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Adhesive Polydopamine Coated Avermectin Microcapsules for Prolonging Foliar Pesticide Retention

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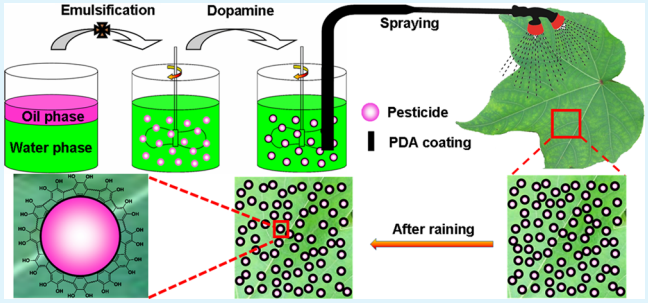
Supporting Information

ABSTRACT: In this work, we report a conceptual strategy for prolonging foliar pesticide retention by using an adhesive polydopamine (PDA) microcapsule to encapsulate avermectin, thereby minimizing its volatilization and improving its residence time on crop surfaces. Polydopamine coated avermectin (Av@PDA) microcapsules were prepared by emulsion interfacial-polymerization and characterized by Fourier transform infrared spectroscopy, energy dispersive X-ray spectroscopy, field-emission scanning electron microscope, and transmission electron microscopy. The *in situ* synthesis route confers Av@PDA microcapsules with remarkable avermectin loading ability of up to 66.5% (w/w). Kinetic study of avermectin release demonstrated that Av@PDA microcapsules exhibit sustained- and controlled-release properties. The adhesive property of Av@PDA microcapsules on different surfaces was verified by a comparative study between Av@PDA and passivated Av@SiO_2 and Av@PDA@SiO_2 capsules with silica shell. Moreover, PDA shell could effectively shield UV irradiation and so protect avermectin from photodegradation, making it more applicable for foliar spraying. Meanwhile, it is determinated that Av@PDA microcapsules have good mechanical stability property.



KEYWORDS: *adhesion, polydopamine, avermectin, emulsion interfacial polymerization*

1. INTRODUCTION

Pesticides are largely used to control weeds, insects, and plant diseases; however, depending on the administration method and climate conditions, only a very small amount of the applied pesticide actually reaches its targets.[1] Most pesticides deposited onto crops are easily volatilized or decomposed under exposure to the sun, and lost or leached into the soil.[2,3] Significant efforts have been exerted in this field to prevent pesticide degradation, and the best-known method to avoid degradation and provide sustained release is encapsulation of the chemicals into a suitable carrier.[4,5]

Several pesticide-delivery systems have been developed and applied in commercial use.[6,7] Although these pesticides are fairly stable, few research studies have paid attention to interaction between pesticides and crops, especially for versatile pesticides sprayed on leaves with different surface properties. A stable and slow- or controlled-release pesticide formulation with strong binding force to leaves will be desirable and efficient for improving residence time on crop surfaces.[8]

Avermectin (Av) is a widely used pesticide, which can be easily dispersed in water to form an emulsion and subsequently sprayed onto different crops, such as corn and cotton. However, Av is easily photo-oxidized, which results in its poor light stability and short half-life.[9,10] Overdosage of Av not only increases costs but also leads to undesirable side effects in both plants and the environment, both of which hinder its wide use in the field.[11] To overcome this challenge, many inorganic materials, such as TiO_2,[12] SiO_2,[4] and various polymers,[13,14] including chitosan[5] and cellulose acetate,[15] are used as carriers to stabilize drug and confer them with controlled-release properties. It is also noted that some complex technologies have to be used to load Av into a carrier previously prepared to achieve high loading capacity.[5,16] Thus, a simple method to encapsulate Av with high loading capacity is desirable. When designing an appropriate encapsulating formulation, interfacial interactions between carriers and crops must be considered to enhance residence times.

An intriguing and natural adhesive polydopamine (PDA) material inspired by mussel is used in many fields. In a weakly alkaline solution (i.e., pH = 8.5), dopamine (DA) and similar compounds[17,18] can self-polymerize to form an adherent PDA coating on virtually any substrate surface,[19−22] thereby

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providing a novel method of achieving capsules.[23,24] Using an oil droplet as a soft template, PDA microcapsules can be prepared via *in situ* emulsion interfacial polymerization.[25] Notably, several reports have demonstrated that PDA can be used to adjust the adhesion properties of material surfaces,[26−29] and PDA microcapsules could be easily adhered on different surfaces similar to a mussel.[30]

In the present work, Av@PDA microcapsules are prepared by *in situ* emulsion interfacial polymerization. The UV-shielding, pH and temperature controlled-release, and adhesive properties of the microcapsules on different surfaces are fully investigated. Results show that the novel microcapsules exhibit excellent stability and controlled-release behavior as well as good adhesive performance on leaves of corn and cotton.

2. EXPERIMENTAL SECTION

2.1. Materials. Avermectin (96.3%), was supplied by Hebei Veyong Animal Pharmaceutical, China. Dopamine hydrochloride (DA) was purchased from Sigma-Aldrich Company. Tris-(hydroxymethyl) aminomethane (TRIS) and hydrochloric acid were purchased from Beijing Chemical Reagents Company, China. Ethanol, *n*-butyl alcohol, and hexadecyl trimethylammonium chloride (CTAC) were analytical chemicals purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd., China. Tetraethyl orthosilicate (TEOS, FuChen Chemical Reagents Factory, Tianjin, China) was purified by vacuum distillation. The cotton and corn leaves were picked from the fields at Shihezi City. Hydrophobic silicon wafers were purchased from Luoyang MCL Electronic Material Co., Ltd., China. Deionized water was prepared with an ion-exchange system.

2.2. Preparation of Av@PDA and Microcapsules. A 1.5 g portion of CTAC (1.5% m/v of water phase) was dissolved in 100 mL of tris-buffer solution (pH = 8.5) in a two-necked flask, and a water solution of the surfactant was obtained. A 0.1 g portion of Av was dissolved in 10.0 mL of *n*-butyl alcohol, and the oil phase was prepared. Immediately, the oil phase was poured into the previous water solution with vigorous mechanical stirring to generate a surfactant stabilized oil/water emulsion. Subsequently, 0.1 g of DA was added and simultaneously stirred at 300 rpm for a further 24 h at room temperature. The precipitate was centrifuged (10 000 rpm) and washed at least thrice with deionized water, and then dried under vacuum at 45 °C for 12 h. The Av@PDA microcapsules were obtained.

2.3. Preparation of Av@SiO_2 Microcapsules. Av@SiO_2 microcapsules were prepared according to the method described in the previous report.[5] A 1.5 g portion of CTAC (1.5% m/v of water phase) was dissolved in 100 mL of tris-buffer solution (pH = 8.5) in a two-necked flask, and a water solution of the surfactant was obtained. A 0.1 g portion of Av was dissolved in 6.0 mL of *n*-butyl alcohol and 4.0 mL of TEOS, and the oil phase was prepared. Immediately, the oil phase was poured into the previous water solution with vigorous mechanical stirring to generate a surfactant stabilized oil/water emulsion. Subsequently, 0.1 mL of concentrated ammonia solution was dropwise added and simultaneously stirred at 300 rpm for 2 h. After it was allowed to age overnight at room temperature, the precipitate was centrifuged (10 000 rpm) and washed at least thrice with deionized water, and then dried under vacuum at 45 °C for 12 h; Av@SiO_2 microcapsules were obtained.

2.4. Preparation of Av@PDA@SiO_2 Microcapsules. Av@PDA@SiO_2 microcapsules were prepared according to the method described in the previous report.[31] A 0.15 g portion of Av@PDA microcapsules was dispersed with 3.0 mL of ethanol in a three-neck round-bottom flask. Then, 280 mL of absolute ethanol, 70 mL of deionized water, and 5.0 mL of concentrated ammonia solution (28 wt %) were added and sonicated for 15 min. Then, 4.0 mL TEOS was added dropwise under continuous mechanical stirring. The system was stirred for 10 h at room temperature. The precipitate was centrifuged (10 000 rpm) and washed thrice successively with deionized water and ethanol, and then dried under vacuum at 45 °C for 12 h to obtain Av@PDA@SiO_2 microcapsules.

2.5. Characterization of the Av@PDA, Av@SiO_2, and Av@PDA@SiO_2 Microcapsules. Energy dispersive X-ray spectroscopy (EDX) was used to determine the elements contained in the samples. Transmission electron microscopy (TEM, Philips CM120 BioTWIN) and a field-emission scanning electron microscope (FE-SEM, SUPRA 55VP, Germany) were used to study the morphology and structures of the samples. The concentration of Av dissolved in the 30% ethanol/water (30:70, v/v) mixture was examined by UV−vis spectrophotometer (UV-3200, Shanghai MeiPuDa Company) at the wavelength 245 nm.

2.6. Determination of Amount of Av Encapsulated in PDA. To determine the amount of Av encapsulated in PDA, the percentages of the Av loading and encapsulated were tested as follows: a certain amount of Av@PDA microcapsules were mixed with 200 mL of ethanol solution for 24 h with magnetic stirring. The concentration of Av was examined by UV−vis spectroscopy (the detailed results of the UV−vis spectrum of Av were shown as Supporting Information in Figure S1). The percentages of Av loading and encapsulation were then calculated from the following equations:[32]

$$\text{avermectin loading} = \frac{\text{mass of avermectin loaded in PDA}}{\text{mass of Av@PDA}} \times 100\%$$

$$\text{avermectin encapsulation} = \frac{\text{mass of avermectin loaded in PDA}}{\text{mass of avermectin}} \times 100\%$$

2.7. Controlled Release of Av. The release behavior of the loaded Av from the prepared samples was investigated. Samples that contain the same amount of Av, including Av technical (Av-Tech), Av emulsifiable concentrate (Av-EC, 5% w/w), and Av@PDA (66.5% w/w) samples, were suspended with 200 mL of an ethanol/water mixture in 250 mL conical flask, respectively, which was used as the release medium to dissolve Av, and then were placed in a constant shaking incubator at a stirring speed of 100 rpm. The cumulative release rate of Av from the microcapsules was calculated by measuring the concentration of Av dissolved in the mixture solution at different times to evaluate the sustained release from Av@PDA microcapsules. To measure the concentration, 2.0 mL of mixture was collected at different intervals from the suspension in the constant shaking incubator. A 2.0 mL portion of supernatant obtained by centrifugation (10 000 rpm) was monitored by UV−vis absorption spectroscopy analysis, and 2.0 mL of mixture was added to the constant shaking incubator.

2.8. UV-Shielding Properties of PDA Carriers for Av. The UV-shielding properties of the produced PDA were performed as follows: Samples that contain the same amount of Av, including Av-Tech, Av-EC (5% w/w), and Av@PDA (66.5% w/w), were mixed with 200 mL of an ethanol/water (30:70, v/v) mixture into the 250 mL beaker, respectively. The samples were exposed to a 40 W germicidal lamp (254 nm) at a distance of 25 cm with a magnetic stirrer, keeping the temperature at room temperature by recirculating water during the experiments. At different intervals, 2.0 mL of solution was extracted and centrifuged to determine the concentration of Av in the solution by UV−vis absorption spectroscopy, and 2.0 mL of mixture was added to beaker. The released amounts of Av were monitored by its absorbance at 245 nm.

2.9. Studies of the Adhesion Properties of Av@PDA Microcapsules. Prior to conducting the test, the hydrophilic silicon wafers were washed. A certain concentration aqueous suspension of Av@PDA microcapsules was prepared and then added onto the surface dish. The cotton leaves, corn leaves, and hydrophilic and hydrophobic silicon wafers were immersed into the solution for 0.5 h, and dried in the air, and then each of the samples was divided into two halves, respectively. One half was washed with deionized water for 0.5 h, with the other doing no treatment. Both were dried under vacuum at 45 °C for 6 h. The same concentration aqueous suspension of Av-

Tech, Av@SiO_2, and Av@PDA@SiO_2 microcapsules was treated by the same process as the Av@PDA microcapsules.

2.10. Determination of the Mechanical Stability of Av@PDA Microcapsules. To examine the mechanical stability of the miscrocapsules, the macroscopic friction test was performed on conventional reciprocating tribometer by recording the friction force.[33] First, the Av@PDA microcapsules were coated on the silicon wafer and dried under gentle vacuum for 24 h. The friction tests were carried out by sliding a steel ball at a sliding velocity of 0.8×10^{-4} m/s under loading of 1 N (Hertzian contact pressure ≈ 0.23 MPa) at 25 °C. The distance of one sliding cycle was 1 cm, the frictional force versus time plot was obtained, and three friction tests were repeated for this sample. Then, SEM was used to observe the change of the microcapsules.

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of Av@PDA, Av@SiO_2, and Av@PDA@SiO_2 Microcapsules. A schematic illustration of the synthesis of Av@PDA microcapsules is shown in Figure 1. During Av@PDA microcapsule formation,

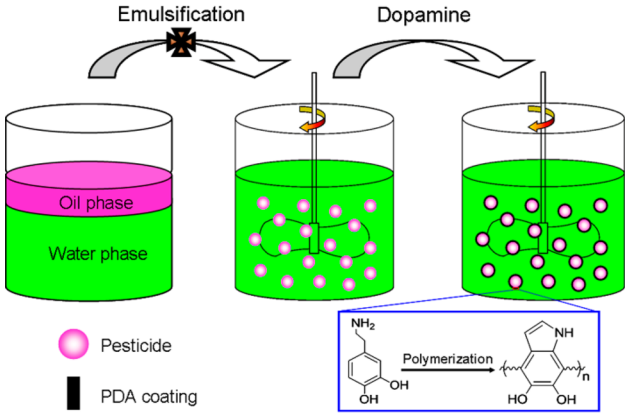

Figure 1. Schematic illustration of the synthesis of Av@PDA microcapsules.

CTAC was used as a surfactant to stabilize oil droplets composed of Av and *n*-butyl alcohol. DA was present in the water−oil interface. Spontaneous oxidative self-polymerization of DA occurs to yield the outer shell of the microcapsules. FTIR spectra were used to confirm the formation of PDA (Figure S2 in the Supporting Information), which is in agreement with the previous report.[34] Dopamine shows many narrow peaks, a feature of a small molecule. From the PDA spectrum, PDA presents only a few intense absorption peaks at 1615 cm^{-1} from aromatic rings, and around 3420 cm^{-1} from catechol −OH groups.

SiO_2 is used as shells to prevent particle clumping because of its chemical inertness and extreme structural stability.[35] In this study, SiO_2 shells were prepared through a versatile sol−gel method to illustrate the adhesive properties of Av@PDA microcapsules. The SEM and TEM images, and EDX spectra of Av@PDA, Av@SiO_2, and Av@PDA@SiO_2 microcapsules, are given in Figure 2. The SEM and TEM images show that both materials have excellent morphologies and uniform particle size distribution. The Av@PDA microcapsules adhered to each other and showed smooth surfaces (Figure 2a,b); their mean size were about 215 nm. By contrast, Av@SiO_2 and Av@PDA@SiO_2 microcapsules were more diffuse and had rough surfaces (Figure 2d,e,g,h), and their mean size were about 220 and 240 nm, respectively. Compared with Figure 2c, a peak of Si (in Figure 2f,i), constituent of SiO_2, was detected obviously by the EDX analysis, which indicates SiO_2 was successfully coated onto Av and the Av@PDA microcapsules.

3.2. Determination of Amount of Av Encapsulated in PDA. Calculated from the aforementioned equations, the amount of Av loaded and encapsulated on the resulting microcapsules was 66.5% and 51.7% (w/w), respectively. Compared with previous reports,[4,5] the ratio of Av loaded in the Av@PDA microcapsules was increased. Thus, a simple method to encapsulate Av with high loading capacity was successfully developed.

3.3. Controlled Release Kinetics. Av release behaviors from the Av@PDA microcapsules were investigated in 30% ethanol/water mixture at different pH and temperatures. Figure 3 shows the release rates of Av-Tech, Av-EC, and Av@PDA at 27 °C. The release of Av-Tech and Av-EC reached equilibrium after 8 and 16 h, respectively, and the cumulative release of Av-Tech and Av-EC was 78.9% and 95.6%, respectively. However, the cumulative release of Av@PDA microcapsules within 220 h was just only 29.3%. Compared with Av-Tech and Av-EC, Av@PDA microcapsules exhibited a longer release time.

3.3.1. Effects of pH Value on the Release Behavior of Av. The effects of pH (3.0, 5.0, 7.0, and 9.0) on the release behavior of Av@PDA microcapsules were studied at 27 °C and at a stirring speed of 100 rpm. Results are shown in Figure 4. The amount of Av released increased with increasing pH. At pH 3.0, about 19% w/w Av (percentage calculated as the release of Av divided by the total loaded Av, w/w) was released into the medium after 120 h. As the pH increased to 9.0, the amount of Av released rose to approximately 71% w/w. This result is probably due to differences in surface charges, i.e., different electrostatic interactions between PDA layers and the Av molecules at different pH values.[36] Av is negatively charged when pH > 3, and PDA layers are protonated at low pH;[37,38] this difference results in electrostatic attraction. At high pH, the amino groups of PDA are deprotonated and become negatively charged, thereby enhancing repulsive forces between Av and PDA. Thus, the release rate of Av increases with increasing pH values.

3.3.2. Effects of Temperature on the Av Release Behavior. Figure 5 shows the effects of different temperatures of the medium on the release behavior of Av@PDA microcapsules at a stirring speed of 100 rpm. Av release was investigated at 27, 37, and 47 °C. The cumulative release of the samples is 27.43%, 49.27%, and 92.07% at 77 h, respectively. The release rate of Av@PDA microcapsules increased with increasing temperature such that more Av could be released within shorter periods of time. Diffusion of Av molecules through the PDA shell intensified at higher temperatures, thereby resulting in easier and quicker Av release from the prepared samples.

3.4. Studies of the UV-Shielding Properties of PDA Carriers for Av. The UV-shielding properties of the PDA carriers were investigated using Av@PDA samples in 30% ethanol/water solution. Samples were exposed to UV light at room temperature under stirring. The remaining concentration of Av in the release medium was measured immediately after UV irradiation by UV−vis spectroscopy. The degradation rates obtained are shown in Figure 6. Av-Tech and Av-EC were completely decomposed by UV irradiation at 4.5 and 10 h, respectively. By contrast, Av remained detectable in the release medium even after 78 h of UV irradiation. The decomposition rate of Av wrapped in microcapsules was much lower than those of Av-Tech and Av-EC. These results clearly demonstrate

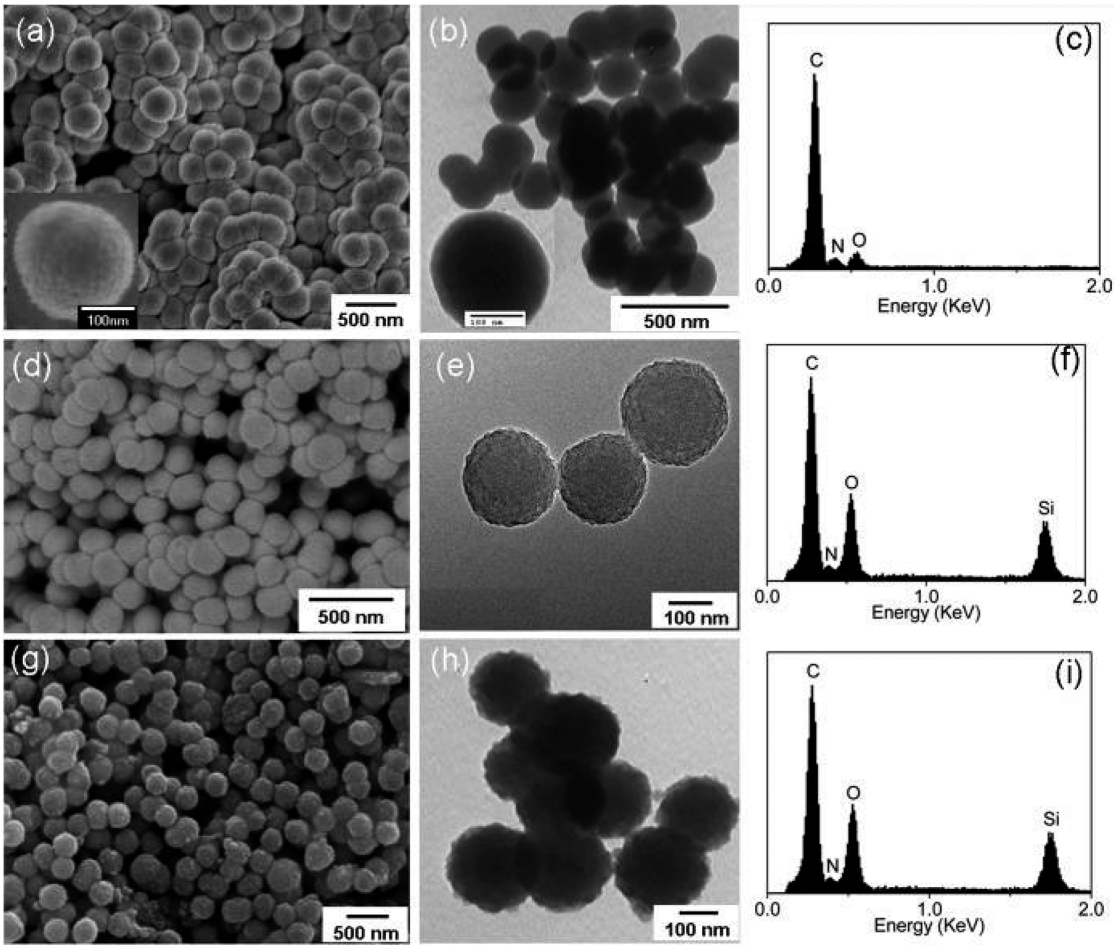

Figure 2. SEM and TEM images and EDX spectra of the microcapsules: (a, b, c) Av@PDA; (d, e, f) Av@SiO_2; (g, h, i) Av@PDA@SiO_2.

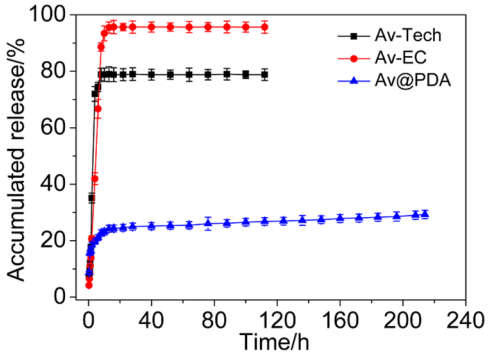

Figure 3. Release curves of Av from Av-Tech, Av-EC, and Av@PDA microcapsules.

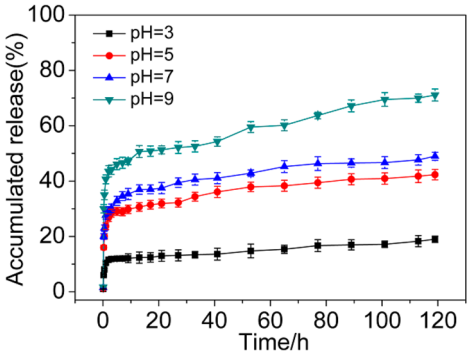

Figure 4. Effects of pH on the release behavior of Av@PDA microcapsules.

that the PDA carriers have remarkable UV-shielding properties, which can significantly improve the efficiency of the loaded Av. Therefore, PDA carriers are promising agents for promoting sustained pesticide release, especially in the presence of photosensitive components.

3.5. Adhesion Properties of Av@PDA Microcapsules. To prove that Av@PDA microcapsules have better adhesion behavior than other pesticide forms, Av-Tech, Av@SiO_2, and Av@PDA@SiO_2 microcapsules were sprayed on the cotton and corn leaves, respectively. The amount of samples remaining on different surfaces was observed to evaluate their adhesion properties. First, the amount of Av-Tech on leaves without or with water washing was observed (shown in Supporting Information Figure S3). Only a small amount of Av-Tech was seen under both conditions which verified that Av-Tech is easy to slide from the leaves. The adhesion behaviors of Av@PDA, Av@SiO_2, and Av@PDA@SiO_2 microcapsules with the same handling on different leaves are shown in Figures 7A–F and 8A–F. Figure 7A,B as well as Figure 8A,B show only a slight decrease in the amount of Av@PDA microcapsules without and with water washing. By contrast, Figure 7C,D as well as Figure 8C,D, reveal that the quantity of Av@SiO_2 microcapsules on leaves was greatly reduced without and with water washing. In order to better illustrate the problem, the

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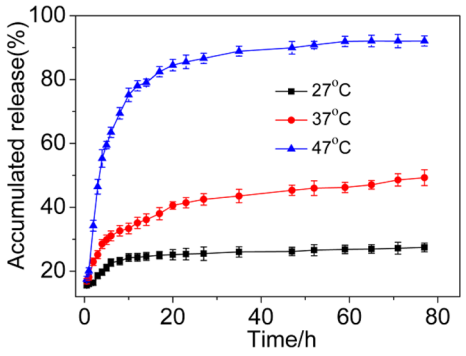

Figure 5. Effect of temperature on the release behavior of Av from Av@PDA microcapsules.

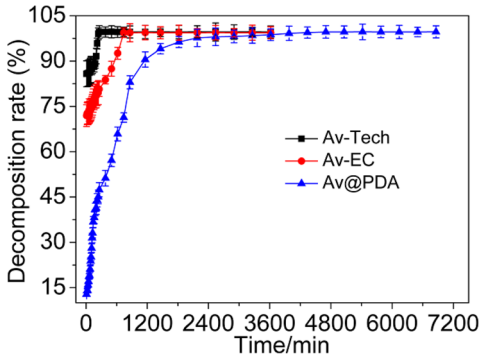

Figure 6. UV-shielding properties of Av-Tech, Av-EC, and Av@PDA microcapsules.

surfaces of Av@PDA microcapsules were deposited with the SiO_2 shell, Figure 7E,F, as well as Figure 8E,F, with the same result. Figures 7A,C,E and 8A,C,E further show that the quantity of Av@SiO_2 and Av@PDA@SiO_2 microcapsules on leaves evidently decreased compared with the quantity of Av@PDA microcapsules. These results indicate that Av@PDA microcapsules have better adhesion properties on cotton and corn leaves than Av-Tech, Av@SiO_2, and Av@PDA@SiO_2 microcapsules.

Although the crop-leaf experiment demonstrated that more Av@PDA microcapsules than Av-Tech, Av@SiO_2, and Av@PDA@SiO_2 microcapsules remained on sprayed leaves, the experiment did not provide strong evidence of the adhesion properties of Av@PDA microcapsules because the leaves generally featured uneven surfaces (SEM images of the blank cotton and corn leaves were shown in Supporting Information Figure S4). To further demonstrate that the Av@PDA microcapsules have excellent adhesion properties, the samples were applied to smooth hydrophilic and hydrophobic silicon wafers. The adhesion behaviors of the microcapsules on the silicon surfaces are shown in Figures 7 (a–f) and 8 (a–f). SEM images (Figures 7a,b and 8a,b) show that the amount of Av@PDA microcapsules barely changed on hydrophilic and hydrophobic silicon wafers without and with water washing. By contrast, the amount of Av@SiO_2 and Av@PDA@SiO_2 microcapsules significantly changed (Figures 7c–f and 8c–f). These results confirm that Av@PDA microcapsules have excellent adhesion, which may be due to PDA with an abundance of catechol groups enhancing its adhesion performance on the crop surfaces. The conclusions are very similar to those reported in a previous study.[26,39]

3.6. Determination of the Mechanical Stability of Av@PDA Microcapsules. In order to investigate the mechanical stability property of microcapsules, the friction tests were carried out on a Japan Xindong HEIDON 14FW reciprocating friction tester. Figure 9a,b shows silicon wafer after friction and the friction curves for point-line contacts friction by steel ball and microcapsules under a load of 1 N, respectively. Figure 9c shows that microcapsules are adhered on steel ball after friction. It is clear that the shape of microcapsules is only slightly deformed and not broken (Figure 9d). This result suggests that Av@PDA microcapsules had good mechanical stability.

4. CONCLUSIONS

In the present study, we developed a novel method for enabling the controlled release of Av by emulsion interfacial polymerization. The proposed microcapsules showed remarkable loading ability for Av (about 66.5% w/w). Av@PDA could effectively protect Av against photodegradation and imparted

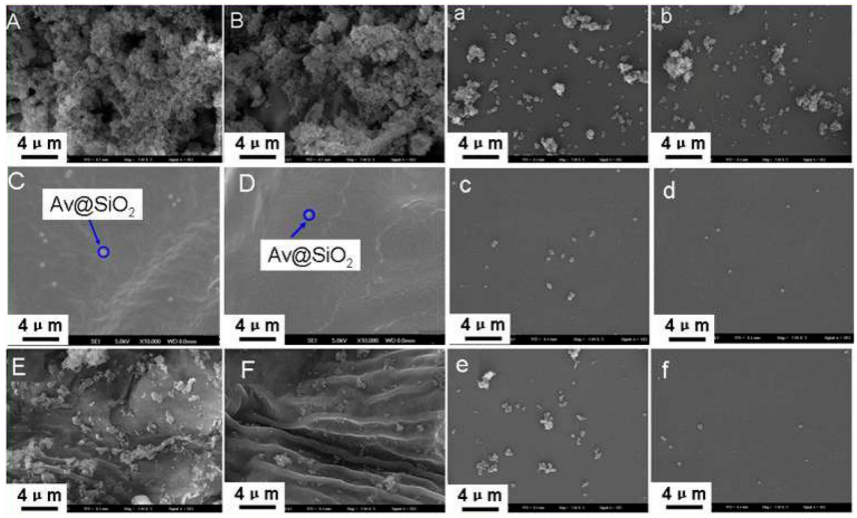

Figure 7. SEM images of the microcapsules on cotton leaves (A, B, C, and D) and hydrophilic silicon wafers (a, b, c, and d): (A, a) Av@PDA; (B, b) Av@PDA with water washing; (C, c) Av@SiO_2; (D, d) Av@SiO_2 with water washing; (E, e) Av@PDA@SiO_2; (F, f) Av@PDA@SiO_2 with water washing.

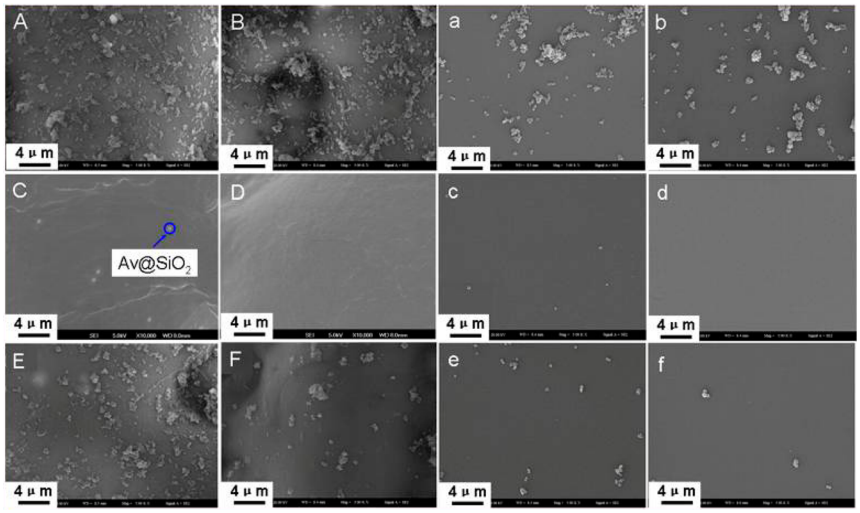

Figure 8. SEM images of the microcapsules on corn leaves (A, B, C, and D) and hydrophobic silicon wafers (a, b, c, and d): (A, a) Av@PDA; (B, b) Av@PDA with water washing; (C, c) Av@SiO_2; (D, d) Av@SiO_2 with water washing; (E, e) Av@PDA@SiO_2; (F, f) Av@PDA@SiO_2 with water washing.

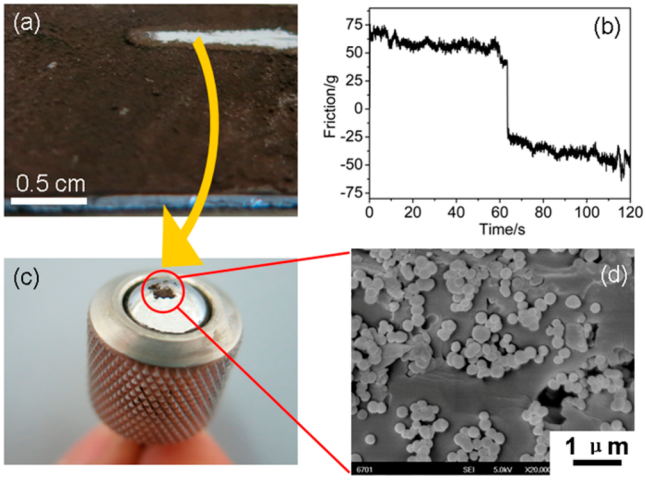

Figure 9. Mechanical property data of Av@PDA microcapsules: (a) images of silicon coated microcapsules substrate after friction; (b) friction curve of Av@PDA microcapsules; (c) photo of microcapsules adhered on steel ball after friction; (d) SEM image of Av@PDA microcapsules after friction.

Av@PDA microcapsules with excellent sustained-release properties. Higher pH values and temperatures intensified Av release. Av showed good adhesion properties and long residence times on cotton and corn leaves. Meanwhile, these microcapsules had good mechanical stability property. Hence, Av@PDA microcapsules may be developed as a resource-saving and environment-friendly pesticide formulation.

■ ASSOCIATED CONTENT

Supporting Information

UV−vis spectrum of Av (Figure S1), FTIR spectra of DA and PDA (Figure S2), SEM images of the Av-Tech on cotton and corn leaves (Figure S3), SEM images of the blank cotton and corn leaves (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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