Preparation and Properties of Bio-Based Polyurethane Controlled Release Urea Coating with Photosensitivity

Lina Zhang, Hongyu Tian,*, Min Zhang,*, Liang Wu, Wusong Guo, Fuli Fang, Xiao Sun, Zijing Zhong, Longxu Du, and Zhiguang Liu

ABSTRACT: In order to improve the photodegradation ability of fertilizer coating material and realize the sustainability of fertilizers, in this study, the commercially available photosensitive iron stearate (FeSt₃) was wet-ground into submicrometer FeSt₃ (SFeSt₃) particles and used in preparation of a SFeSt₃-modified bio-based polyurethane (PU)-coated controlled release urea (PU-SFe-CRU). The results showed that after 1 month photodegradation, the coating material had significant yellowing, the oxygen content of SFeSt₃-modified PU (PU-SFe) increased by 56.89%, and its structure became more porous and looser than PU. The thermal stability of PU-SFe decreased, and more intermediate products were produced after exposure to UV light. The germination experiment showed that PU-SFe before and after photodegradation (up to 60 mg/L) had no adverse effect on the seed germination and bud growth of rice. Additionally, PU-SFe had a significantly higher Cr adsorption capacity after photodegradation due to the increase of the oxygen-containing group and specific surface. This study provides a theoretical basis for the research and development of photodegradable environment-friendly controlled release urea.

1. INTRODUCTION

The nitrogen (N) use efficiency of common N fertilizers is only 20–30%,¹ and the unused N will be lost through volatilization, leaching, and other ways.²,³ This not only causes economic losses but also causes environmental problems such as water eutrophication, soil hardening, and air pollution.⁴,⁵ Controlled release urea (CRU) can reduce environmental pollution by improving the nitrogen use efficiency to further achieve sustainable development of agriculture.⁶

Coating material is the key to the nitrogen release characteristics and quality of CRUs. Compared with the fragile inorganic coating materials such as sulfur, polymers are strong and mechanical wear-resistant.⁷,⁸ In addition, nitrogen release rates of polymer-coated CRU meet the dynamic nutrient requirement of crops better. Therefore, polymers have been widely used in CRU coatings in recent years. However, petrochemical coating materials are all persistent and their long-term application poses potential environmental risks.⁶ Studies show that coating materials reduce biodiversity and bio-richness¹⁰ and in turn affect nutrient cycling in soil¹⁰ and eventually crop growth. Recently, bio-based materials with better degradability have attracted much attention.¹¹,¹² Lu et al. showed improved degradability of a coating material after modification with liquefied wheat straw and better degradability of liquefied starch-based polyurethane (PU).¹³,¹⁴ Liu et al. prepared a novel bio-based coating material using waste frying oil-based polyol and isocyanate and evaluated its degradation performance.¹⁵ Compared with petrochemical PU, bio-based PU have the advantages of low cost, easy access, and low environmental impact, but their degradation is still slow under field conditions.¹⁶,¹⁷ Urgun-Demirtas et al. documented no significant mass loss of PU in a 10 week laboratory soil incubation experiment at 25 °C.¹⁸ Tian et al. showed a merely 5.05% degradation rate of bio-based PU during a 9 month incubation experiment.¹⁹ Therefore, the degradability of bio-based PU needs to be further improved.

Photodegradation is a simple and easy-to-implement method of degradation.²⁰ Photocatalytic technology has been successfully used to treat air and wastewater pollutants²¹–²³ including plastics.²⁴,²⁵ Under ultraviolet (UV) light, PU degrades mainly through chain breaking and oxidation. Photosensitizers can accelerate PU photodegradation as they generate free radicals under UV light, which attack the macromolecular chain of PU.²⁶,²⁷ Iron stearate (FeSt₃) is a cheap and environmentally friendly photosensitizer. In
addition, it has the highest photosensitivity among stearates and has no environmental impact after degradation. Previous research showed that incorporation of rigid particles, nanoparticles in particular, can effectively improve the microstructure and enhance the hardness of polymers.4,28 Therefore, when ground FeSt$_3$ is incorporated to bio-based coating materials, the nitrogen release behavior of CRUs is expected to be affected due to the improved microstructure and enhanced hardness of coating materials. In addition, degradation of coating materials at the soil surface after the complete release of nutrients is expected to be accelerated due to the photosensitivity of FeSt$_3$. According to Yu et al., the specific surface area of FeSt$_3$-modified coating material increases as it breaks down into debris, and heavy metals in soil would be adsorbed on its surface and immobilized.29 Consequently, less heavy metal would accumulate in crops and move through the food chain.

Many studies have been conducted on the degradation of coating materials,13,14 but few have been performed on the degradation of photosensitizer-modified coating materials. This study was aimed to develop an environmentally friendly CRU coated with photodegradable FeSt$_3$-modified bio-based material. First, FeSt$_3$ was wet-ground to submicrometer particles (SFeSt$_3$). Then, controlled release urea (CRU) fertilizer was produced using urea, polyaryl polymethylene isocyanate (PAPI), castor oil, and SFeSt$_3$. The effects of SFeSt$_3$ on coating properties were studied, and the influences of the coating ratio, PAPI proportion, and SFeSt$_3$ proportion on nitrogen release rate were investigated using the surface response model. Finally, the degradability, phytotoxicity, and Cr adsorption capacity of the SFeSt$_3$-modified coating were evaluated.

2. RESULTS AND DISCUSSION

2.1. Changes in Coating Morphology and Hydrophobicity after Photodegradation. As can be seen from the photos of PU and PU-SFe before (Figure 1a,c) and after photodegradation (Figure 1b,d), PU was milky white (Figure 1a), and PU-SFe was pale red (Figure 1c), which was related to the red color of SFeSt$_3$. After a month of photodegradation, both PU (i.e., PUUV) and PU-SFe (i.e., PU-SFeUV) turned darker and yellower (Figure 1b,d), which may be due to the formation of monoquinoneimine and diquinoneimine during the UV-degradation of PU.30−32 The formation of these structures is caused by the oxidation of methylene between two benzene rings in the polyurethane structure under the action of UV light and oxygen. In addition, yellowing may also be related to the increase of carbonyl.32,33 The higher the content of carbonyl, the darker the color of the coating material. All these results show that the yellowing of coating color is closely related to its photodegradation. Compared with PUUV, the color of PU-SFeUV was darker, indicating that SFeSt$_3$ had accelerated the UV-degradation of PU.

The SEM images showed the smooth surfaces of PU and PU-SFe (Figure 1e,g), indicating that the addition of SFeSt$_3$ did not change the surface morphology of the coating. After 1 month photodegradation, the surfaces of PU and PU-SFe became rough (Figure 1f,h), indicating changes in surface structure of PU during UV-degradation.34,35 It is proved that UV light may cause the destruction of the coating material structure. Compared with PUUV, the surface of PU-SFeUV was rougher and cracked, indicating that the addition of SFeSt$_3$ resulted in stronger photodegradation of the coating.36

Figure 1. Photos (a–d), surface (e–h) and cross-section (i–l) scanning electron microscope (SEM) images, and water contact angle images (m–p) of the coatings of controlled release urea fertilizers. Column 1: polyurethane (PU); column 2: PU after 1 month photodegradation (PUUV); column 3: submicrometer FeSt$_3$-modified PU (PU-SFe); and column 4: PU-SFe after 1 month photodegradation (PU-SFeUV).
The cross-section SEM images of PU and PU-SFe showed a compact structure of the coatings (Figure 1i,k). After photodegradation, a few pores were observed in PU, while a large number of pores with diameters of 0.1–1 μm were observed in PU-SFe. These pores may be caused by gases produced during photodegradation. A porous structure after photodegradation was also reported by Yang et al.; it is clearly pointed out that the pores in the membrane shell are caused by the gas produced in the process of photodegradation, which further indicates that the existence of these holes will make the structure of the coating material become loose, and it is easier to further degrade. By adding SFeSt3 to the polyethylene system, it has been proved by UV light test that the presence of SFeSt3 can significantly promote the photodegradation of polyethylene, resulting in the structure of polyethylene looseness, thus greatly accelerating its biodeterioration. The much more porous and looser structure of PU-SFe after UV aging compared with PU may also be related to the SFeSt3 particles evenly distributed in PU. The particles of SFeSt3 are photosensitive, and when UV-irradiated, they generate free radicals to attack the macromolecular network of PU, resulting in the rapid degradation of the polymer around and consequently pores in the coating. The pores can provide space for water storage and niches for microorganism growth, which is conducive to the subsequent biodeterioration of PU.

After photodegradation, the water contact angle of PU decreased by 23.9% to 53.4° (PUUV) (Figure 1n), while that of PU-SFe decreased by 59.8% to 36.7° (PU-SFeUV) (Figure 1p). Photodegradation can significantly degrade the water contact angle of PU materials, which is consistent with the results of previous studies. Yari et al. proved that the intermediate products produced in the degradation process can reduce the surface water contact angle of PU by UV aging test. David et al. determined the water contact angle of PU with different UV light times and found that the water contact angle of PU gradually decreased with the extension of the light time, indicating that the reduction of water contact can be used to prove the photodegradation of the material. The decreases in the water contact angle for PU and PU-SFe after photodegradation may be caused by the increase of hydrophilic groups in their structure or the roughening of their surfaces, or it could be a combination of both. The SEM and water contact angle images showed that when subjected to photodegradation, PU-SFe changed from hydrophobic to hydrophilic with a rough surface and a porous structure, which is conducive to microorganism growth and the subsequent biodeterioration of PU.26

2.2. Changes in O Content, O/C Ratio, and FTIR Spectra of the Coatings before and after Photodegradation. Surface oxygen distributions of PU and PU-SFe before and after photodegradation are shown in Figure 2. The O content of PUUV (27.40%) increased by 35.38% compared with that of PU (20.24%) (Figure 3a), while the O content of PU-SFeUV (32.68%) was increased by 56.89% compared with that of PU-SFe (20.83%). In addition, the O content of PU-SFeUV was significantly higher than that of PUUV, indicating that photodegradation had caused oxidation of PU and much stronger oxidation of PU-SFe. The O/C ratio of PUUV decreased by 23.9% to 53.4°, whereas that of PU-SFe decreased by 59.8% to 36.7° (Figure 1p). Photodegradation changes in the O/C ratio also indicate oxidation of PU and much stronger oxidation of PU-SFe caused by photodegradation. The addition of SFeSt3 increased the O/C ratio of UV-irradiated PU, indicating that SFeSt3 incorporation had stimulated the photo-oxidation degradation of PU. The reason may be that the addition of SFeSt3 promotes the surface disintegration of the coating material, thus increasing the contact area of the coating material with air and UV light and further promoting the photo-oxidative degradation of the coating material.

In the FTIR spectra of the coatings, O–H stretching vibration related absorption peaks at 3326, 3338, 3331, and 3234 cm⁻¹ were observed for PU, PU-SFe, PUUV, and PU-SFeUV, respectively (Figure 3b). The O–H peak of PU did not change much after photodegradation, whereas that of PU-SFe became much wider and larger, indicating that SFeSt3 addition had promoted −OH formation during photodegradation. The increase in −OH, an important hydrophilic group, will lead to higher hydrophilicity, which explains the decrease in the water contact angle of PU-SFe after photodegradation (Figure 1). The absorption peaks at 2800–2930 cm⁻¹ are related to methyl and methylene stretching vibration.13 The absorption peak at 2270 cm⁻¹ is related to the isocyanate group.41 The isocyanate peak of PUUV became smaller as compared with PU, indicating that photodegradation had caused partial degradation or transformation of the isocyanate groups in PU. In contrast, the peak of the isocyanate group disappeared in the PU-SFeUV spectrum, indicating that photodegradation had caused complete degradation or transformation of the isocyanate groups in PU-SFe. The peak at 1720 cm⁻¹ for PU-SFe was significantly enhanced after photodegradation. As this peak is related to the C=O stretching vibration, its enhancement indicates the occurrence of photo-oxidation and a Norrish reaction with such products as aldehydes and ketones. The peak at 1052 cm⁻¹, which is related to the C=C stretching vibration in the benzene ring, did not change significantly in PU but was significantly weakened in PU-SFe after photo-
degradation, which indicates that the benzene ring was subjected to a much stronger attack when UV-irradiated with the presence of SFeSt3. The peak at 1223 cm\(^{-1}\), which is related to C\(\cdots\)O\(\cdots\)C, was greatly weakened for PU-SFe after photodegradation, indicating that the presence of SFeSt3 had promoted the cleavage of the C\(\cdots\)O\(\cdots\)C bond in PU-SFe. This may be caused by the attack of free radicals produced by SFeSt3 under UV light. The resulted exposed oxygen may attract protons to form \(\cdot\)OH, which explains the wider and larger \(\cdot\)OH peak at 3234 cm\(^{-1}\) discussed previously and the improved hydrophilicity of PU-SFe as compared with PU. The weakening of the peak at 1042 cm\(^{-1}\), corresponding to N\(\cdots\)H and C=O, indicates structural changes in PU-SFe after photodegradation,\(^{13}\) which is conducive to the subsequent degradation of PU.

2.3. Thermal Stability Changes of the Coatings.

Thermogravimetric analysis (TGA) thermograms of PU, PU-SFe, PUUV, and PU-SFeUV are shown in Figure 4a,b. The pyrolysis of PU and PU-SFe can be divided into three stages of rapid decomposition (Figure 4c). Both PU and PU-SFe were stable up to approximately 240 °C and completely degraded at approximately 670 °C. For PU and PU-SFe, a 20% weight loss occurred at 349.5 and 343.6 °C, respectively. This 20% weight loss may be due to the loss of small groups and volatile substances.\(^{41}\) PU and PU-SFe lost 50% of their mass at 486.5 and 522.3 °C, respectively. Both PU and PU-SFe lost 80% of their mass at approximately 600 °C, which may be attributed to the decomposition of such functional groups as N\(\cdots\)H and C=O. The pyrolysis of PU and PU-SFe was completed at 694 and 661 °C, respectively. The UV-irradiated PU (i.e., PUUV) and PU-SFe (i.e., PU-SFeUV) decomposed completely at 702 and 622 °C, respectively. Photodegradation did not significantly affect the final pyrolysis temperature of PU but significantly lowered the final pyrolysis temperature of PU-SFe by 39 °C. The thermal stability of polymers mainly depends on the degree of cross-linking.\(^{19}\) The cross-linking in

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**Figure 3.** Oxygen (O) contents, O/C ratios (a), and Fourier transform infrared (FTIR) (b) spectra of the coatings: polyurethane (PU), submicrometer FeSt3-modified PU (PU-SFe), UV-irradiated PU (PUUV), and UV-irradiated PU-SFe (PU-SFeUV).

**Figure 4.** Thermogravimetric analysis of polyurethane (PU) and submicrometer FeSt3-modified PU (PU-SFe) between 25 and 800 °C (a). Thermogravimetric analysis of UV-irradiated PU (PUUV) and UV-irradiated PU-SFe (PU-SFeUV) between 25 and 800 °C (b). Thermal analysis curves of polyurethane (PU) and submicrometer FeSt3-modified PU (PU-SFe) between 25 and 800 °C (c). Thermal analysis curves of UV-irradiated PU (PUUV) and UV-irradiated PU-SFe (PU-SFeUV) between 25 and 800 °C (d).
PU-SFeUV may have been weakened to a greater extent by photodegradation due to the photosensitization of SFeSt₃, as evident by the porous and loose structure (Figure 1). Therefore, PU-SFeUV displayed a lower final pyrolysis temperature.

The maximum degradation rate of PUUV was recorded at 588.4 °C, whereas that of PU-SFeUV was recorded at 569.5 °C (Figure 4d), which was 18.9 °C lower. This indicates that the addition of SFeSt₃ accelerated the photodegradation of PU, resulting in the destruction of the structure of PU-SFeUV, which became loose and finally promoted the thermal degradation.¹³ Both PU and PU-SFe had obvious pyrolysis at 447.8–498.7 °C, but PUUV and PU-SFeUV showed no obvious pyrolysis at this temperature range. According to Liu et al. PU pyrolysis at 447.8–498.7 °C is mainly due to the cleavage of N–H.¹³ As these bonds had been cleaved during photodegradation (Figure 4d), no more bond cleavage would occur in PUUV and PU-SFeUV at this temperature range during thermal degradation, which explains the lack of substantial pyrolysis. These results indicate that SFeSt₃ can promote the photo-oxidation decomposition and in turn reduce the thermal stability of PU.

2.4. Photodegradation Products Identified by GC/MS.

GC/MS was used to identify the organic intermediates produced during the photodegradation of coatings. A series of new substances were indentified from the UV-irradiated coatings (Figure 5). n-Heptanoic acid and methyl palmitate, whose retention times were 7.71 and 17.58 min, respectively, were indentified in PUUV but not in PU. Eight compounds, including n-heptanal (5.12 min), n-hexanoic acid (6.40 min), N-methylpyrrolidone (7.22 min), p-heptanolide (8.76 min), n-hexadecane (13.75 min), heptadecane (17.56 min), palmitic acid (18.02 min), and N-(1,3-dimethyl-butyl)-n'-phenyl-1,4-phenylenediamine (23.29 min), were indentified in PU-SFeUV but not in PU-SFe. More degradation products were indentified from PU-SFeUV than from PUUV, indicating that the addition of SFeSt₃ had accelerated the photodegradation efficiency of PU. In addition, n-heptanoic was indentified in PUUV, whereas n-heptanal, which is the oxidation product of n-heptanoic, was indentified in PU-SFeUV, demonstrating that PU-SFe had undergone faster and stronger photo-oxidation than PU. The mass spectrogram and structure diagram of the substances produced during the degradation of the coating material are listed in Figure. S2.
The reason for the variety of intermediate products produced by PU-SFeUV is that the added SFeSt₃ plays the role of a photosensitizer. The mechanism of SFeSt₃ playing its role was listed as follows:

\[
\text{Fe(OOCR')}_3 \xrightarrow{hv} \text{Fe(OOCR')}_2 + \text{CR'OO}^- \quad (1)
\]

\[
\text{CR'OO}^- \xrightarrow{hv} \text{R'} + \text{CO}_2 \quad (2)
\]

where R' represents C₁₇H₃₅ and SFeSt₃ produces alkyl radicals (R') after being exposed to UV light. It is because the Fe 3d orbital electrons easily generate electron transfer, producing a free radical; the free radical would attack the N=C and C=O of the polymer chain; and then, the polymer chain would produce new long-chain free radicals. Long-chain free radicals will undergo peroxidation and chain scission and decompose into ketones, aldehydes, phenols, and other macromolecular free radicals according to Norrish I and Norish II type reactions. In this process, the long polyurethane chain will be degraded. The specific photodegradation mechanism is listed in Figure 6.

2.5. Phytotoxicity of the Coatings. The seed germination experiment is commonly performed to evaluate phytotoxicity of chemicals. In this study, the germination of rice seeds was not affected by the coating suspension solutions with a concentration up to 60 mg/L (Figure 7). The germination rates after 96 h incubation in the treatments with a coating concentration of 60 mg/L were 90.00% (CK, without coating), 86.67% (PU), 90.83% (PU-SFe), 91.34% (PUUV), and 89.46% (PU-SFeUV) (Figure 7). There were no significant differences in the germination rate between different coatings or different coating concentrations. The results showed that neither PU nor SFeSt₃-modified PU was toxic to plant growth. In addition, their photodegradation products were not toxic to plant growth, either. Therefore, SFeSt₃ can be incorporated in PU to accelerate its degradation in the field after nutrient has been completely released without toxicity to plants. A similar result was also reported by Lian et al. Lian et al. conducted hydroponic experiments on wheat by adding 10 mg/L polystyrene microplastics (0–100 nm) to water and proved that microplastics did not significantly affect the germination rate of wheat seeds under this addition level. Although the addition materials are different, the germination rate of rice will not be significantly affected when the addition amount is 60 mg/L in this experiment, and the coating material amount of 60 mg/L can be accumulated to this amount only after 5 years of practical application of fertilization without any degradation. However, bio-based materials undergo photodegradation and biodegradation over a 5 year period, so it takes longer for the amount of coating to accumulate to 60 mg/L in the soil. This experiment proved that the bio-based coating materials before and after photodegradation did not have significant adverse effects on the growth of rice within the scope of usage in this experiment.

After 96 h incubation, rice bud length of the PU and PU-SFe treatments was not significantly different from that of CK (Figure 7c). However, rice bud length of the PUUV and UV-irradiated PU-SFe (PU-SFeUV) at different concentrations (0 (CK), 15, 30, and 60 mg/L) showed that the photodegraded PU-SFeUV treatments were significantly larger than that in CK (Figure 7d). The reasons need further investigation. This may be because the coating material produces some undetected substances that could be absorbed by the rice during the process of photodegradation.
The results showed that although the suspension solutions of the coatings contained such harmful substances as n-heptanoic acid (Figure 5), their concentrations must be too low to adversely affect the seed germination and growth of rice.19

2.6. Kinetics of Cr Adsorption by the Coatings. As shown in Figure 8, the adsorption amount of Cr increased rapidly in the initial 36 h and then slowed down. The reason is that the adsorption sites on the coating surface became saturated with time. The adsorption equilibrium was reached after 84 h. The adsorption capacity of the coatings was significantly improved after photodegradation, which was consistent with the previous studies.25−46 Lin et al.’s results showed that the adsorption capacity of Pb by polypropylene particles could be significantly improved after UV irradiation, and the importance of the increase of oxygen-containing functional groups on the surface of the material to its adsorption capacity was expounded.47 The Cr adsorption capacities of PU and PU-SFe were 85.60 and 88.94 mg/g, whereas those of PUUV and PU-SFeUV were 93.27 and 109.87 mg/g, respectively. The higher Cr adsorption capacity of PUUV and PU-SFeUV may be related to the increase of oxygen-containing functional groups or the increase of specific surface area due to pores (Figure 1). The immobilization of heavy metal ions such as Cr by the coatings can reduce heavy metal bioavailability and uptake by plants.

Three common kinetic models were used to fit the Cr adsorption data to understand the adsorption mechanisms (Figure 9). The correlation coefficients ($R^2$) between the experimental data and the simulated data of each model are listed in Table S2.

![Figure 8](image院院士.png)

**Figure 8.** Adsorption amount of Cr with time by the coatings of polyurethane (PU), UV-irradiated PU (PUUV), submicrometer FeSt3-modified PU (PU-SFe), and UV-irradiated PU-SFe (PU-SFeUV).

Of the three models, the pseudo-second-order model best described the Cr adsorption dynamics of the coatings with significant correlation coefficients, indicating that Cr was adsorbed by the coatings mainly via ion exchange (Table S1).

According to the intra-particle diffusion model, adsorption is a complex process with three steps, including external diffusion, particle internal diffusion, and adsorption of the solute at the adsorption site of the adsorbent.48 The linear fit of the intra-particle diffusion model did not pass the origin (Figure 9k,l), which indicates that Cr adsorption by the coatings was controlled by particle internal diffusion and external diffusion.

2.7. Effects of the Coating Ratio and Proportion of PAPI and SFeSt3 on the Nitrogen Release Characteristics of PU-SFe-CRUs. The nitrogen release rate of PU-SFe-CRUs was significantly affected by the coating ratio (Figure 10a). The larger the coating ratio was, the slower the nitrogen was released. After 1 day of incubation, the nitrogen release rates were 95.24, 9.91, and 0% for the PU-SFe-CRUs with coating ratios of 1.32, 3.00, and 4.68%, respectively. After 84 days of incubation, the cumulative nitrogen release rates were 80.97 and 37.05% for the coating ratios of 3.00 and 4.68%, respectively. At a very low coating ratio (e.g., 1.32%), the urea fertilizer particles may not be fully coated, and nitrogen is

![Figure 9](image院士.png)

**Figure 9.** Linear fitting graphs of adsorption kinetic models: pseudo-first-order kinetic model (a−d), pseudo-second-order kinetic model (e−h), and intra-particle diffusion model (i−l) of PU, PUUV, PU-SFe, and PU-SFeUV.
readily released from the unwrapped part, resulting in a rapid nitrogen release. The higher coating ratios (i.e., 3.00 and 4.68%) gave the PU-SFe-CRUs better performance in the slow release of nitrogen. The results were consistent with previous studies. In the scope of coated in this experiment, the release rate of nitrogen was slower with the increase of coating ratio.

The proportion of SFeSt$_3$ in coating significantly affected the nitrogen release of the fertilizer (Figure 10b). The nitrogen release rates for the CRU with SFeSt$_3$ proportions of 0.20, 0.70, and 1.20% were 4.56, 9.91, and 14.03% after 1 day of incubation, 5.99, 11.43, and 18.59% after 7 days of incubation, and 16.12, 29.68, and 44.96%, respectively, after 28 days of incubation. The results showed that the content of SFeSt$_3$ affected the nutrient release rate of fertilizer throughout the nutrient release period. By measuring the microstructure of cross sections of different fertilizer coatings (Figure 11), it was shown that the more SFeSt$_3$ content, the faster the release rate of fertilizer nitrogen was because excessive SFeSt$_3$ would affect the film formation reaction of coating materials, leading to the formation of pores in the membrane shell during the culture process and accelerating the release of nitrogen. In the process of fertilizer production, we can make use of this characteristic to prepare special slow and controlled release fertilizers for crops with different nutrient requirements by adjusting the proportion of SFeSt$_3$.

When the PAPI proportion was 66.82%, the nitrogen release rate reached 95.24% after only 1 day of incubation (Figure 10c). When the proportion of PAPI was 33.18 and 50.00%, the nitrogen release behavior of the two kinds of Pu-SFe-CRU was consistent with that of CK. When the content of PAPI was 33.18%, the release rate of fertilizer nitrogen was significantly faster than that of CK and CRU with PAPI proportion of 50.00%. The analysis reason might be that when the proportion of PAPI was 33.18%, the $-\text{NCO}$ group was not enough to fully react with $-\text{OH}$, and the remaining $-\text{OH}$ caused the hydrophile of coating material, thus leading to the accelerated release of fertilizer nitrogen. This was different from the results of a previous study, which may be because different types of polyols were used in coating.

Surface response models were developed according to Table S2 to further explore the influences of coating ratio ($A$), proportion of submicrometer FeSt$_3$ (SFeSt$_3$) in coating ($B$), and proportion of polyaryl polymethylene isocyanate (PAPI) in coating ($C$) on the nitrogen release rate of the controlled release urea fertilizers (CRUs) coated with SFeSt$_3$-modified polyurethane. Polyurethane is the product of the reaction between PAPI and castor oil. CK is polyurethane-coated CRU with no SFeSt$_3$ added to the coating.

$$Y_i = 8.96 - 24.50A + 12.09B - 5.88C - 2.67AB + 9.74AC - 7.87BC + 12.60A^2 + 9.81B^2 - 0.95C^2, \quad (R^2 = 0.8936) \quad (3)$$

Figure 10. Influences of the coating ratio (a), proportion of submicrometer FeSt$_3$ (SFeSt$_3$) in coating (b), and proportion of polyaryl polymethylene isocyanate (PAPI) in coating (c) on the nitrogen release rate of the controlled release urea fertilizers (CRUs) coated with SFeSt$_3$-modified polyurethane. Polyurethane is the product of the reaction between PAPI and castor oil. CK is polyurethane-coated CRU with no SFeSt$_3$ added to the coating.

Figure 11. Scanning electron microscope (SEM) images of the cross section of coatings, with 0.20% SFeSt$_3$ proportion (a), 0.70% SFeSt$_3$ proportion (b), and 1.20% SFeSt$_3$ proportion (c) respectively (the fertilizer after 7 days incubation in water).
\[ Y_2 = 11.38 - 28.39A + 19.32B - 3.95C + 5.94AB - 4.74AC - 4.99BC + 16.25A^2 + 17.81B^2 + 3.18C^2, \]
\[ (R^2 = 0.9267) \]  
\[ Y_3 = 33.08 - 24.95A + 18.37B + 3.90C + 15.27AB - 0.97AC - 0.48BC + 9.41A^2 + 14.47B^2 + 2.33C^2, \]
\[ (R^2 = 0.9215) \]

In terms of their influence on the nitrogen release rate of PU-SFe-CRUs, the three factors were in the order of coating ratio > the proportion of PAPI > the proportion of SFeSt3 (eqs 3–5).

3. CONCLUSIONS

In this study, a novel photodegradable, bio-based PU-coated CRU was successfully prepared by modification of PU with SFeSt3. SFeSt showed excellent photosensitivity in the process of UV irradiation. After 1 month of UV irradiation, the oxygen content of coating increased by 56.89%, the O/C ratio increased by 88.46%, and the structure of the coating became loosened. The effects of UV light and SFeSt3 photosensitivity on the groups and structures of the coating significantly changed the process of thermogravimetry and significantly reduced the temperature of the coating. In addition, the intermediate products of photodegradation of coating have no adverse effect on the germination of rice seeds. The SFeSt3-modified PU, especially after UV-irradiation, displayed high Cr adsorption capacity and Cr fixation ability. CRUs with SFeSt3-modified coatings are easy to prepare and are expected to be commercially available and broadly used in the future. This study can provide reference for the development of the next generation of environmentally friendly CRUs.

4. EXPERIMENTAL SECTION

4.1. Materials. Iron stearate was purchased from Shandong Weifang Youhe Auxiliary Co., Ltd; castor oil (acid value: 1.2% mg KOH/g, hydroxyl value: 164 mg KOH/g) was obtained from Tianjin Kaitong Chemical Industry Co., Ltd; PAPI (–NCO mass fraction of 31.1%) was purchased from Yantai Wenhua Polyurethane Co., Ltd.; urea (3–5 mm and 46% N) was purchased from Shandong Hualu Hengsheng Chemical Co., Ltd., China. Anhydrous ethanol was purchased from Xinxiang Zhengxin Chemical Industry Co. Ltd, Shandong province.

4.2. Preparation of SFeSt3 and SFeSt3-Modified CRUs. For the preparation of SFeSt3, FeSt3 was mixed with anhydrous ethanol at a ratio of 1:10 (w/w), ground with a ball mill (Beijing Galloping Scientific Instrument Co., Ltd., Beijing, China) at 800 r/min for 15 min, and vacuum-dried.

For the preparation of SFeSt3-modified bio-based PU-coated CRUs (PU-SFe-CRUs), urea, PAPI, castor oil, and SFeSt3 at ratios listed in Table S2 were used. First, 1 kg urea (79.9% of the particles >3.5 mm) was placed in a rotary drum and heated at 70 ± 5 °C for about 10 min. Then, the mixture of PAPI, castor oil, and SFeSt3 was uniformly sprayed onto the urea particles in the drum and cured for 5–8 min for the production of PU from PAPI and castor oil. This step was repeated until the mixture was completely used. The prepared CRUs were cooled to room temperature. A total of 20 PU-SFe-CRUs were prepared. These PU-SFe-CRUs had a coating ratio of 1.32–4.68%, PAPI proportion in coating of 33.18–66.82%, and SFeSt3 proportion in coating of 0.2–1.2%. For comparison purpose, another two CRUs were prepared as well as with a coating ratio of 3% and PAPI proportion in a coating of 50%: one without SFeSt3 or FeSt3 (PU-CRU) while the other with FeSt3 at 0.7% in coating (PU-Fe-CRU).

The CRU with a coating ratio of 3.00%, PAPI proportion of 50.00%, and SFeSt3 proportion of 0.70% was the PU-SFe-CRU used in all experiments in this study except the nitrogen release experiment where other PU-SFe-CRUs were also used as specified below.

4.3. Determination of Particle Size and Hardness. The particle size of FeSt3 and SFeSt3 was measured with a particle size analyzer (Mastersizer 2000, Marvin, UK; Zeta sizer Nano ZS90, Seymour, USA, US). The particle hardness of urea, PU-CRU, PU-SFe-CRU, and PU-Fe-CRU was determined with a particle hardness meter (FT-803, Ruike Weiye Instrument Co., Ltd., Zhejiang, China).

4.4. Nitrogen Release Experiment. A nitrogen release experiment was conducted to investigate the effects of the coating ratio, SFeSt3 proportion, and PAPI proportion on nitrogen release characteristics of the PU-SFe-CRUs. For the effect of the coating ratio, PU-SFe-CRUs with coating ratios of 1.32, 3.00, and 4.68%, PAPI proportion of 50.00%, and SFeSt3 proportion of 0.70% were used. For the effect of SFeSt3 proportion, PU-SFe-CRUs with a coating ratio of 3.00%, PAPI proportion of 50.00%, and SFeSt3 proportions of 0.20, 0.70, and 1.20% were used. For the effect of PAPI proportion, PU-SFe-CRUs with a coating ratio of 3.00%, SFeSt3 proportion of 0.70%, and PAPI proportions of 33.18, 50.00, and 66.82% were used. The nitrogen release rates of the above mentioned PU-SFe-CRUs and PU-CRU (CK) were measured according to the standard method HG/T 4216-2011. Briefly, 10 g CRU were put into a bottle containing 200 mL deionized water and placed in a biochemical incubator at 25 ± 0.5 °C. The solution was sampled after 1, 3, 5, 7, 14, 28, 56, and 84 days of incubation for the determination of the refractive index using a refractometer (RX-5000, ATAGO Co., Ltd, Tokyo, Japan) until the cumulative nitrogen release rate was larger than 80%.

4.5. UV-Degradation Experiment. The two CRUs, PU-CRU and PU-SFe-CRU were ground with a grinding machine (Yongkang PBO Hardware Products Co., Ltd., Zhejiang, China) and sieved with a 2 mm sieve to obtain their coatings (>2 mm), PU and PU-SFe, respectively. The coatings were washed repeatedly with deionized water to remove urea, oven-dried at 50 °C, and put in a chamber with UV lights (45 W) at 35 °C for 30 days (Figure 12). The UV-irradiated PU and PU-SFe were referred to as PUUV and PU-SFeUV, respectively.
4.6. Characterization. The surface and cross section of the coatings before and after photodegradation were observed using a scanning electron microscope (SEM) (QUANTA250, FEI Company, Oregon, USA). The cross-section of the coating was taken after freezing the coating in liquid nitrogen for half an hour and then slicing it with a scalpel blade. The water contact angle was measured using a contact angle meter (JC2000A, Jianduan Photoelectricity Technology Co., Ltd., Shanghai, China). Thermal stability of the coatings was evaluated by thermogravimetric analysis (TGA) with a DTG60A instrument (Shimadzu Corporation, Tokyo, Japan). The surface element distribution was visualized with an energy dispersive X-ray spectroscopy (EDX) coupled with SEM. Oxygen (O) content was quantified, and carbon (C) content was determined. Fourier transform infrared (FTIR) spectra of the coatings were recorded using a Thermo Nicolet 380 FTIR spectrometer (Thermo Nicolet Corporation, Maine, USA) at a scanning range from 4000 to 400 cm⁻¹. The coatings were extracted with acetone (12.5 g/L) for 2 h, and UV-degradation products in the extracts were identified using a TSQ8000 gas chromatography-mass spectrometer (GC/MS) (Thermo Fisher Scientific, Germany) with a C18 column. High-purity helium was used as the carrier gas at a flow rate of 1 mL/min, and the injection volume was 1 μL. The mass detector was operated in the electron impact (EI) ionization mode at 70 eV, and the range of mass spectrometry scanning was 45–450 amu. Data were collected 5 min after injection. The ion source temperature was 280 °C. At least five scans were performed for each peak, with no longer than 0.7 s for each scan.

4.7. Phytotoxicity Experiment. Coatings treated and untreated with UV light (i.e., PU, PU-SFe, PUUV, and PU-SFeUV) were ground, passed through a 100-mesh sieve, and mixed with deionized water to prepare suspension solutions of 0 (CK), 15, 30, and 60 mg/L for each coating. The coating material concentration setting refers to the experimental design of Tian et al.¹⁹

Vigorous seeds of rice (Oryza sativa L.) with uniform size were disinfected with 2% NaClO₄ solution for 30 min under continuous stirring and rinsed with deionized water for 5–7 times. The disinfected rice seeds were soaked in deionized water for 24 h, cleaned, and seeded in Petri dishes (with a lid) lined with two layers of filter paper and preloaded with 10 mL of the above suspension solution sequences, with 30 seeds in each dish and four replicates for each treatment. The dishes were placed in an incubator at 25 °C in the dark. Germination (radicle protrusion of 2 mm) was recorded every 24 h until at least 80% of the seeds in the 0 mg/L treatment (CK) had germinated.

4.8. Cr Adsorption Experiment. In 100 mL conical flasks, 40 mL 100 mg/L Cr solution and 10 mg PU, PU-SFe, PUUV, and PU-SFeUV were added and shaken at 150 r/min and 25 ± 2 °C. The concentration of Cr in the solution was determined at different incubation times. Three replicates were conducted for this experiment.

The Cr adsorption kinetic data were fitted with the pseudo-first-order model (eq 6), pseudo-second-order model (eq 7), and intra-particle and diffusion model (eq 8):

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  
\[ \frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) \times t \]  
\[ q_t = k_3 t^{1/2} + C \]  

where \( q_e \) (mg/g) and \( q_t \) (mg/g) represent the amounts of adsorbed Cr at equilibrium and time \( t \), respectively, and \( k_1 \) (L/min), \( k_2 \) (g/mg-min), and \( k_3 \) (mg/g-min^{1/2}) are rate constants.

4.9. Statistical Analysis. Data were analyzed using analysis of variance (ANOVA) followed by Duncan’s multiple range test of SAS package, version 9.2 (SAS Institute, Cary, NC, USA). Graphs were plotted using Origin 8.6. Differences were considered significant at \( p < 0.05 \).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06432.

Particle size of SFeSt₃ and particle hardness of CRUs; design table of the surface response model; effects of the coating ratio, proportion of SFeSt₃, and proportion of PAPI on the initial release rate, 7 day release rate, and 28 day cumulative release rate of fertilizer; intermediate products of photodegradation; model fitting details of Cr adsorption by coatings; photodegradation behavior of coating materials under different dosages of photosensitizer; the influence of coating material dosage on its adsorption capacity (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Hongyu Tian – National Engineering Research Center for Efficient Utilization of Soil and Fertilizer Resources, College of Recourses and Environment, Shandong Agricultural University, Taian 271018, China; Email: thy0634@qq.com

Min Zhang – National Engineering Research Center for Efficient Utilization of Soil and Fertilizer Resources, College of Recourses and Environment, Shandong Agricultural University, Taian 271018, China; orcid.org/0000-0002-7838-3393; Email: minzhang-2002@163.com

**Authors**

Lina Zhang – National Engineering Research Center for Efficient Utilization of Soil and Fertilizer Resources, College of Recourses and Environment, Shandong Agricultural University, Taian 271018, China

Liang Wu – Key Laboratory of Crop Specific Fertilizer, Ministry of Agriculture and Rural Affairs, Xinyangfeng Agricultural Technology Co Ltd., Jingmen, Hubei 448001, China

Wusong Guo – Key Laboratory of Crop Specific Fertilizer, Ministry of Agriculture and Rural Affairs, Xinyangfeng Agricultural Technology Co Ltd., Jingmen, Hubei 448001, China

Fuli Fang – Key Laboratory of Crop Specific Fertilizer, Ministry of Agriculture and Rural Affairs, Xinyangfeng Agricultural Technology Co Ltd., Jingmen, Hubei 448001, China

Xiao Sun – National Engineering Research Center for Efficient Utilization of Soil and Fertilizer Resources, College of Recourses and Environment, Shandong Agricultural University, Taian 271018, China

Zijing Zhong – National Engineering Research Center for Efficient Utilization of Soil and Fertilizer Resources, College of Recourses and Environment, Shandong Agricultural University, Taian 271018, China

ACS Omega 2022, 7, 8558–8569
Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.1c06432

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS
This work was supported by the Key R&D Program of Shandong Province (Public Welfare Special Project), "Development and application of growth-promoting and stress-resistant slow-controlled release fertilizer" (grant no. 2019GNC106011) and Xinyangfeng Technical Cooperation Project, Research on Development and Application Technology of Slow and Controlled Release Fertilizer (grant no. 010-380953).

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