water with 0.1% Tween 80, and then 4 mL of the aqueous suspension was exposed to UV light (365 nm) under stirring at 25 °C. Technical Hex solution, non-irradiated Nps, and distilled water were used as controls. *Rhizoctonia solani* cakes (5 mm in diameter) were placed into the center of potato dextrose agar (PDA) petri dishes with Nps (50, 100, and 200 mg/L). The dishes were incubated for 14 days at 28 °C and each colony diameter was measured every 24 h. The relative inhibition rates against the fungi were calculated according to the colony diameters.

2.12. Biosafety Evaluation

Human embryo skin fibroblast cells (CCC-ESF-1 cells) were seeded in 96-well plates in triplicate and cultured in DMEM medium supplemented with 10% FBS and 1% penicillin/streptomycin at 37 °C for 24 h. Then, CCC-ESF-1 cells were treated with different concentrations (0, 31.25, 62.5, 125, 250, and 500 μ g/mL) of BMMs/Azo/ β -CD for 24 h, and the cell viability was evaluated using a cell counting kit (CCK8, Dojindo, Japan). *E. coli* was cultured in LB culture medium with different concentrations (0, 31.25, 62.5, 125, 250, and 500 μ g/mL) of BMMs/Azo/ β -CD Nps at 37 °C for 24 h, and the *E. coli* concentrations were determined by UV–Vis absorptiometry at 600 nm. All tests were carried out at least in triplicate.

2.13. Data Analysis

The data were analyzed using SPSS 20.0 statistical analysis software (SPSS, Chicago, IL, USA). All experiments were performed three times. Statistical significance was determined as $p < 0.05$.

3. Results and Discussion

3.1. Morphological Observations

Figure 2 shows SEM images of BMMs, BMMs/Azo, Hex@BMMs/Azo, and Hex@BMMs/Azo/ β -CD. The Nps had spherical shapes and were not destroyed due to the encapsulations of Hex, Azo, and β -CD. The particle sizes, zeta-potential values, and PDIs were further measured by DLS analysis (Table 1). After Hex was loaded and the mesopore surface was grafted with Azo/ β -CD, the average particle size of Nps increased from 269.8 ± 6.8 nm (BMMs) to 387.2 ± 3.8 nm (Hex@BMMs/Azo/ β -CD). The highest PDI value, i.e., 0.153 ± 0.02 , indicated that the Nps had better mono-dispersity and stability. Owing to the presence of -OH on the surface of the mesoporous silica, the zeta potential of BMMs was -13.93 ± 1.57 mV. After the modification of azobenzene, the zeta-potential value of BMMs/Azo increased to -8.42 ± 1.71 mV because of the neutralization of the amino groups present on the surface of the modified azobenzene. After loading Hex, the zeta-potential value of Hex@BMMs/Azo/ β -CD Nps decreased to -16.97 ± 0.95 mV, due to the negative charge of Hex, indicating that the pesticide Hex was successfully loaded into the Nps.

3.2. Structure and Interaction Analysis

The structure of the Nps was also tested by XRPD and the results are shown in Figure 3A. BMMs had an obvious (100) crystal-plane diffraction peak at $2\theta = 1.86^\circ$, which is the characteristic peak of BMMs, indicating that it had a highly ordered, double-hole structure. After grafting the modified azobenzene, BMMs/Azo exhibited the same (100) crystal-plane diffraction peak, indicating that the BMMs/Azo Nps still maintained an ordered mesoporous structure. After Hex was loaded into the BMMs, the peak intensity

decreased from 1.99° to 1.97° , and the d value moved from 44.09 to 44.85 nm. This is because the Hex in the channel reduced the scattering between the mesoporous channels and the pore wall. The strength of the XRPD peaks ($2\theta = 2^\circ$) of the β -CD-coated Hex@BMMs/Azo Nps decreased significantly, and the shape broadened, showing that the mesoporous structure was affected, and β -CD was successfully encapsulated into the system.

Figure 2. SEM images of different nanoparticles. (A-a,A-b) BMMs, (B-a,B-b) BMMs/Azo, (C-a,C-b) Hex@BMMs/Azo, (D-a,D-b) Hex@BMMs/Azo/ β -CD.

Table 1. The mean diameters and distributions of nanoparticles based on BMMs.

Nps	Mean Size (nm)	PDI	Zeta Potential (mV)
BMMs	269.8 ± 6.8	0.062 ± 0.03	-13.93 ± 1.57
BMMs/Azo	367.4 ± 3.3	0.144 ± 0.01	-8.42 ± 1.71
Hex@BMMs/Azo	553.4 ± 4.1	0.123 ± 0.04	-16.77 ± 1.60
Hex@BMMs/Azo/ β -CD	387.2 ± 3.8	0.153 ± 0.02	-16.97 ± 0.95

Figure 3. XRPD patterns (A), FTIR (B), N₂ adsorption/desorption isotherms (C), and BET surface areas and pore volumes (D) of BMMs, BMMs/Azo, Hex@BMMs/Azo, and Hex@BMMs/Azo/β-CD.

The FTIR spectra of BMMs, BMMs/Azo, Hex@BMMs/Azo, and Hex@BMMs/Azo/β-CD were determined to evaluate the Nps' structural changes with various functional groups (Figure 3B). BMMs exhibited three characteristic peaks at 1082, 780, and 810 cm^{-1} that were anti-symmetrical and symmetrical stretching-vibration peaks of Si–O–Si groups. The absorption bands at 1644 and 1419 cm^{-1} were the stretching-vibration peaks of the –CONH– group and the vibration peaks of the C=C group in the aromatic ring respectively, indicating that the modified Azo was successfully grafted onto the surface of BMMs. The characteristic absorption peak of Hex at 3227 cm^{-1} and the absorption peak with increasing intensity at 1082 cm^{-1} suggested that the pesticide Hex was adsorbed in the pores of mesoporous silica through van der Waals forces and hydrogen bonds. The loading content of Hex in Nps was also tested by HPLC, and the loading ratios of Hex (27.3%) in Hex@BMMs/Azo/β-CD were obtained. To investigate the porosity, pore surface areas, and pore volumes of the nano-delivery system, nitrogen adsorption/desorption measurements were performed. As shown in Figure 4C, the N₂ adsorption/desorption isotherms of BMMs, BMMs/Azo, Hex@BMMs/Azo, and Hex@BMMs/Azo/β-CD belong to the Langmuir IV isotherm with two hysteresis loops. The first hysteresis loop, at $0.2 < P/P_0 < 0.4$, rose rapidly owing to monolayer adsorption of nitrogen. The second hysteresis loop appeared at $P/P_0 = 0.8–0.95$, indicating that the capillary tube of the particle accumulation pore had been condensed. The corresponding pore-size distribution revealed that the Nps had a dual-model structure and two pore sizes (Figure 3C, inset). After the loading of Hex molecules and the modification of Azo/β-CD in BMMs, the shape of the adsorption isotherm remained basically unchanged compared with BMMs, indicating that the mesoporous structure of the sample still existed. However, the BET specific surface area and pore volume of Hex@BMMs/Azo/β-CD significantly decreased, implying that Hex molecules occupied a significant number of pores and surface sites of Nps (Figure 3D). These observations further suggested that the modified Azo interacted with Si–OH groups, and that Hex was successfully loaded into Hex@BMMs/Azo/β-CD Nps.

Figure 4. TG (A), XPS (B), and element distributions (C) of Hex@BMMs/AZO/β-CD and the control samples.

The loading rate of the Hex@BMMs/Azo/β-CD Nps was determined by TG analysis. The TG curves of nanoparticles are shown in Figure 4A. The mass loss of all samples mainly included two stages. The first stage was the evaporation of water in the samples before 150 °C, and the second weight-loss peak occurred at the stage from 150 to 800 °C due to the decomposition of organic components incorporated in the samples. The weight losses of BMMs/Azo and Hex@BMMs/Azo were 8.1% and 32.8%, respectively. Hence, the loading rate of Hex@BMMs/Azo was about 24.7%, which was approximately consistent with the result of HPLC. After β-CD was grafted to the surface of Hex@BMMs/Azo Nps, the weight loss was 39.5%, proving that Hex was successfully loaded into Azo-functionalized BMMs and β-CD played a good encapsulation role.

To analyze the chemical elements on the surface of nanoparticles, the samples were characterized by XPS. As shown in Figure 4B, the surface of BMMs nanoparticles mainly contains two elements, Si and O. The binding energies of approximately 533.08 and 104.06 eV belong to O1s and Si2p, respectively. The weak emerging signal at 285.08 eV was attributed to C1s, which was a residual component after the calcination of the CTAB template. In the BMMs/AZO spectrum, the C1s peak was more intense than that of BMMs and a new signal of N1s was observed at the binding energy of 401.08 eV, confirming that Azo was successfully modified on the surface of BMMs. Furthermore, a new peak of Cl2p appeared at 201.08 eV in the spectrum of Hex@BMMs/Azo, compared with BMMs/Azo, indicating that BMMs/Azo nanoparticles were successfully loaded with Hex. The element components of Hex@BMMs/Azo/β-CD were completely consistent with those of Hex@BMMs/Azo. Due to the coating of β-CD, the thickness of the surface of Hex@BMMs/Azo increased, resulting in the weakening of the absorption peak intensity of Hex@BMMs/Azo/β-CD nanoparticles. In addition, the result of EDS analysis (Figure 4C)

showed that the elements of Si, O, C, N, and Cl were all distributed in Hex@BMMs/Azo/ β -CD, which further proved the successful preparation of the nano-pesticide system.

3.3. Foliage Adhesion of Hex

Adhesion experiments were conducted to prove that the Hex@BMMs/Azo/ β -CD nano-delivery system had better adhesion behavior on the leaf surfaces. As shown in Figure 5, the contact-angle values of Hex@BMMs/Azo Nps and Hex@BMMs/Azo/ β -CD Nps were $83.89^\circ \pm 0.36^\circ$ and $71.64^\circ \pm 0.41^\circ$ respectively, which were obviously lower than those of Hex technical solution ($103.62^\circ \pm 0.37^\circ$) and deionized water ($105.57^\circ \pm 0.48^\circ$). The data showed that Azo/ β -CD-coated Hex@BMMs microcapsules exhibited excellent adhesion properties. Compared with deionized water and technical Hex, the contact angles of the Nps were reduced because the hydroxyl groups on the surface of BMMs increased the infiltration of the nano-delivery system on the leaf surface. The smaller contact angle of Hex@BMMs/Azo/ β -CD Nps was due to the properties of β -CD, including internal hydrophobicity and external hydrophilicity. After mesoporous silica was modified by β -CD, the hydrophilicity of the silica surface increased and the contact angle decreased, which improved the water solubility of the Nps and the adhesion of Nps on leaves.

Figure 5. The contact angles of Hex@BMMs/Azo (A), Hex@BMMs/Azo/ β -CD (B), technical Hex (C), and deionized water (D).

3.4. Photo-Responsive Property

To verify that β -CD could self-assemble with BMMs/Azo to form a gatekeeper for the controlled-release of pesticide, we detected the UV absorption spectra of BMMs, BMMs/Azo, and BMMs/Azo/ β -CD under UV irradiation. As shown in Figure 6A, compared with BMMs, an obvious UV absorption peak appeared at 357 nm after the modification of Azo, indicating that Azo was successfully grafted on the surface of BMMs. When β -CD was capped onto the nanoparticles' surface, the UV peak intensity was higher than that of BMMs/Azo. This was mainly because the electron cloud density of the Azo-conjugated system was interfered by the higher electron cloud in the inner cavity of β -CD molecules, resulting in the decrease of electron transition energy and the increase of absorption intensity of the conjugated system, which led to the enhancement of BMMs/Azo/ β -CD absorption spectrum intensity.

Figure 6. UV–Vis spectra of BMMs/Azo/β-CD and control samples (A). UV–Vis spectra of Azo after different radiation: UV (365 nm) light radiation for 0, 30, and 60 min (B), Vis (450 nm) light irradiation for 0, 30, 60, 90, 120, 150, and 180 min after UV irradiation (120 min) (C).

We further investigated the effect of light on the *trans/cis*-isomers of Azo molecules. The UV absorption spectra of BMMs, BMMs/Azo, and BMMs/Azo/β-CD nanoparticles were detected by UV–Vis spectroscopy. After nanoparticles were radiated by UV light, the peak at 357 nm decreased with increasing time from 0 to 60 min (Figure 6B), indicating that the UV light could induce *trans-cis* transformation of Azo molecules. Under the following Vis light radiation, the peak intensities showed contrasting trends (Figure 6C), suggesting that the Vis light radiation could induce *cis-trans* transformation of Azo molecules. Especially from 90 to 120 min, a significant transition appeared in the nano-system, implying that *cis*-Azo structures were mostly converted to *trans*-Azo structures under the irradiation of visible light, and the detached β-CD recombined with BMMs/Azo again. As a result, Azo in BMMs/Azo/β-CD Nps exhibited *trans-cis* reversible photoisomerization, which could be mutually transformed from a *trans* structure to a *cis* structure under the alternating irradiation of UV–Vis light, which was consistent with previous reports [22,33]. In addition, BMMs-Azo Nps were repeatedly irradiated many times, and no “fatigue” to light was observed, indicating that the nanomaterial had good reversible light-responsive capability.

3.5. Release Behavior

3.5.1. Effect of Light Intensity

To investigate the controlled-release performance of Hex from Hex@BMMs-Azo-CD under UV light, Hex@BMMs-Azo-CD Nps were irradiated under different UV-light intensities (150, 300, and 500 W at 365 nm). As shown in Figure 7A, the release of Hex from the microcapsules under UV irradiation was faster than that in darkness. This was because the Hex@BMMs-Azo-CD Nps were endowed with irreversible “gatekeeper” systems, and Azo underwent *trans-* to *cis*-isomerization under UV irradiation. The “cap” of the pesticide-carrying non-complex that blocked the mesopores was opened, and Hex molecules were released from the pores, indicating that the nano-pesticide delivery system responded to light stimulation. Compared with the control with a release rate of only 6.37% in darkness, Hex was released rapidly from the Nps within 100 min of illumination. After 360 min, the release ratios of Hex reached 41.5%, 58.3%, and 79.0% at light intensities of 150, 300, and 500 W, respectively. In addition, the Azo-modified BMMs carrier was more sensitive to UV light with increasing light intensity, and the Hex-release rate was obviously increased, which further showed that UV light was the dominant driving force for Hex release. In short, these results demonstrated that Hex could be released from Hex@BMMs-Azo-CD Nps via stimulation by UV light.

3.5.2. Effect of pH

The release behaviors of Hex@BMMs-Azo-CD Nps were investigated at different pH values (4.0, 7.0, and 9.0). The sustained-release curves of pesticide at various pH values are shown in Figure 7B. The cumulative release rate gradually increased as the pH value

decreased. At pH 4, the Hex-release rate reached 66.58% at 360 min. After 360 min, the release rate of Hex@BMMs-Azo-CD Nps at pH 4 was 66.9%, and those at pH 7 and pH 9 were 58.3% and 40.4%, respectively. This was mainly due to the grafting of β -CD on the surface of the Nps. CD is relatively stable under alkaline and neutral conditions, but is easily hydrolyzed under acidic conditions. After the sealed “cap” was opened by hydrolysis, Hex molecules were easily released from the mesopores. In addition, excessive hydrogen ions in the acid solution will be added to the N=N bond of azobenzene, resulting in a pH response.

Figure 7. Cumulative release curves with different intensity UV light (A) and different pH (B), and kinetic fitting models of Hex@BMMs/Azo/ β -CD nanoparticles (C). Error bars represent standard deviation from the mean ($n = 3$).

3.5.3. Release Kinetics Analysis

To further elucidate the effect of pH on the mechanism of Hex sustained release from Hex@BMMs-Azo-CD NPs, we studied the release kinetics using the zero-order kinetics model, first-order kinetics model, Higuchi kinetics model, and Ritger-Peppas kinetics model (Figure 7C). Table 2 presents the values of parameters and the regression coefficients (R^2).

Table 2. Release parameters of HEX at different pH values.

pH	Fitting Methods	Kinetic Equation	Determination Coefficient, R^2
4.0	Zero-order fitting	$Q = 0.1176t + 29.65$	0.8576
	First-order fitting	$Q = 59.58(1 - e^{-0.0224t})$	0.9098
	Higuchi fitting	$Q = 2.79t^{1/2} + 16.425$	0.9577
	Ritger–Peppas fitting	$Q = 11.45x^{n_1}$	0.9827
7.0	Zero-order fitting	$Q = 0.1326t + 18.64$	0.8392
	First-order fitting	$Q = 56.74(1 - e^{-0.0129t})$	0.9899
	Higuchi fitting	$Q = 3.17t^{1/2} + 3.596$	0.9457
	Ritger–Peppas fitting	$Q = 5.09x^{n_2}$	0.9509
9.0	Zero-order fitting	$Q = 0.0914t + 12.93$	0.8873
	First-order fitting	$Q = 39.36(1 - e^{-0.0125t})$	0.9743
	Higuchi fitting	$Q = 2.14t^{1/2} + 2.879$	0.9687
	Ritger–Peppas fitting	$Q = 3.52x^{n_3}$	0.9789

Note: Q is the fractional release of pesticide, t is the elapsed time, R^2 is the high value of the linear regression coefficient, and n is the release exponent, where n_1 , n_2 , and n_3 are 0.308, 0.426, and 0.425, respectively.

Regardless of acidic or alkaline conditions, the R^2 value of the Ritger–Peppas kinetic equation was higher than those of the other three mathematical models, indicating that the Ritger–Peppas kinetic model was more suitable for the release behavior of Hex. The values of n in acidic and alkaline environments were 0.308 and 0.425 respectively, and both values, which were lower than 0.45, proved that the Hex release in Hex@BMMs/Azo/ β -CD mainly followed Fick diffusion, and the concentration was the main influencing factor in the slow-release process. However, under neutral conditions, the R^2 value of the first-order kinetic equation was the highest, and the release of Hex conforms to the first-order kinetic model, implying that the release of Hex was closely related to concentration.

3.6. Bioactivity Test

Figure 8 shows the bioactivity of Hex@BMMs/Azo/ β -CD plotted against concentrations of *Rhizoctonia solani* ranging from 50 to 200 mg/L. Compared with the negative control, the inhibition rates were 40.3% (non-irradiated Nps), 60.1% (irradiated Nps), and 56.8% (technical Hex) respectively, at the Hex-as-an-active-ingredient concentration of 50 mg/L at 14 days, due to the sustained release of Hex in the nano-delivery systems. In addition, the control efficiencies of UV-irradiated samples were significantly higher than those of non-UV-irradiated samples and technical controls, indicating that UV irradiation significantly improved the release of Hex in the nano-delivery systems. This result is consistent with previous reports [23,34]. In short, the UV-stimuli-responsive Nps exhibited a better and more sustained antibacterial activity against *Rhizoctonia solani* than technical Hex.

Figure 8. Digital images (A) and inhibitory rates (B) of Hex@BMMs/Azo/ β -CD nanoparticles against *Rhizoctonia solani* at 14 days.

3.7. Biosafety Evaluation

To further evaluate the biological safety of nanocarriers, the toxicological effects of different concentrations of BMMs/Azo/ β -CD on CCC-ESF-1 cells and *E. coli* were studied. Figure 9 shows that different concentrations of BMMs/Azo/ β -CD Nps had little influence on the growth and metabolism of CCC-ESF-1 cells and *E. coli*, indicating that an Azo-modified nano-pesticide loading system had excellent biological safety.

Figure 9. Biosafety evaluation of different concentrations of BMMs/Azo: (A) *Escherichia coli* suspension OD₆₀₀, (B) photograph of *Escherichia coli* colony, (C) CCC-ESF-1 cell survival rate, and (D) photograph of CCC-ESF-1 cell. (a) Control, (b) 31.25 µg/mL, (c) 62.55 µg/mL, (d) 125 µg/mL, (e) 250 µg/mL, and (f) 500 µg/mL.

4. Conclusions

In this work, we prepared a novel UV-responsive nano-pesticide delivery system by the sol–gel method. Azo was modified and grafted with BMMs, and then the fungicide Hex was loaded into mesoporous silica by adsorption. The Hex@BMMs/Azo/ β -CD Nps had a uniformly spherical morphology and good dispersibility in water. The nanocomplex showed excellent photo-responsive controlled-release performance owing to the strong host–guest complex between the *trans*-Azo and β -CD, which was used to control Hex release from BMMs under UV–Vis irradiation. In addition, the release of Hex in Nps was promoted in an acidic environment by varying the pH of the structure. The Ritger–Peppas kinetic model was a better fit for the release behavior of Hex. The carrier displayed good adhesion on leaf surfaces, and was biologically benign. The sustained fungicidal efficacy against *Rhizoctonia solani* indicated that Hex@BMMs/Azo/ β -CD nanoparticles could effectively improve the utilization of Hex and decrease pesticide residue. Therefore, this work provides a promising approach to reduce the risk to the environment, and promote the development of green agriculture in the future.

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