

Mussel-Inspired Thermosensitive Polydopamine-*graft*-Poly(*N*-isopropylacrylamide) Coating for Controlled-Release Fertilizer

Zhiyuan Ma,[†] Xin Jia,^{*,†} Jiamei Hu,[†] Zhiyong Liu,[†] Heyun Wang,[†] and Feng Zhou[‡]

[†]School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Key Laboratory for Chemical Materials of Xinjiang Uygur Autonomous Region, Shihezi University, Shihezi 832003, People's Republic of China

[‡]State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

S Supporting Information

ABSTRACT: A thermoresponsive release multi-element compound fertilizer was first reported on the basis of a polydopamine-*graft*-poly(*N*-isopropylacrylamide) bilayer coated on a salty core by a combination of dopamine chemistry and surface-initiated atom transfer radical polymerization techniques, and the control of nutrient release in response to the environmental temperature was investigated. The successfully synthesized stimuli-responsive fertilizers were confirmed by transmission electron microscopy (TEM), Fourier transforms infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and gel permeation chromatography (GPC). The release of elements from fertilizer was determined by an inductively coupled plasma (ICP) emission spectrometer. The thermosensitive fertilizers exhibit outstanding stimuli-responsive permeability to encapsulated nutrients, and the release rate of coated elements can be tailored by the ambient temperature. They can release nutrients easily at $T < \text{lower critical solution temperature (LCST)}$ but slow at $T > \text{LCST}$. This strategy of grafting thermoresponsive polymer brushes on polydopamine (Pdp)-coated substrates is useful to prepare a stimuli-responsive release system, which can adjust the release rate according to different conditions, and will be effective and promising in the research and development of a stimuli-sensitive controlled-release system.

KEYWORDS: *Thermoresponsive, polydopamine, PNIPAm, ATRP, controlled-release fertilizer*

■ INTRODUCTION

Fertilizers have been used to supply nutrients in growing media for many years, and they are added to soil to supply one or more plant nutrients essential to the growth of plants.^{1,2} However, the nutrients of a common fertilizer is lost to the environment easily and cannot be abundantly taken up by plants, which results in the contamination of water, air, etc.³ An effective way to improve nutrient use efficiency while reducing the environmental hazards is using slow- or controlled-release fertilizers (SCRFs), contributing to the sustainable development of agriculture and the environment.^{4–7} In comparison to traditional fertilizers, SCRFs have many advantages. For example, decreasing the loss rate of the fertilizer, supplying sustainable nutrients, and minimizing potential negative effects associated with overdosage.^{8,9} Coated fertilizers, encapsulating the fertilizer core with various materials,^{10,11} are the major categories of the SCRFs. Although many coating materials have been reported,^{12–15} SCRFs, which could tune the release rate of nutrients according to different ambient conditions, were barely reported, because it is hard to find multifunctional materials that could be used as both a barrier and a stimuli-sensitive layer. Moreover, sometimes temperatures are used in connection with day length to manipulate the plant growth. In this sense, the development of a thermoresponsive encapsulated fertilizer according to the temperature is urgent and essential.

Recently, inspired by the adhesive properties of mussel proteins, the Messersmith group introduced a facile strategy to

deposit a polydopamine (Pdp) layer on different substrates by spontaneous self-polymerization in weak alkaline solution.^{16–18} In addition, a variety of secondary immobilization reactions using the Pdp coating as a base or “primer” led to versatile coatings being reported, including grafted polymer brushes, metal films, etc.^{19–23} Therefore, it is probable that the design and preparation of the stimuli-responsive fertilizer with a “polydopamine-*g*-polymer brush” structure, a Pdp inner layer and a grafted stimuli-sensitive polymer brush corona, could provide a simple and effective approach to realize functionalization of the fertilizer. In addition, surface-initiated atom transfer radical polymerization (SI-ATRP), a well-established controlled/“living” radical polymerization technique that has been used successfully in a Pdp-based initiator,^{24–26} has received considerable interest from industry and academia. Poly(*N*-isopropylacrylamide) (PNIPAm), one of the most widely investigated temperature-responsive polymers, exhibiting a lower critical solution temperature (LCST) of about 32 °C in water, is widely used in controlled-release systems,^{27–29} and the ATRP technique has been successfully carried out to obtain a well-defined PNIPAm system.^{30,31} Such chemistry features could be used for feasibly designing a temperature switch with “Pdp-*g*-PNIPAm”.

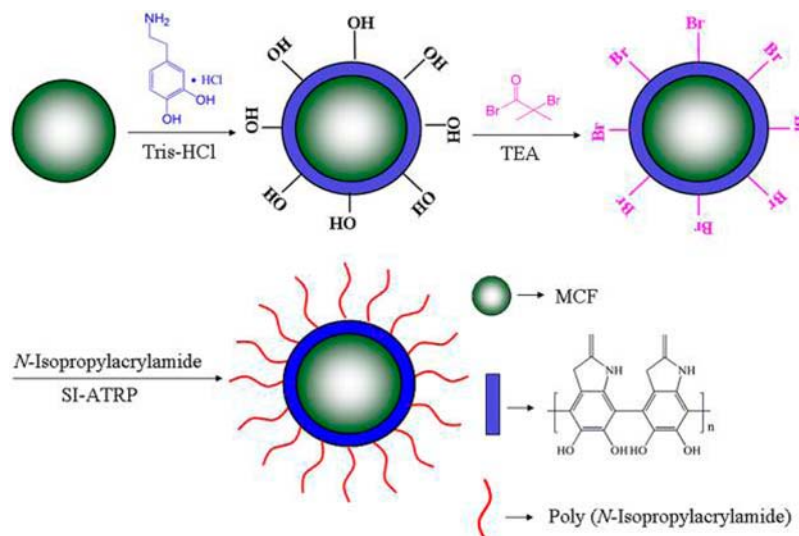
Received: September 3, 2013

Revised: December 3, 2013

Accepted: December 5, 2013

Published: December 5, 2013

Scheme 1. Schematic Illustration of the ATRP Grafted with PNIPAm from Pdop-Coated Fertilizers



On the basis of our previous works,^{24,32,33} we developed a new “polydopamine-graft-polymer brush” to realize thermoresponsive release of a coated fertilizer. The Pdop layer was first deposited on the salty core, providing copper, potassium, and phosphorus. Subsequently, the SI-ATRP was employed to graft NIPAm on the Pdop layer. The effect of the temperature on the release behavior of elements from the coated fertilizer is systematically studied in water. The results revealed that the Pdop-*g*-PNIPAm coating, composed of a Pdop inner layer and a thermosensitive PNIPAm outer shell, has excellent thermoresponsive release properties, and such thermo-induced switching can be used to control the release kinetics of the entrapped nutrients. This technology is facile and effective, and this strategy will be promising in development of SCRFs.

EXPERIMENTAL SECTION

Materials. Dopamine hydrochloride (Aldrich), copper(I) bromide (98%, Aldrich), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), 2-bromoisobutyl bromide (BIBB, 97%, Alfa Aesar), and *N,N*-dimethylaminopyridine (DMAP, 99%, Alfa Aesar) were used as received, without further purification. *N*-Isopropylacrylamide (NIPAm, 97%, Aldrich) was recrystallized twice from a toluene/hexane solution (50%, v/v) and dried under vacuum prior to use. Triethylamine (TEA, 97%, Tianjin Shengmiao Fine Chemical, Ltd.) was dried over calcium hydride for 12 h prior to distillation under nitrogen. All of the water used was deionized, and all other chemicals were analytical-grade and used as received.

Preparation of Multi-element Compound Fertilizer (MCF). The procedure for the synthesis of the double copper potassium pyrophosphate trihydrate, a multi-element compound fertilizer (MCF), is in accordance with the reported procedure.³⁴ The synthesis was carried out by adding the copper sulfate solution (0.1 M) to the potassium pyrophosphate solution (0.1 M) under vigorous stirring at 25 °C. After aging for 24 h, the solid was filtered and dried.

Preparation of Pdop-Coated Multi-element Compound Fertilizer (PCMCF). A total of 200 mg of dopamine hydrochloride was dissolved in 200 mL of Tris-HCl (10 mM, pH 8.5). Then, 2 g of MCF powder was added. The reaction solution was stirred for 24 h. The resultant product was centrifuged, washed with water several times, and dried under vacuum at 45 °C. To obtain PCMCF with a certain thickness of the Pdop layer, the number of inner-coating deposition cycles was designed 3 times.³³ The coating procedure was repeated the same way.

Preparation of Pdop-Coated Multi-element Compound Fertilizer Supported Initiator (PCMCF-Br). A 100 mL round-

bottom flask containing PCMCF (2.0 g), CH₂Cl₂ (20.0 mL), TEA (1.0 mL), and DMAP (0.5 g) was evacuated and filled with argon 3 times. Subsequently, 20.0 mL of CH₂Cl₂ containing 1.0 mL of BIBB was added dropwise at 0 °C for 1 h. The mixture was reacted for 23 h at room temperature to produce the supported initiator. After centrifugation and thoroughly washing with acetone and then with a methanol/water (1:1 v/v) mixture, the solid was dried under vacuum. These coated fertilizers with a supported initiator were denoted as PCMCF-Br.

Preparation of Pdop-*g*-PNIPAm-Coated Multi-element Compound Fertilizer (PPCMCF). A Schlenk flask containing PCMCF-Br (1.0 g) and CuBr (50.2 mg, 0.36 mmol) was sealed with a rubber plug and evacuated and filled 3 times with Ar. A solution of NIPAm (3.96 g, 36.0 mmol) and PMDETA (220 μL, 1.05 mmol) in a mixed solvent of H₂O/MeOH (6.3 mL, 1:1, v/v) was added in a flask, degassed by a freeze-pump-thaw cycle 3 times, and injected to the Schlenk flask with double-ended needles performed under inert gases. The flask was immersed in an oil bath at 65 °C, and its contents were stirred for 24 h. The polymerization was terminated by exposing the reaction flask to air and exhaustively rinsed with water and methanol to remove residual catalyst. PPCMCF was obtained by centrifugation, washing, and drying overnight under vacuum.

Techniques of Characterization. Transmission electron microscopy (TEM) measurements were carried out on a Hitachi H-600 microscope. Fourier transform infrared spectroscopy (FTIR) studies were recorded on KBr pellets with a Nicolet Avata360 spectrophotometer. Thermogravimetric analysis (TGA) was conducted on a Netzsch STA449F3 instrument with a heating rate of 10 °C/min in a N₂ flow. Molecular weights and molecular weight distributions of the polymer coating were determined by a gel permeation chromatography (GPC) system equipped with a Waters 2414 refractive index detector and PLgel 5 μm Mixed-C columns, eluted with tetrahydrofuran (THF) at 40 °C (1 mL/min). The content of Cu, K, and P were analyzed by an inductively coupled plasma (ICP) emission spectrometer using Thermo Scientific 6000 Series.

Release Behavior of PPCMCF in Water. The release behavior of copper (Cu), potassium (K₂O), and phosphorus (P₂O₅) from different fertilizers in water was determined as follows: 0.2 g of fertilizer was enclosed into dialysis bags [molecular weight cut-off (MWCO) = 15 000]. Then, the bags were put into conical bottles with 200 mL of aqueous solution and shaken at the temperatures of 25 °C (*T* < LCST) and 37 °C (*T* > LCST). During 80 days, 5.0 mL of the solution was withdrawn from conical bottles every 5 days. After microwave-assisted digestion in the presence of catalyst, the contents of Cu, K, and P in the solution were determined with ICP and the same volume of fresh medium was added to the incubated system to maintain a constant amount of solvent.

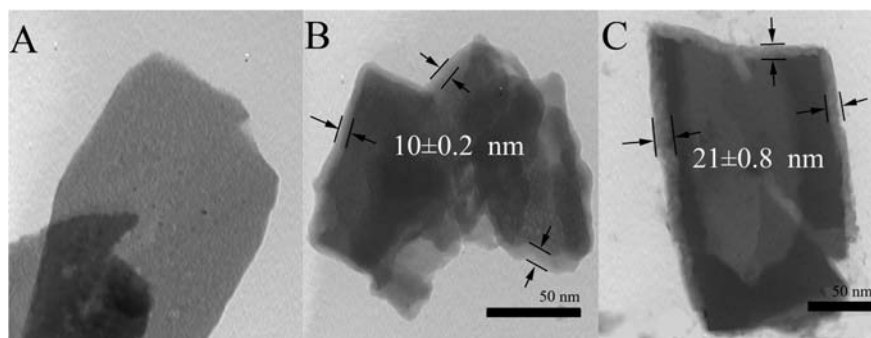


Figure 1. TEM image of (A) MCF, (B) PCMCF, and (C) PPCMCF.

RESULTS AND DISCUSSION

Preparation and Characterization of PPCMCF. The fabrication strategy involves three key steps, as shown in Scheme 1. PCMCF was first prepared by deposition of dopamine on the salty core. After immobilization of the initiator for the ATRP on the Pdop coating, fertilizers with a thermosensitive corona grafting from the Pdop substrate were prepared by ATRP grafted with PNIPAm.

Figure 1 shows the TEM images of products. In comparison to the salty core (Figure 1A), a coating with an average thickness of about 10 nm was observed as a light shell and coated on the dark flaky MCF (Figure 1B). The encapsulation boundary is clear, because the Pdop film is successfully coated on MCF. The growth profile of Pdop is in agreement with our previous work.³³ After ATRP of Pdop initiated by NIPAm, thermoresponsive fertilizers were formed and the layer thickness increases to about 21 nm (Figure 1C).

Figure 2 shows the FTIR spectra of Pdop, PNIPAm, and Pdop-g-PNIPAm layer without a salty core. Ethylenediaminete-

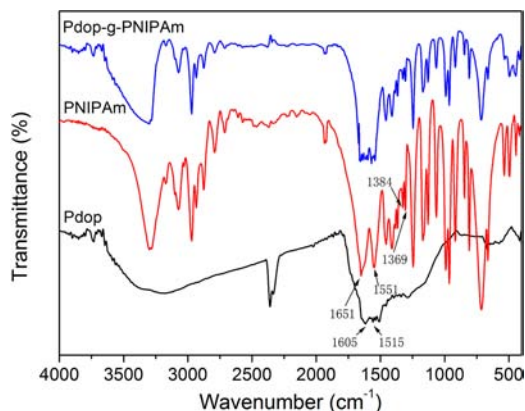


Figure 2. FTIR spectra of samples.

traacetic acid (EDTA) was used to remove the MCF core. Pdop has characteristic bands at 1515, 1605, and 3200–3500 cm^{-1} because of the indole/indoline structures and N–H/O–H bonds, as reported previously.^{32,35} For PNIPAm, the peaks at 1651 and 1551 cm^{-1} are ascribed to the amide I band (stretching vibration of C=O) and amide II band (stretching vibration of N–H). Both of the peaks at 1384 and 1369 cm^{-1} with the same intensity are the characteristic deformation vibration peaks of C–H bonds in the methyl groups of isopropyl. Moreover, for Pdop-g-PNIPAm coating, the infrared analysis results show that the characteristic groups of both Pdop and PNIPAm exist in the products. It is noted that some

changes come over the peak shift and the change of the peak. The red-shifted absorption band occurred at 3300 cm^{-1} with the change of the peak at 1500–1700 cm^{-1} , which corresponds to the Pdop-g-PNIPAm structures.

The relative amount of Pdop-coating and -grafted PNIPAm of controlled-release fertilizers was investigated with TGA and depicted in Figure 3. The weight loss of the MCF is 13.21% at

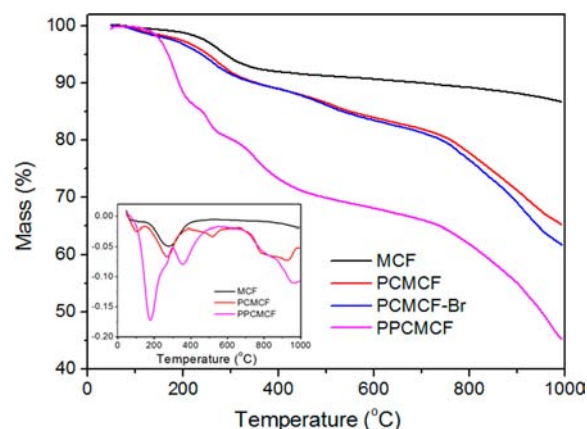


Figure 3. TGA and DTG (inset) curves of samples.

temperatures up to 1000 °C. After modification with Pdop, a 34.72% weight loss was noted. This indicates that the percentage of Pdop of PCMCF is 21.51%. The weight loss of PCMCF–Br and PPCMCF are 38.06 and 57.28 wt %, respectively. In this sense, the difference between PCMCF and PCMCF–Br corresponds to 0.182 mmol of initiator groups per gram of initiator-coated fertilizers. A comparison of TGA data for PCMCF and PPCMCF suggests that ~22.5 wt % of the hybrid is due to the grafted polymer. TGA curves verify that the thermoresponsive brushes were successfully grafted from PCMCF, and the success of the present strategy can be extended to prepare controlled-release fertilizers with stimuli-responsive polymer brushes. The differential thermogravimetry (DTG) curves revealed characteristic differences in the coating of the fertilizers, as shown in the inset of Figure 3. It is clear that the bilayer structure presents interactions and a shift in DTG peaks is observed for PCMCF and PPCMCF. However, it is noted that the weight loss of PPCMCF seems not to correspond to TEM images, in which the thickness of the polymer is about 21 nm. We think that MCF is two-dimensional (2D) and flake-shaped crystals, as shown in Figure 1A. Microscopic PPCMCF is embedded in a polymer base (panels B and C of Figure 1). It is reasonable from the structure

of PPCMCF and the ratio of the monomer to PPCMCF. Therefore, it is reasonable to realize the difference between TGA and TEM.

After an alkaline-etching method,^{19,36} the results of the grafting polymerization of PNIPAm from PCMCF were further obtained using GPC (Figure 4). Oligodopamine, which can

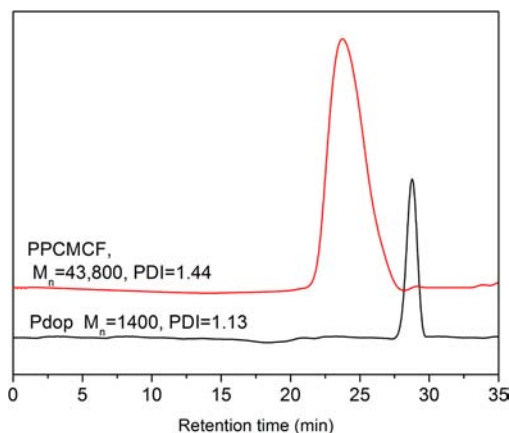


Figure 4. GPC traces of polymer retrieved from stimuli-responsive release fertilizers.

dissolve in THF, could be retrieved from P Dop with a strong alkaline solution, and the water-soluble inorganic solution was removed with adequacy of dialysis (MWCO = 500).³² The GPC curve with a narrow molecular weight distribution ($M_w/M_n < 1.5$) confirmed that the polydopamine-graft-polymer brush coating was prepared via ATRP of NIPAm from a P Dop-based ATRP initiator. The results demonstrated that PNIPAm brushes are grafted on PCMCF successfully.

The characteristics of controlled-release fertilizers are presented in Table 1. The determined contents of Cu, K₂O,

Table 1. Characteristics of Controlled-Release Fertilizers

fertilizers	P ₂ O ₅ (g/g)		K ₂ O (g/g)		Cu (g/g)	
	calcd ^a	meas ^b	calcd ^a	meas ^b	calcd ^a	meas ^b
MCF	0.412	0.421	0.0701	0.0796	0.286	0.287
PCMCF	0.324	0.316	0.0550	0.0597	0.225	0.228
PPCMCF	0.231	0.229	0.0392	0.0401	0.160	0.162

^aCalculated values. ^bMeasured values determined by ICP.

and P₂O₅ are almost consistent with the calculated values. The total amount of salt contained was determined using a sample digestion method for evaluating nutrient contents in PPCMCF. The contents of Cu, K, and P in the fertilizers were determined with ICP, after microwave-assisted digestion in the presence of a catalyst. The release behaviors of nutrients from fertilizer were determined, as discussed above.

Controlled-Release Behavior of PPCMCF. The nutrient release of the fertilizer is slow and does not reach equilibrium after 80 days, because MCF is a salt with relatively low water solubility. The release curve was obtained by plotting the concentration of elements normalized with the highest value versus time. The results indicate that the controlled-release fertilizers with a P Dop-g-PNIPAm coating have an excellent stimuli-responsive release behavior according to the temperature.

First, we investigated the release behaviors of nutrients from MCF, PCMCF, and PPCMCF at 25 and 37 °C, which are below and above the LCST of PNIPAm, respectively. Although the overall diffusion rate of elements was very slow, the thermosensitive solubility of the PNIPAm corona clearly made a difference. Figure 5 shows the release behavior of copper from

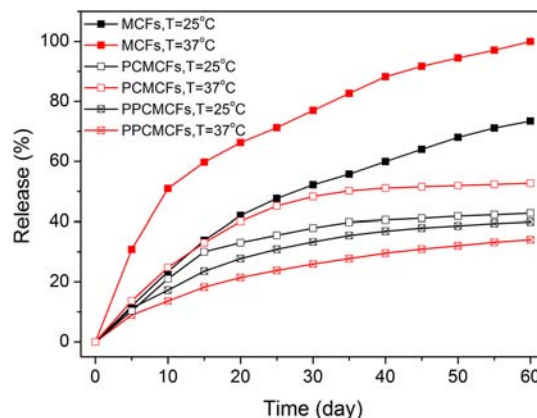
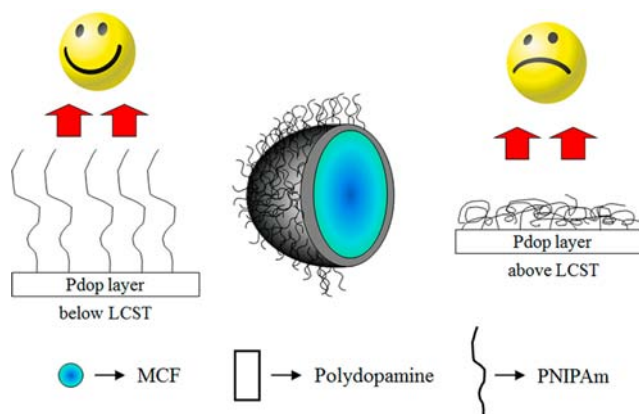


Figure 5. Stimuli-responsive release behavior of Cu from fertilizers at different temperatures.

fertilizers in different temperature solutions. The accumulative release rate of copper from MCF based on the relative intensity is 100 wt % (37 °C) and 73 wt % (25 °C) within 60 days. For PCMCFs, the release rate decreased to 52 wt % at 37 °C and 42 wt % at 25 °C. The results show that the P Dop coating could control the release behavior of entrapped nutrients, which are close to our previous studies.³³ It is noted that the accumulative release rate of Cu at high temperatures is faster than that at low temperatures, because an increase in the temperature represents an increase in the average molecular speed and diffusion occurs faster at higher temperatures. However, for PPCMCFs, the release rate appears faster at temperatures below LCST and the maximum achievable release of Cu is significantly lower at 37 °C than that at 25 °C. The accumulative release rates of Cu from PPCMCF at 37 and 25 °C are 33 and 39%, respectively. This difference in the release kinetics should originate from the thermal switch behavior of the PNIPAm layer, as shown in Scheme 2. At 37 °C, PNIPAm brushes are in a collapsed state, which makes the nutrient permeability of the multilayered

Scheme 2. Stimuli-Responsive Release Behaviors of PPCMCFs



polymeric coating low and slows the release rate of elements across the brush. In contrast, at 25 °C, thermosensitive chains are soluble, which opens the channel of the bilayer and favors release. Moreover, the release behavior of K and P has the same tendency (see Figure S1 of the Supporting Information). The Pdp inner layer plays a key role in both controlling the nutrient release and polymer-brush-grafted supports, and the PNIPAm thermosensitive corona could control the nutrients across the Pdp-g-polymer brush film according to the temperature.

The release rate of nutrients from an encapsulated fertilizer cannot be stopped at 37 °C, but the obviously slowed rate and the reduced amount of released elements make it possible to thermally switch the release of nutrients by switching the ambient temperature below and above the LCST. This control is demonstrated by the result presented in Figure 6. In a further

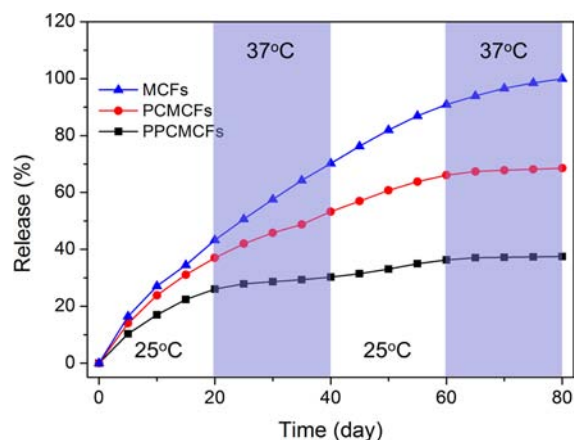


Figure 6. Stimuli-responsive release profile of Cu from PPCMCF recorded by switching the temperature between 25 and 37 °C.

experiment, PPCMCF was immersed in water at 25 °C. At first, the swollen PNIPAm corona allowed for the release of elements to release in a favorable condition, as is visible from the fast increase in the accumulative release. After 20 days of nutrient release, the temperature of solution was heated to 37 °C and the release became much slower because of the collapsed PNIPAm brushes. It is noted that, when the temperature cooled to 25 °C again, the faster release kinetics was recovered, and when heated to 37 °C for a second time, the release rate slowed again. This ability to turn on and slow the nutrient release by switching the ambient temperature makes these stimuli-responsive-coated systems highly attractive. With a further study on the effect of the medium temperature on the release of other nutrients (K and P), the results show that the temperature resulted in changing the release of elements (see Figure S2 of the Supporting Information). However, in a parallel test, the release curves of MCF and PCMCF show an upward tendency over time without a slowing step. This demonstrates that thermoresponsive polymer brushes would be challenging to prevent the nutrient release according to the temperature and these “polydopamine-g-polymer brushes” may be interesting for applications where a control of the release rate is mostly desired.

Last, a comparison of thermoresponsive release data for nutrients from PPCMCFs at 25 and 37 °C and switching data is shown in Figure 7. During the first 20 days, the accumulative release rate of Cu from PPCMCF at “switching” is almost

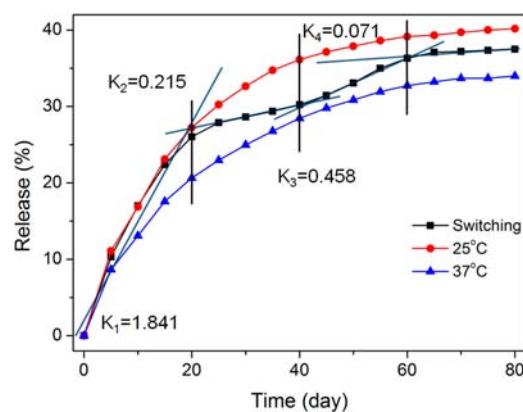


Figure 7. Thermoresponsive release behavior of Cu at different temperatures.

identical to 25 °C (the slope of the line is 1.841) and obviously faster than that at 37 °C, because the soluble thermoresponsive chains open the channel of the brushes and favor the release of elements. However, for the switching curve, when the temperature of medium was turned to 37 °C at the 20th day, the collapsed PNIPAm slowed the release rate ($K_2 = 0.215$) and diminished the rate from 36 wt % (25 °C) to 30 wt %. When the switch data cooled to 25 °C again, a faster release was recovered ($K_3 = 0.458$) and a 6% increase is obviously faster than that at 37 °C (only 3%). In the last 20 days, the solution temperature was turned to 37 °C again and a smoother release curve was obtained ($K_4 = 0.071$). A further experiment on thermoresponsive release of K and P is shown in Figure S3 of the Supporting Information. The results further imply that the release curves obtained certify that Pdp-g-PNIPAm-coated stimuli-responsive release fertilizers can control the nutrient release by adjusting the solution temperature.

A Pdp-g-PNIPAm-coated stimuli-responsive release MCF via mussel-inspired initiator ATRP was successfully prepared. The multifunctional layer formed by the Pdp inner shell and thermosensitive PNIPAm outer corona exhibited stimuli-responsive permeability for encapsulated nutrients depending upon the temperature. The Pdp-g-PNIPAm layers can release elements easily, at $T < LCST$. In contrast, they can reduce nutrient release, at $T > LCST$. The results showed that the Pdp-g-PNIPAm-coated controlled-release fertilizers with excellent thermoresponsive release could be expected to be promising in the research and development of coated fertilizers. Moreover, we could accomplish responsiveness to different external stimulus goals via changing the outer polymer brushes.

■ ASSOCIATED CONTENT

📄 Supporting Information

Stimuli-responsive release behavior of (A) K and (B) P from fertilizers at different temperatures (Figure S1), stimuli-responsive release profile of (A) K and (B) P from fertilizers recorded by switching temperature between 25 and 37 °C (Figure S2), and thermoresponsive release behavior of (A) K and (B) P from PPCMCF at different temperatures (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jiaxin@shzu.edu.cn.

Funding

This work was supported by the National Natural Science Foundation of China (21264013).

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Akelah, A. Novel utilizations of conventional agrochemicals by controlled release formulations. *Mater. Sci. Eng., C* **1996**, *4*, 83–98.
- (2) Wu, C. S. Promoting fertilizer use via controlled release of a bacteria-encapsulated film bag. *J. Agric. Food Chem.* **2010**, *58*, 6300–6305.
- (3) Davidson, E. A. The contribution of manure and fertilizer nitrogen to atmospheric nitrous oxide since 1860. *Nat. Geosci.* **2009**, *2*, 659–662.
- (4) Solihin; Zhang, Q. W.; Tongamp, W.; Saito, F. Mechanochemical route for synthesizing KMgPO_4 and NH_4MgPO_4 for application as slow-release fertilizers. *Ind. Eng. Chem. Res.* **2010**, *49*, 2213–2216.
- (5) Jin, S. P.; Yue, G. R.; Feng, L.; Han, Y. Q.; Yu, X. H.; Zhang, Z. H. Preparation and properties of a coated slow-release and water-retention biuret phosphoramidate fertilizer with superabsorbent. *J. Agric. Food Chem.* **2011**, *59*, 322–327.
- (6) Bandyopadhyay, S.; Bhattacharya, I.; Ghosh, K.; Varadachari, C. New slow-releasing molybdenum fertilizer. *J. Agric. Food Chem.* **2008**, *56*, 1343–1349.
- (7) Zhao, G. Z.; Liu, Y. Q.; Tian, Y.; Sun, Y. Y.; Cao, Y. Preparation and properties of macromolecular slow-release fertilizer containing nitrogen, phosphorus and potassium. *J. Polym. Res.* **2010**, *17*, 119–125.
- (8) Guo, M. Y.; Liu, M. Z.; Liang, R.; Niu, A. Z. Granular urea-formaldehyde slow-release fertilizer with superabsorbent and moisture preservation. *J. Appl. Polym. Sci.* **2006**, *99*, 3230–3235.
- (9) Ni, B. L.; Liu, M. Z.; Lu, S. Y.; Xie, L. H.; Zhang, X.; Wang, Y. F. Novel slow-release multielement compound fertilizer with hydroscopicity and moisture preservation. *Ind. Eng. Chem. Res.* **2010**, *49*, 4546–4552.
- (10) Xie, L. H.; Liu, M. Z.; Ni, B. L.; Zhang, X.; Wang, Y. F. Slow-release nitrogen and boron fertilizer from a functional superabsorbent formulation based on wheat straw and attapulgite. *Chem. Eng. J.* **2011**, *167*, 342–348.
- (11) Wang, W. B.; Wang, A. Q. Synthesis, swelling behaviors, and slow-release characteristics of a guar gum-g-poly(sodium acrylate)/sodium humate superabsorbent. *J. Appl. Polym. Sci.* **2009**, *112*, 2102–2111.
- (12) Ni, B. L.; Liu, M. Z.; Lu, S. Y. Multifunctional slow-release urea fertilizer from ethylcellulose and superabsorbent coated formulations. *Chem. Eng. J.* **2009**, *155*, 892–898.
- (13) Liang, R.; Liu, M. Z.; Wu, L. Controlled release NPK compound fertilizer with the function of water retention. *React. Funct. Polym.* **2007**, *67*, 769–779.
- (14) Mulder, W. J.; Gosselink, R. J. A.; Vingerhoeds, M. H.; Harmsen, P. F. H.; Eastham, D. Lignin based controlled release coatings. *Ind. Crops Prod.* **2011**, *34*, 915–920.
- (15) Jarosiewicz, A.; Tomaszewska, M. Controlled-release NPK fertilizer encapsulated by polymeric membranes. *J. Agric. Food Chem.* **2003**, *51*, 413–417.
- (16) Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. Mussel-inspired surface chemistry for multifunctional coatings. *Science* **2007**, *318*, 426–430.
- (17) Lee, H.; Lee, B. P.; Messersmith, P. B. A reversible wet/dry adhesive inspired by mussels and geckos. *Nature* **2007**, *448*, 338–341.
- (18) Zhang, L.; Wu, J.; Wang, Y.; Long, Y.; Zhao, N.; Xu, J. Combination of bioinspiration: A general route to superhydrophobic particles. *J. Am. Chem. Soc.* **2012**, *134*, 9879–9881.
- (19) Kang, S. M.; Rho, J.; Choi, I. S.; Messersmith, P. B.; Lee, H. Norepinephrine: Material-independent, multifunctional surface modification reagent. *J. Am. Chem. Soc.* **2009**, *131*, 13224–13225.
- (20) Fan, X.; Lin, L.; Dalsin, J. L.; Messersmith, P. B. Biomimetic anchor for surface-initiated polymerization from metal substrates. *J. Am. Chem. Soc.* **2005**, *127*, 15843–15847.
- (21) Yang, H.; Lan, Y.; Zhu, W.; Li, W.; Xu, D.; Cui, J.; Shen, D.; Li, G. Polydopamine-coated nanofibrous mats as a versatile platform for producing porous functional membranes. *J. Mater. Chem.* **2012**, *22*, 16994–17001.
- (22) Li, C. Y.; Wang, W. C.; Xu, F. J.; Zhang, L. Q.; Yang, W. T. Preparation of pH-sensitive membranes via dopamine-initiated atom transfer radical polymerization. *J. Membr. Sci.* **2011**, *367*, 7–13.
- (23) Wu, J.; Zhang, L.; Wang, Y.; Long, Y.; Gao, H.; Zhang, X.; Zhao, N.; Cai, Y.; Xu, J. Mussel-inspired chemistry for robust and surface-modifiable multilayer films. *Langmuir* **2011**, *27*, 13684–13691.
- (24) Ma, Z. Y.; Jia, X.; Hu, J. M.; Zhang, G. X.; Zhou, F.; Liu, Z. Y.; Wang, H. Y. Dual-responsive capsules with tunable low critical solution temperatures and their loading and release behavior. *Langmuir* **2013**, *29*, 5631–5637.
- (25) Ma, Z. Y.; Jia, X.; Zhang, G. X.; Hu, J. M.; Zhang, G. X.; Liu, Z. Y.; Wang, H. Y.; Zhou, F. pH-responsive controlled-release fertilizer with water retention via atom transfer radical polymerization of acrylic acid on mussel-inspired initiator. *J. Agric. Food Chem.* **2013**, *61*, 5474–5482.
- (26) Kohri, M.; Kohma, H.; Shinoda, Y.; Yamauchi, M.; Yagai, S.; Kojima, T.; Taniguchi, T.; Kishikawa, K. A colorless functional polydopamine thin layer as a basis for polymer capsules. *Polym. Chem.* **2013**, *4*, 2696–2702.
- (27) Xie, D. H.; Ye, X. D.; Ding, Y. W.; Zhang, G. Z.; Zhao, N.; Wu, K.; Cao, Y.; Zhu, X. X. Multistep thermosensitivity of poly(*N*-propylacrylamide)-*block*-poly(*N*-isopropylacrylamide)-*block*-poly(*N,N*-ethylmethylacrylamide) triblock terpolymers in aqueous solutions as studied by static and dynamic light scattering. *Macromolecules* **2009**, *42*, 2715–2720.
- (28) Feng, J. J.; Zhang, P. P.; Wang, A. J.; Liao, Q. C.; Xi, J. L.; Chen, J. R. One-step synthesis of monodisperse polydopamine-coated silver core-shell nanostructures for enhanced photocatalysis. *New J. Chem.* **2012**, *36*, 148–154.
- (29) Bazin, G.; Zhu, X. X. Understanding the thermo-sensitivity of crystalline colloidal arrays formed by poly(styrene-*co*-*N*-isopropylacrylamide) core-shell microspheres. *Soft Matter* **2012**, *8*, 1909–1915.
- (30) You, Y. Z.; Kalebaila, K. K.; Brock, S. L.; Oupický, D. Temperature-controlled uptake and release in PNIPAM-modified porous silica nanoparticles. *Chem. Mater.* **2008**, *20*, 3354–3359.
- (31) Plunkett, K. N.; Zhu, X.; Moore, J. S.; Leckband, D. E. PNIPAM chain collapse depends on the molecular weight and grafting density. *Langmuir* **2006**, *22*, 4259–4266.
- (32) Ma, Z. Y.; Jia, X.; Zhang, G. X.; Hu, J. M.; Zhang, X. L.; Liu, Z. Y.; Wang, H. Y.; Zhou, F. pH-responsive controlled-release fertilizer with water retention via ATRP of acrylic acid on mussel-inspired initiator. *J. Agric. Food Chem.* **2013**, *61*, 5474–5482.
- (33) Jia, X.; Ma, Z. Y.; Zhang, G. X.; Hu, J. M.; Liu, Z. Y.; Wang, H. Y.; Zhou, F. Polydopamine film coated controlled-release multielement compound fertilizer based on mussel-inspired chemistry. *J. Agric. Food Chem.* **2013**, *61*, 2919–2924.
- (34) Ciopec, M.; Muntean, C.; Negrea, A.; Lupa, L.; Negrea, P.; Barvinschi, P. Synthesis and thermal behavior of double copper and potassium pyrophosphate. *Thermochim. Acta* **2009**, *488*, 10–16.
- (35) Dreyer, D. R.; Miller, D. J.; Freeman, B. D.; Paul, D. R.; Bielawski, C. W. Elucidating the structure of poly(dopamine). *Langmuir* **2012**, *28*, 6428–6435.
- (36) Kang, S. M.; Park, S.; Kim, D.; Park, S. Y.; Ruoff, R. S.; Lee, H. Simultaneous reduction and surface functionalization of graphene oxide by mussel-inspired chemistry. *Adv. Funct. Mater.* **2011**, *21*, 108–112.