Supporting Information

Controlled-release Fertilizers with Ultralow Coating Content

Dunsheng Liang^{*a,b*}, Hebo Shi^{*a,b*}, Qiming Lu^{*a,b*}, Rafael L. Quirino^{*c*}, Chaoqun Zhang^{*a,b**}

^aKey Laboratory for Biobased Materials and Energy of Ministry of Education, College of Materials and Energy, South China Agricultural University, 483 Wushan Road, Guangzhou 510642, China.

^bGuangdong Laboratory for Lingnan Modern Agriculture, Guangzhou 510642, China

^cChemistry Department, Georgia Southern University, Statesboro, GA, 30460, USA.

*Corresponding author. E-mail: <u>zhangcq@scau.edu.cn</u>, <u>nwpuzcq@gmail.com</u>

Experimental Section/Methods

Materials

Castor oil (CO), with hydroxyl value of 208 mg of KOH/g of oil was purchased from Guangzhou Xinye Trading Co., Ltd (China). Polymethylene diisocyanate (PMDI, 30.5 wt.% NCO) was provided by Wanhua Chemical Group Co., Ltd. (China). Urea granule (with a granule size of approximately 2.8-4.5 mm) was purchased from Offshore Oil Toshima Co., Ltd (China). Magnesium chloride hexahydrate, ammonia, stearic acid, and cetyltrimethylammonium bromide were purchased from Tianjin Zhiyuan Chemical Co., Ltd. (China), Shanghai Zhenpin Chemical Co., Ltd. (China), Shanghai Boka Chemical Technology Co., Ltd. (China), and Tianjin Fuchen Chemical Co., Ltd. (China), respectively. Paraffin wax was purchased from Shanghai Yiyang Instrument Co., Ltd. (China). All raw materials were used without further purification.

Preparation of nano Mg(OH)₂ particles

Hierarchically nanostructured Mg(OH)₂ particles were synthesized from MgCl₂ and NH₄OH via an anti-deposition route. Typically, 7.5 g of MgCl₂.6H₂O and 75 mL of ethanol were mixed to form a homogenous solution at 70 °C, under gentle agitation. 0.06 g of cetyltrimethylammonium bromide was added as the nucleation agent. The mixture was then added, drop-wise, into a NH₄OH solution (41.7 g, 18.7-21%) under agitation over the course of 15 min. Agitation continued for 90 min after addition. Finally, the resulting mixture was maintained at room temperature for 5 h, followed by filtration and washing with ethanol to obtain white Mg(OH)₂ particles (yield: 74.92%).

Preparation of stearic acid-Mg(OH)₂ (STA-Mg(OH)₂) particles

Superhydrophobic STA-Mg(OH)₂ particles were obtained by an acid-base reaction between STA and Mg(OH)₂. 1.61 g of Mg(OH)₂ and 0.86 g of STA were dispersed into 90 mL of ethanol, and then stirred at 60 °C for 30 min. After filtration, washing with ethanol twice, and drying at 60 °C for 2 h, superhydrophobic STA-Mg(OH)₂ particles were obtained (yield: 71.36%).

Preparation of castor oil-based polyurethane films and nanocomposite films

Polyurethane films were prepared by the reaction between castor oil and PMDI with an OH:NCO molar ratio of 1.0:1.2. First, 3.20 g of castor oil and 1.80 g of PMDI were mixed

under vacuum (0.1 kPa) for 3 min and left undisturbed for another 4 min, resulting in a prepolymer. The pre-polymer was then cast on a glass plate with dimensions of 100 mm×200 mm (length×width). After that, pre-determined amounts of superhydrophobic STA-Mg(OH)₂ was deposited on the surface of the pre-polymer and cured at 80 °C for 30 min to obtain the superhydrophobic film. Paraffin wax was dissolved in *n*-hexane and the liquid was uniformly sprayed onto the surface of above superhydrophobic film by via spray nozzle at the atomizing pressure of 2.0 bars. Finally, the nano-composite film was obtained by condensation treatment at 50 °C for 10 min to remove the *n*-hexane. The samples were named PU-x-xx, where PU represented polyurethane, x represented the weight percentage of STA-Mg(OH)₂ powder to PU, and xx represented the weight percentage of paraffin wax to PU. By adjusting the content of STA-Mg(OH)₂ powder and paraffin, nano-composite films with tailorable performance were obtained.

Preparation of PU-coated urea granules

The coated fertilizer was prepared with polyurethane and polyurethane nanocomposites as the coating materials by a drum coating technique (as shown in Scheme S1). First, the castor oil derivatives and PMDI were stirred under vacuum (0.1 kPa) for 3 min to obtain the polyurethane pre-polymer. Then, the pre-polymer was poured into 200 g of urea granules in the rotating-drum with a rotating rate of 45 rad/min and the mixture was cured at 80 °C for 10 min to obtain the first-layer coating of coated fertilizer (0.5 wt.% of polyurethane relative to urea). The above coating process was repeated two times to obtain the second-layer coating and third-layer coating. After three layers of pre-polymer coatings, STA-Mg(OH)₂ particles were deposited to modify the third coating and cured at 80 °C for 30 min. Then, paraffin wax dissolved in n-hexane was applied on the surface of the coated urea granules and dried at 50 °C for 10 min to obtain the coated fertilizer. By adjusting the contents of polyurethane prepolymer, STA-Mg(OH)₂ particles, and paraffin wax, different samples were obtained and named PCUy-yy-yyy, where PCU stands for polyurethane-coated urea, "y" represents the coating content, and "yy" and "yyy" represent the weight percentages of STA-Mg(OH)₂ powder and paraffin wax to polyurethane, respectively.



Scheme S1 Preparation of the coated fertilizer from polyurethane with dual modification technique.

Characterization

The structure of STA-Mg(OH)₂ powders was characterized by a Nicolet 380 FTIR spectrometer (Thermo Scientific, Japan). The sample was mixed with KBr powder and compressed to form a clear pellet, then characterized at a wave number range of 400-4000 cm⁻¹ and a resolution of 4 cm⁻¹. The surface and cross-sectional morphology of coated fertilizers were characterized using a JEOL JSM-6380LA Quanta 200 scanning electron microscope. The water contact angle (WCA) of the coating was tested using a JC2000C1 goniometer (POWEREACH, China) at room temperature and averaged after three parallel tests using deionized water (5 μ L). A X-ray diffractometer (XRD, XD-2X/M4600, China) with monochromatic CuK α radiation was used to investigate crystalline phases observable in the angular range of 10°< 20 <80° with a stepping rate of 10°/min. X-ray photoelectron spectroscopy (XPS, Thermo K-alpha) with Al-K α radiation was employed to analyze elements and functional groups.

Nutrient release characteristics of PCUs

The nutrient release characteristics of the PCUs prepared were determined according to ISO18644-2016. Briefly, a sample of 10.0 g was incubated in an Erlenmeyer flask containing 200 mL of distilled water at room temperature. 200 mL of releasing media was collected and equal volume of fresh releasing media was added at pre-determined time intervals until the nitrogen cumulative release rate of fertilizers reached over 80%. The N release rates were calculated after 1 day, 3 days, 5 days, 7 days, 14 days, 28 days, 35 days, and 42 days according to the Kjeldahl method. The nitrogen amounts in the releasing media were measured at 430 nm using a UV spectrophotometer (Metash, China). Nitrogen cumulative release rate was calculated as follows.

Nitrogen cumulative release rate (%) =
$$\frac{m}{m_0} \times 100$$

Where " m_0 " and "m" are the total nitrogen amounts of the controlled-release fertilizer and the nitrogen cumulative amounts of the controlled-release fertilizer at pre-determinded time intervals. Nitrogen cumulative release rate after immersion for 24 hours was defined as the initial N release rate. N release longevity of each sample was established as the time required for the cumulative nutrient release to achieve 80%.". The tests for all PCUs were performed in triplicate and the nutrient release rate reported was the average value for all samples.

The kinetic release data of the controlled-release fertilizer was analyzed for goodness of fit with the four classic mathematical models, including Zero-order kinetic model, First-order kinetic model, Higuchi model and Korsmeyer-Peppas model as summarized in Table S1.

Model	Equations	Y	X
Zero-order kinetic	$\frac{R_t}{R_{\infty}} = kT - R_0$	$\frac{R_t}{R_{\infty}}$	Т
First-order kinetic	$\frac{R_t}{R_{\infty}} = R_0 e^{kT}$	$\log(\frac{R_t}{R_{\infty}})$	Т
Higuchi	$R_t = P T^{0.5}$	R _t	$T^{0.5}$
Korsmeyer-Peppas	$\frac{1}{R_{\infty}} - K_0 I$	$\overline{R_{\infty}}$	logT

Table S1. Mathematical models used to evaluate the release kinetics of CRFs

$$\frac{R_t}{R_{\infty}} = kT^n \qquad \qquad \log(\frac{R_t}{R_{\infty}})$$

Where R_t stands for the nutrient cumulative release rate after time T. $R\infty$ and R_0 are cumulative nutrient release rate to achieve 80% and the initial N release rate of coated fertilizer, respectively. K and n represent the release rate constant and the release exponent for the fertilizer release mechanism. The values of k, n, and R^2 were calculated by linear curve fitting using OriginPro9. When 0 < n < 0.5, the semipermeable coating membrane exhibited a Fickian diffusional release mechanism. When 0.5 < n < 1 and n > 1, a non-Fickian transport and a super Case II transport were observed for the Korsmeyer-Peppas kinetic model, respectively.

Swelling rate

The swelling rate was measured by the drainage method. Briefly, 1.0 g of the coated fertilizer was placed in a beaker with 20 mL of deionized water. The sample was removed after 0 days, 1 day, 3 days, 5 days, 7 days, 10 days, 14 days, and 21 days and dried using paper towel. The coated fertilizer was finally put into a graduated cylinder with 4.0 mL of deionized water and the change in volume was recorded. The swelling rate was calculated as follows.

Swelling rate
$$(\%) = \frac{V}{V_0} \times 100$$

Where " V_0 " and "V" are the original volume of the coating material and the volume of the coated fertilizer after soaking. The characterization was carried-out in triplicate.

Pot experiment

Red soil was obtained from South China Agricultural University and was air-dried before being ground into particles with a diameter of less than 2 mm. Samples without urea (Control group), with 0.3 g of urea (Black group), and PCU1.5-6-20 were added to the top of 210 g of dry soil, and covered with 40 g of dry soil in a plastic pot (8.5 cm x 9 cm x 7.5 cm, height x top diameter x bottom diameter). Two seeds (Zhongnong 488) were placed in the soil and another 40 g of soil were added. Sufficient deionized water was added to maintain the soil at 30-40% humidity. After germination, 50 mL of deionized water were added every two days, and the leached solution was collected to determine urea concentration. On the twentieth day, corn seedlings were collected and their fresh weight, dry weight, seedling height, and root length were measured.

Statistical analysis

Statistical comparisons were analyzed in one-way analysis of variance (ANOVA) by the Statistical Package for the Social Sciences (SPSS, version 23.0) software to calculate standard deviations (SD). Statistical significance: *p < 0.05, **p < 0.01, ***p < 0.005.



Fig. S1 The FTIR of sample. The FTIR spectra of STA, $Mg(OH)_2$ and STA- $Mg(OH)_2$ at a wave number range of 1300-1800 cm⁻¹, respectively.



Fig. S2 The FTIR spectra of castor oil (CO), polymethylene diisocyanate (PMDI), and polyurethane (PU), respectively.



Fig. S3 Surface topography of coated fertilizers encapsulated with PU nanocomposites. (a, b, c and d) Surface view of the controlled-release fertilizer PCU1.5-0-0, PCU1.5-3-0, PCU1.5-6-0 and PCU1.5-9-0, respectively.



Fig. S4 Cumulative N release rate of controlled release fertilizer in water at 25 °C. Release curves of PCU with (a) different content of STA-Mg(OH)₂ and (b) different content of wax.



Fig. S5 Nutrient content in eluent for pot experiment.



Fig. S6 (a and b) The image of PCU1.5-0-0, PCU1.5-6-0 and PCU1.5-6-20 in the water,

respectively.

Table S2. Surface roughness

Sample Surface roughness (nm)

PU1.5-0-0	14
PU1.5-6-0	142
PU1.5-6-20	125

Table S3. Pot experiment results

Sample	Fresh weigh	Dry weigh	Root length	Seeding length
	(g)	(g)	(cm)	(cm)
Control	1.13±0.24	0.16±0.02	19.8±10.6	42.0±12.40
Black	1.19±0.56	0.18±0.06	16.6±6.32	43.3±8.40
PCU1.5-6-20	2.04±0.34	0.23±0.03	32.3±5.52	63.2±6.31