



Minerva Access is the Institutional Repository of The University of Melbourne

Author/s:

Mazaheri, Omid

Title:

Metal-Phenolic Networks: From Fundamental to Agricultural Applications

Date:

2022

Persistent Link:

<https://hdl.handle.net/11343/326448>

Terms and Conditions:

Terms and Conditions: Copyright in works deposited in Minerva Access is retained by the copyright owner. The work may not be altered without permission from the copyright owner. Readers may only download, print and save electronic copies of whole works for their own personal non-commercial use. Any use that exceeds these limits requires permission from the copyright owner. Attribution is essential when quoting or paraphrasing from these works.

Metal-Phenolic Networks: From Fundamental to Agricultural Applications

Omid Mazaheri

ORCID ID: 0000-0002-9749-9842

Doctor of Philosophy

December 2022

Faculty of Veterinary and Agricultural Sciences

&

Department of Chemical Engineering

The University of Melbourne

*A thesis submitted in total fulfilment of the requirements for the
degree of Doctor of Philosophy at the University of Melbourne*

Abstract

Urea, as a nitrogen-rich fertilizer, plays a vital role in increasing and maintaining soil fertility, and crop yield. The efficiency of urea as a fertilizer reduces through ammonia volatilization, nitrification, denitrification, nitrate leaching to groundwater, and runoff. Nitrogen loss can be reduced through controlled-release ureas (CRUs), which can control the physicochemical release of urea in soil. Materials used for the fabrication of CRUs are mostly non-biodegradable polymers, which further spread pollutants into the environment. In an effort to reduce environmental impact, this thesis investigated the possibility of using metal-phenolic networks (MPNs) as a means of coating urea such that the MPN coating provides a physical barrier against water, controlling urea dissolution and release into soils.

Self-assembly of MPNs in a non-aqueous solvent (acetonitrile) on urea granules was first conducted to engineer thickness-tunable coatings. Tannic acid and iron ions were chosen as model compounds for the assembly of MPNs. Varying operational conditions were assessed to determine the underlying mechanism for which MPNs were formed. Specifically, parameters, including the MPN self-assembly method, solution aging time, metal-to-ligand molar ratio, precursor concentration, and processing temperature all influenced the formation kinetics, thickness, and surface roughness of the films. Upon placement of coated urea granules in water the complete dissolution of urea occurred within 3-5 hours. The release rate of urea in water was controlled *via* the pH-dependent behavior of the self-assembled MPNs.

Although urea coated with MPNs could control the dissolution of urea, the fabrication of CRU involved the use of solvent, which makes it not ideal for large-scale manufacturing processes where the volume of liquid media required makes handling difficult. Thus, in the second effort, a one-step mechanochemical grinding approach was utilized to synthesize MPNs in the absence of solvent. After an investigation of the mechanism of MPN formation in solvent-free

conditions, the fabricated material demonstrates tunable mechanical resistance and stiffness that adjust with aging and thermal post-treatments. It is demonstrated that the encapsulated urea within MPNs can prolong the release period of nitrogen in the soil by up to 9 days depending on the type of post-treatment applied.

This work provides a systematic understanding of the possible formation of MPNs using the self-assembly coating technique in non-aqueous media on urea granules (chapter 3) and encapsulation of urea in the MPN matrix (chapter 4). These simple fabrication methods open new chapters for utilizing environmentally friendly materials to control-the release of urea. The implementation of environmentally friendly materials is a key consideration in addressing the challenge of more sustainable and socially responsible agricultural production.

Declaration

This is to certify that:

- (i) This thesis comprises only my original work except where indicated in the Preface;*
- (ii) Due acknowledgment has been made in the text to all other material used; and*
- (iii) This thesis is less than 100,000 words in length, exclusive of tables, bibliographies, appendices, and footnotes.*

Omid Mazaheri

Faculty of Veterinary and Agricultural Sciences
Department of Chemical Engineering
The University of Melbourne

Preface

This thesis is comprised of five chapters. *Chapter 1* is the introduction, followed by the literature review (*Chapter 2*) which summarizes previous research work. *Chapters 3* and *4* are research experiments and discussions. The main contents in these chapters have been published (chapter 3) or are under revision for publication (chapter 4). *Chapter 5* is the general conclusions and outlook, which highlights the key findings and suggests directions for further research.

The candidate was the primary author of all manuscripts. The candidate was responsible for designing and conducting the experiments, collecting, analyzing, and interpreting the data, and writing the original manuscripts. The co-authors were involved in improving the experimental design, conducting some characterizations, and editing the manuscripts. Overall, *Chapters 3* and *4* contain 70% of my original research studies.

Chapter 3 of this thesis has been published in the following article:

O. Mazaheri, M.S. Alivand, A. Zavabeti, S. Spoljaric, S. Pan, D. Chen, F. Caruso, H.C. Suter, and K.A. Mumford, Assembly of Metal–Phenolic Networks on Water-Soluble Substrates in Nonaqueous Media, *Advanced Functional Materials*, **2022**, 32, 2111942.

The manuscript of *Chapter 4* is under revision for publication

Publications

The following publications have been produced during the PhD candidature:

- **O. Mazaheri**, M.S. Alivand, A. Zavabeti, S. Spoljaric, S. Pan, D. Chen, F. Caruso, H.C. Suter, and K.A. Mumford, Assembly of Metal–Phenolic Networks on Water-Soluble Substrates in Nonaqueous Media, *Adv. Funct. Mater.*, **2022**, 32, 2111942.
- M.S. Alivand, **O. Mazaheri**, Y. Wu, A. Zavabeti, G.W. Stevens, A.C. Scholes, and A.K. Mumford, Engineered Assembly of Water-Dispersible Nanocatalysts Enables Low-Cost and Green CO₂ Capture, *Nat. Commun.*, **2022**, 13, 1249.
- M.S. Alivand, **O. Mazaheri**, Y. Wu, A. Zavabeti, G.W. Stevens, C.A. Scholes, A.K. Mumford, Water-Dispersible Nanocatalysts with Engineered Structures: The New Generation of Nanomaterials for Energy-Efficient CO₂ Capture, *ACS Appl. Mater. Interfaces*, **2021**, 13, 57294.
- M.S. Alivand, **O. Mazaheri**, Y. Wu, A. Zavabeti, G.W. Stevens, C.A. Scholes, Catalytic Solvent Regeneration for Energy-Efficient CO₂ Capture, *ACS Sustainable Chem. Eng.*, **2020**, 8, 51, 18755.
- A. Dashti, **O. Mazaheri**, F. Amirkhani, A.H. Mohammadi, Molecular Descriptors-Based Models for Estimating Net Heat of Combustion of Chemical Compounds, *Energy*, **2020**, 217, 119292.
- M.S. Alivand, **O. Mazaheri**, Y. Wu, G.W. Stevens, C.A. Scholes, K.A. Mumford, Preparation of Nanoporous Carbonaceous Promoters for Enhanced CO₂ Absorption in Tertiary Amines, *Engineering*, **2020**, 6, 1381.
- R.J. Kalbasi, F. Rahmati, **O. Mazaheri**, Overcoming Acid–Base Copolymer Neutralization Using Mesoporous Carbon and its Catalytic Activity in the Tandem Deacetalization–Knoevenagel Condensation Reaction, *Res. Chem. Intermed.*, **2020**, 46, 3413.
- A. Reyhani, **O. Mazaheri**, M.S. Alivand, K.A. Mumford, G. Qiao, Temporal Control of RAFT Polymerization via Magnetic Catalysis, *Polym. Chem.*, **2020**, 11, 2838.
- M.S. Alivand, **O. Mazaheri**, Y. Wu, G.W. Stevens, C.A. Scholes, K.A. Mumford, Development of Aqueous-Based Phase Change Amino Acid Solvents for Energy-Efficient CO₂ Capture: the Role of Antisolvent, *Appl. Energy*, **2019**, 256, 113911.
- M.S. Alivand, **O. Mazaheri**, Y. Wu, G.W. Stevens, C.A. Scholes, K.A. Mumford, Development of Aqueous-Based Phase Change Amino Acid Solvents for Energy-Efficient CO₂ Capture: the Role of Antisolvent, *Data in Brief*, **2019**, 27, 104741.
- M.S. Alivand, M. Najmi, N.H.M.H. Tehrani, A. Kamali, O. Tavakoli, A. Rashidi, M.D. Esrafil, E. Ghasemy, **O. Mazaheri**, Tuning the Surface Chemistry and Porosity of Waste-Derived Nanoporous Materials Toward Exceptional Performance in Antibiotic Adsorption: Experimental and DFT Studies, *Chem. Eng. J.*, **2019**, 374, 274.

Acknowledgments

First of all, I would like to thank *A/Prof. Helen C. Suter* as my primary supervisor for allowing me to do the PhD research. I am so grateful for her supervision and guidance throughout my PhD candidature not only because of the valuable academic advice but also for her being emotionally supportive during the difficult times. She gave me the freedom and support to do research that I was interested in. Along with Helen, I would like to express my sincere gratitude to *A/Prof. Kathryn A. Mumford* for her continuous encouragement and unfailing support and step-by-step guidance during my whole candidature. I am incredibly appreciative of your guidance throughout my PhD and for helping me transition into the next phase of my career. Also, I would also like to express my appreciation to my co-supervisor *Prof. Deli Chen* for his generous help and continuous support. He always encouraged me to participate in academic activities and establish connections with other scholars. To my committee chair, *Prof. Jizheng (Jim) He* thank you for your continuous support and feedback.

To the member of Caruso Nanoengineering Group at the Department of Chemical Engineering, I also extend a huge thanks. I especially recognize *Prof. Frank Caruso* for kindly welcoming me into his labs. He taught me how to find interesting questions and accordingly design experiments to solve them. I would also like to thank *Dr. Roya Khalil* from Incitec Pivot Fertiliser for helpful discussions on industrial concepts of the works and *Dr. Steve Spoljaric*, *Dr. Shuaijun Pan*, *Dr. Chan-Jin Kim*, *Dr. Jingqu Chen*, *Mr. Abhishek Mondal*, and *Mr. Junnan Lu* for helpful discussions in *chapter 3* of this thesis. Additional thanks go to *Dr Ali Zavabeti*, *Dr. Alex Duan*, and *Dr. Jay Black* for conducting characterizations from my materials and analytical advice.

To all of my colleagues in the Faculty of Veterinary and Agricultural Sciences and the Department of Chemical Engineering, thank you for making this journey memorable. I would like to especially acknowledge *Dr. Masood S. Alivand* for his friendship and continuous insight over the last few years through different collaborative projects. I would like to express my sincere gratitude to *Rebecca V. McQuillan* for her friendship and enthusiastic presence in the office hours endured with an extremely positive attitude. It has been an absolute pleasure working with all of you.

The financial support offered by “the University of Melbourne - Melbourne Research Scholarship” is particularly appreciated. I am also honored to have received the Rowden White award during my candidature. I would also like to acknowledge the partial financial support of the Australian Research Council (ARC) Industrial Transformation Research Program funding scheme (IH200100023), the ARC Linkage Project funding scheme (LP160101417), and the ARC Discovery Project funding scheme (DP200100713).

And lastly, to all of my family and friends in Australia, the United States, and Iran who have stood by me and provided me with encouragement when I needed it most. I am especially forever indebted to my mother *Sousan* and my brother *Amir*, who have supported me in my study abroad and provided me with feedback, insight, and unconditional love. Finally, I am very grateful to thank *Oranous* for her unconditional love, countless encouragement, and endless support. She is the one who understands me best, celebrates every small achievement for me, and faces all the difficulties with me. Thanks for having you in my most wonderful years.

Table of Contents

Abstract.....	i
Declaration.....	iii
Preface.....	iv
Publications.....	v
Acknowledgments.....	vi
1 Introduction	1
1.1 Research background	3
1.2 Significance and Scope of Thesis.....	4
1.3 Objectives of the study	5
2 Literature review.....	7
2.1 Controlled-release Fertilizer (CRF) and its classification.....	9
2.1.1 Organic compounds (inhibitors, nutrient-rich natural compounds, and urea derivatives)	10
2.1.2 Physical barriers.....	11
2.1.3 Sulfur-based CRFs	11
2.1.4 Mineral-based CRFs	12
2.1.4.1 Polymer-based CRFs	13
2.1.4.2 Hydrophobic CRFs	14
2.1.4.3 Polysaccharides	28
2.1.4.4 CRFs from Hydrogel Polymers.....	29
2.2 Fabrication methods of CRFs.....	35
2.3 Mixing-type CRFs.....	35
2.4 Coated-type CRFs	37
2.5 The release mechanism of CRFs.....	38
2.6 Metal-Phenolic Networks.....	40
2.7 Conclusion.....	40
3 Assembly of Metal–Phenolic Networks on Water-Soluble Substrates in Nonaqueous Media	42
3.1 Abstract	44
3.2 Introduction	44
3.3 Results and Discussion.....	47
3.3.1 MPN Formation in Acetonitrile	47
3.4 Factors Influencing MPN Formation and Growth	54

3.4.1	Effect of Solution Aging Time	54
3.4.2	Effect of Precursor Ratio	56
3.4.3	Effect of Precursor Concentration	59
3.4.4	Effect of MPN Deposition Cycles	61
3.4.5	Effect of Temperature	61
3.5	Release Profile of Urea from Urea Granules@MPN Samples.....	62
3.6	Conclusion.....	65
3.7	Supplementary Information.....	67
3.7.1	Experimental Section.....	67
3.7.1.1	Materials	67
3.7.1.2	Methods	67
3.7.1.3	Characterization.....	74
3.7.1.4	Figures	81
3.7.1.5	Tables.....	113
4	Encapsulation of Urea into Metal-Phenolic Networks as Controlled-Release Urea: A Mechanochemical approach.....	116
4.1	Abstract	118
4.2	Introduction	119
4.3	Results and Discussion.....	122
4.3.1	Mechanochemical formation of MPN	122
4.3.2	Aging and thermal treatment of urea@MPN _{Ti}	126
4.3.3	Bulk properties of urea@MPN _{Ti} following aging and thermal treatments.....	128
4.3.4	Structural and lattice properties of urea@MPN _{Ti} after aging and thermal treatments.....	131
4.3.5	Agricultural application of urea@MPN as controlled-release urea.....	133
4.4	Conclusion.....	138
4.5	Supplementary Information.....	138
4.5.1	Experimental Section.....	138
4.5.1.1	Materials	138
4.5.1.2	Methods	139
4.5.1.3	Characterization.....	142
5	Conclusion and outlooks	147
5.1	Thesis summary.....	149
5.2	Recommendations for future work.....	151
6	References	154

List of Figures

Figure 1.1. Main processes of the nitrogen cycle in soil and the pathways of N uptake and loss, and different pathways to control the urea release, hydrolysis, and nitrification.	4
Figure 2.1. Classification of controlled-release fertilizer (CRF) according to the different materials used in the synthesis. Non-polymer and polymer-based materials are highlighted in gray and green, respectively.	10
Figure 2.2. Schematic illustration of double layered coating of urea granules using bio-based polyurethane and nano lauric acid copper. Adapted with permission from ref 62. Copyright 2019 Royal Society of Chemistry.	21
Figure 2.3. 3D reconstruction images and polarization micrograph of modified urea granules (D1 and D2) with the water phase highlighted blue and the air phase highlighted purple. The air phase (purple) is extracted and highlighted (D3 and D4); schematic of common superhydrophobic controlled-release mechanisms (E1–E4), and nano lauric acid copper-modified coated urea granules (F1–F4). Adapted with permission from ref 62. Copyright 2019 Royal Society of Chemistry.	22
Figure 2.4. Modification of frying oil to produce bio-based polyurethane and coating it on the urea granules. Adapted with permission from ref 64. Copyright 2017 American Chemical Society.....	25
Figure 2.5. (upper) schematic of the CRU formation, (lower) (A) optical image of coated urea granules with polymer before (left) and after (right) fluorine functionalization, (B) model diagram of the CRU, (C) schematic of the CRU after being immersed in water. Adapted with permission from ref 66. Copyright 2017 American Chemical Society.....	28
Figure 2.6. Fabrication of CRU using wheat straw as bio-based polysaccharides. Adapted with permission from ref 67. Copyright 2017 Royal Society of Chemistry.....	29
Figure 2.7. Examples of cellulose etherification using etherification agents. (a) epichlorohydrin, (b) monochlorotriazinyl-cyclodextrin, and (c) acrylamide and benzyl chloride. Adapted with permission from ref 8. Copyright 2019 Elsevier.....	34
Figure 2.8. The common methods to fabricate CRFs.	37
Figure 2.9. Diffusion mechanism of CRFs; (step 1) covering a solid fertilizer using a polymer, (step 2) water penetrating the coating, (step 3) solid fertilizer dissolution and increasing the osmotic pressure inside the coated granules, (step 4) swallowing coating membrane and release the fertilizer [From Haifa slide presentation [103]].	39
Figure 2.10. The mechanism of nutrient release from hydrogel materials. Adapted with permission from ref 8. Copyright 2019 Elsevier.	39
Figure 3.1. Influence of solution aging time on Fe ^{III} –TA complex formation in acetonitrile before the addition of urea granules. (a) Photograph of Fe ^{III} –TA solutions showing solution color changes as a function of solution aging time. (b) UV–Vis spectra of Fe ^{III} –TA solutions at different solution aging times. (c) Schematic illustration of the formation of Fe ^{III} –TA complexes in acetonitrile solution at different solution aging times. (d) UV–vis spectra of Fe–TA solution at different solution aging times after addition of 1,10-phenanthroline indicator. All data are for systems prepared with a final concentration of 2.3 mM TA and an M:L molar ratio of 1.5:1 at 25 °C.....	50
Figure 3.2. Formation of MPN film on urea granules. (a) UV–Vis spectrum of Fe ^{III} –TA solution in acetonitrile after immersion of urea granules; the highlighted area (500–665 nm)	

corresponds to the LMCT band of the Fe^{III} -TA complexes. (b) Raman spectrum of the MPN film deposited on the urea granules. (c) XPS pattern of the MPN film deposited on the urea granules (Fe 2p area). (d–g) SEM images of the surfaces of urea granules@MPN showing the time-dependent growth of an MPN film on urea granules following immersion of the urea granules in the Fe^{III} -TA solution: 0 min (uncoated urea granule) (d); 15 min (e); 30 min (f); and 45 min (g). The inset in (g) shows an SEM cross-section image of urea granules@MPN. All data are for systems prepared with a final concentration of 2.3 mM TA, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min at 25 °C.....54

Figure 3.3. Influence of solution aging time on Fe^{III} -TA particle formation in acetonitrile after the addition of urea granules into the Fe^{III} -TA solution. (a, b) Fe^{III} -TA particle growth and population distribution (number weight) using solution aging times of 1 and 60 min, as measured by FBRM. (c, d) SEM images of the surface of MPN films coated on urea granules prepared using solution aging times of 1 and 60 min. Scale bars are 250 μm . All data are for systems prepared with a final concentration of 2.3 mM TA and an M:L molar ratio of 1.5:1 at 25 °C. 55

Figure 3.4. Influence of precursor ratio on MPN film formation after addition of urea granules into the aged solution. (a) Surface roughness of the MPN films prepared at different M:L molar ratios, as measured by AFM (the inset shows a representative SEM image of the external surface of an MPN film on urea granules prepared at an M:L ratio of 1.5:1; scale bar is 100 μm). (b) Corresponding thickness profiles of MPN films prepared at different M:L ratios, as measured from the cross-section SEM images. Inset shows a schematic representation of the film thickness. (c) Thermograms of MPN films prepared at different M:L molar ratios. (d) Schematic representation of the interactions of gallic acid units of TA with Fe^{III} and different types of bond breakage during heating of the MPN film. (e) M:L molar ratio profiles of the MPN films measured by XPS (bar graph) and Fe content in the MPN films measured by ICP-AES (yellow line) as a function of the theoretical M:L molar ratio in mixed solutions. All data are for systems prepared with a final concentration of 2.3 mM TA and a solution aging time of 15 min at 25 °C. 58

Figure 3.5. Influence of precursor concentration on MPN film formation. (a–c) FBRM analysis of growth of Fe^{III} -TA particles and their population distribution in Fe^{III} -TA solutions of varying TA concentrations (insets show the corresponding SEM images of the surface morphology of the MPN films coated on urea granules (scale bars are 100 μm)). (d) Size distribution of Fe^{III} -TA particles formed in Fe^{III} -TA solutions of varying TA concentrations. (e) Corresponding thickness profiles of the MPN films prepared using Fe^{III} -TA solutions of varying TA concentrations, as measured from the cross-section SEM and optical profiler images (inset shows an optical profiler image of an MPN film prepared with 4.7 mM TA) (scale bar is 50 μm). (f) MPN content in urea granules@MPN prepared using Fe^{III} -TA solutions of varying TA concentrations and Fe content in MPN films obtained using Fe^{III} -TA solutions of varying TA concentrations, followed by removal of urea granules. All data are for systems prepared using an M:L molar ratio of 1.5:1 and a solution aging time of 15 min at 25 °C. 60

Figure 3.6. Effect of deposition cycle and temperature on MPN film formation. (a, b) Micro-CT images of an MPN film on a urea granule after the 1st and 10th MPN film deposition cycles, and (c, d) corresponding cross-section images of urea granules@MPN sectioned in half and (e, f) volume reconstruction of the micro-CT data from approximately 1500 scan projections. (g) Thickness profiles of MPN films prepared at different temperatures, as

measured from the cross-section SEM images and optical profiler images (inset shows a micro-CT image of a sample prepared at 60 °C). Scale bars in all micro-CT images are 1 mm. All data are for systems prepared with a final TA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min.....61

Figure 3.7. Cumulative release rate of urea in water at 25 °C, measured by colorimetric method, from urea granules@MPN samples prepared (a) using different MPN deposition cycles and (b) at different solution temperatures. Samples were prepared at a TA concentration of 2.3 mM, M:L molar ratio of 1.5:1, and a solution aging time of 15 min. The temperature used for the samples examined in **Figure 3.7a** was 25 °C. 65

Figure 4.1. Urea-mediated coordination-driven assembly of MPN via grinding. (a) Schematic illustration of the preparation of urea@MPN via grinding of urea, TA, and Ti^{IV} precursors and possible complexation states of TA- Ti^{IV} . (b) UV-Vis DRS spectra of urea, TA, TA- Ti^{IV} , and urea@MPN after grinding; the highlighted area (400–700 nm) corresponds to the LMCT band of the TA- Ti^{IV} complexes. (c) XPS patterns of the TA- Ti^{IV} complexes and urea@MPN (Ti 2p area). (d) XPS patterns of the TA, TA- Ti^{IV} complexes, and urea@MPN (O 1s area). (e) Raman spectra of urea-TA, TA- Ti^{IV} complexes, and urea@MPN. (f-h) SEM images of the surfaces of TA, ground urea, and urea@MPN. Scale bars are 10 μm . (i) HAADF and EDX mapping images of urea@MPN. Scale bars are 5 μm 125

Figure 4.2. Influence of aging and thermal treatments on physicochemical properties of urea@MPN. (a) UV-Vis DRS spectra and (b-c) High resolution XPS spectra of N 1S and C 1S areas of fresh, aged, and heated urea@MPN samples. (d) ν_1/ν_2 ratio profiles (bar graph) and $\Delta\nu_1-\nu_2$ difference (black line) of TA- Ti^{IV} , fresh, aged, and heated urea@MPN samples measured by Raman spectroscopy. (e) FTIR spectra of urea-TA, fresh, aged, and heated urea@MPN samples. (f) Crystallinity degree of TA- Ti^{IV} , fresh, aged, and heated urea@MPN samples measured by XRD from $2\theta = 5-80$ 127

Figure 4.3. Influence of aging and thermal treatments on the mechanical and bulk properties of urea@MPN samples. (a) Compressive stress-strain curves, (b) calculated required energy for 25% deformation, and (c) corresponding Young's modulus values from elastic regions of compression tests of urea, fresh, aged and heated samples. (d) and (e) DSC and TGA, respectively, from fresh, aged, and heated urea@MPN samples. (f) Water contact angle measured from urea, fresh, aged, and heated samples. (g-h) Micro-CT images from urea@MPN samples after aging and thermal treatments, respectively (inset show the cross-section images). (i) volume reconstruction of the micro-CT data from ≈ 1200 scan projections from aged and heated samples. 131

Figure 4.4. Structurally modulated urea crystals in urea@MPN via aging and thermal treatments. (a,b) SEM images of the surface of samples after aging and heating processes. (c) A schematic of urea crystals in the urea@MPN samples after aging and heating treatments. TEM (d,e), SAED (f,g), high-resolution TEM (h,i), and HAADF-mapping images (j,k) of urea@MPN after aging and heating treatments, respectively. Inset in f and j represents the atomic structure of urea crystals. 133

Figure 4.5. Cumulative release rate of urea in soil, measured by colorimetric protocol, from urea@MPN samples as shown in (a) using different treatments (b), MPN contents (c), and metals (d). Cumulative release rate of urea at (e) different environmental temperature, and (f) moisture content of the soil from urea@MPN_{Ti} prepared with 40% MPN content. Three experiments were investigated for each sample, with the data shown as the mean $\pm$ standard deviation.....136

Figure 4.6. Physical property changes of urea@MPN after being in contact with water and soil. Water-holding capacity of urea@MPN_{Zr} and urea@MPN_{Ti} prepared using different content of MPN(a). Water-holding capacity of the soil after applying different percentages of urea@MPN (b), and water-retention of soil after mixing with urea@MPN. 137

List of Schemes

Scheme 2.1. Synthesis mechanism of polyurethane using castor oil Adapted with permission from ref 61. Copyright 2012 American Chemical Society.	20
Scheme 2.2. The structure of common crosslinking agents used for preparation of polyurethane.....	23
Scheme 2.3. Modification of vegetable fatty acid oils to polyols by (a) transition metal carbonylation, (b) oxidation method, (c) transesterification reaction, (d) ammonolysis, and (e) epoxy ring-opening method. Adapted with permission from ref 7. Copyright 2022 Elsevier.	24
Scheme 2.4. Schematic illustration of polyurethane synthesis using soybean oil. Adapted with permission from ref 65. Copyright 2019 Elsevier.	26
Scheme 2.5. The general process for the preparation of cottonseed polyurethane. Adapted with permission from ref 66. Copyright 2017 American Chemical Society.	27
Scheme 2.6. Esterification of cellulose using (a) ethylenediaminetetraacetic dianhydride, (b) butyric acid and acetic anhydride, and (c) chloroacetyl chloride. Adapted with permission from ref 8. Copyright 2019 Elsevier.	32
Scheme 2.7. Preparation of the IPN using the “Grafting from” method using cellulose and AAc/AAM monomers. Adapted with permission from ref 8. Copyright 2019 Elsevier	35
Scheme 3.1. Schematic illustration of the MPN assembly protocol used to coat urea granules (water-soluble substrate) in acetonitrile solution. (a) Overview of the different steps involved in the formation of an MPN coating onto urea granules: step 1, iron and tannic acid solutions are mixed to generate Fe^{III} –TA complexes; step 2, the solution is aged, possibly resulting in the conversion of Fe^{III} –TA complexes into Fe^{III} –acetonitrile complexes; step 3, urea granules are introduced into the aged solution for the MPN coating to proceed. (b) MPN coating proceeds via multiple interfacial interactions between the urea granules and TA, iron, and Fe^{III} –TA complexes; Fe^{III} –TA particle aggregation; and subsequent deposition of the Fe^{III} –TA particles and fusion onto the urea granules.	48
Scheme 4.1. Schematic illustration of the mechanochemical coordination-driven assembly of MPN followed by encapsulation of urea crystals. The high friction conditions produced by mechanochemical grinding provide the required energy for creation of TA- Ti^{IV} coordination in solid-state. The heating treatment changes the structural rearrangement of urea crystals and MPNs.	122

CHAPTER 1

Introduction

This chapter provides background information relevant to the work contained within this thesis. It introduces the importance of nitrogen fertilizer use in agriculture and its cycling in soil and the need for developing controlled-release urea. It also identifies the motivations and research objectives for the work that follows.

This Page Intentionally Left Blank

1.1 Research background

With the projected rapid growth in global population to 10 billion by 2050, nitrogen-based fertilizers are in high demand to maintain adequate food supply as nitrogen is a predominant nutrient required by crops [1]. Urea as a nitrogen-rich (~46% N) and low-cost chemical, is the most common nitrogen fertilizer used in agriculture; however, the high solubility and rapid hydrolysis of urea leads substantial (up to 70%) lost to the environment through ammonia volatilization, nitrate leaching to groundwater, nitrification, denitrification, and runoff (**Figure 1.1**) [1-3], contributing to ecological and environmental issues at global scales including water pollution, climate change, eutrophication, biodiversity loss, stratospheric ozone depletion, and public health problems [4]. For example, the impact of 1 kg of N_2O (as one of the main hazardous species produced through denitrification) on warming the atmosphere is almost 300 times that of 1 kg of carbon dioxide [5]. Thus, increasing the efficiency by which plants are able to utilize urea fertilizer to ensure food security is necessary for sustainable agriculture. In this context, substantial efforts have been directed toward developing enhanced-efficiency urea. Different approaches including controlled-release ureas (CRUs), urease inhibitors, and nitrification inhibitors are employed to achieve the goal [6]. Controlling the dissolution of urea is one way of reducing the rate at which plant available nitrogen is produced via hydrolysis and nitrification, to maximize plant uptake and minimize loss. CRUs, in which a physical barrier regulates the dissolution of urea, have been designed to meet the predicted needs of plants for nitrogen through external stimuli such as pH, soil moisture, and temperature [1]. Polymer-based materials are widely used as either coatings on urea granules or to embed urea in a matrix [6]. Polymers provide suitable surface properties such as mechanical strength and hydrophobicity. However, the use of polymers has been restricted due to complicated synthesis protocols, prohibitive cost, and non-biodegradability. Research frontiers have shifted towards using environmentally friendly bio-based materials such as vegetable oils, polysaccharides, and

polyphenols [7, 8]. Natural polyphenols that are ubiquitous in plants are of particular interest as controlled-release coatings due to being relatively inexpensive [9]. In addition, polyphenols display high adherence through physical and chemical bonding, which provides a uniform assembly on surfaces [9]. Therefore, polyphenols are widely compatible structural motifs for engineering materials such as CRUs.

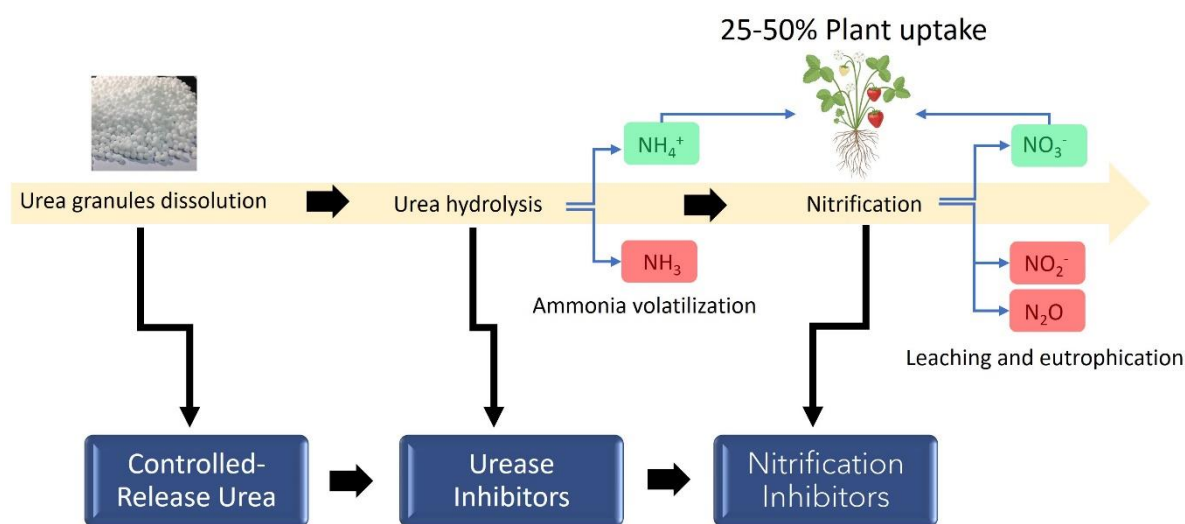


Figure 1.1. Main processes of the nitrogen cycle in soil and the pathways of N uptake and loss, and different pathways to control the urea release, hydrolysis, and nitrification.

1.2 Significance and Scope of Thesis

CRUs have attracted broad interest owing to their potential to enhance urea efficiency. However, their use in farms is limited because the current technology relies on using non-biodegradable and expensive polymers. As a result, developing a novel environmentally friendly and low-cost CRU could be a game-changer for making significant changes in soil N cycling over the next decade. The control of urea dissolution is the first stage among different methods (i.e. controlled-release ureas, urease inhibitors, and nitrification inhibitors) for reducing the N loss and increasing the N uptake by plants. Providing bio-degradable platforms for the fabrication of CRUs is highly desirable from the viewpoint of environmental and economical scopes to ensure food security. This thesis begins with an introductory *Chapter 1*,

which covers the research background, significance, scope, and objectives of the study. *Chapter 2* reviews and classifies the materials and fabrication methods used for preparing CRUs. This thesis particularly explores a new class of controlled-release urea using the engineering coating of polyphenols. *Chapters 3 and 4* are experimental studies, and the assembly of polyphenols in the presence of metals under solvent or solvent-free conditions is addressed. Understanding the mechanism of formation of polyphenolic coatings on urea plays a pivotal role for tunable assembly of polyphenols, which influences the urea release profile. Thus, the formation mechanism of phenolic assemblies is systematically assessed. After optimization of the coating process, the efficiency of encapsulated urea as a controlled-release urea is evaluated in water and soil under different environmental conditions. *Chapter 5* provides an overall conclusion and outlook on using MPNs as CRUs.

1.3 Objectives of the study

Given the nature of the problem, the main objective of this research is to introduce metal-phenolic networks (MPNs) technology for the first time as a coating for controlled-release of urea. Thus, assembly of MPNs in non-aqueous solvent and solvent-free conditions on urea particles was addressed and following this a performance evaluation of the materials as CRUs in water and soil conducted.

The objectives in research *chapter 3* are:

- To explore the assembly of the MPNs on urea granules in non-aqueous solvents, finding the formation mechanism of MPNs.
- To evaluate the release profile of urea from MPN coated urea in water.

The objectives in research *chapter 4* are:

- To investigate the formation of MPNs at solvent-free conditions *via* a mechanochemical approach in the presence of urea and evaluate the MPN-urea changes after aging and heating treatments.
- To assess the urea release profiles of prepared materials as CRUs in soil under different environmental conditions.

CHAPTER 2

Literature review

This chapter summarizes the literature surrounding controlled-release fertilizers. This includes an overview of research conducted to date, discussion of the underlying materials and fabrication methods used as control release fertilizers, as well as comparing the varying types of chemicals and operation conditions that affect the release profile of fertilizers. As the purpose of this thesis is the fabrication of controlled-release urea, by ending the literature review, more specific papers related to the manufacturing of CRUs are chosen to be discussed. From this discussion, limitations associated with the release profile of fertilizers are identified.

This Page Intentionally Left Blank

2.1 Controlled-release Fertilizer (CRF) and its classification

Controlled-release Fertilizers (CRFs) are fertilizers coated with engineered materials to facilitate control over the dissolution rate of nutrient by providing physical barriers surrounding the fertilizer particles, where the thickness of the coatings is primarily responsible for regulating the penetration of water into the coated fertilizer. Importantly, CRFs aim to regulate the release of nutrients to match crop demand. The terms controlled-release fertilizer and slow-release fertilizer (SRF) are often used interchangeably. However, Trenkel and Shaviv stated distinct differentiations between both terms [10, 11]. For SRFs, the release of the nutrient is not predictable, however the release pattern for CRFs can be predicted by knowledge of key elements such as pH, temperature, and moisture of soil. An ideal CRF is a system that is prepared using natural material(s) with minimal potential pollution impacts to the soil, and controls the nutrient release based on the plant requirements. CRFs can be categorized by their materials. **Figure 2.1** presents a comprehensive classification structure including organic compounds, inorganic nutrients, and physical barriers [6, 8, 11-13]. The chart is divided into non-polymer and polymer-based materials, which are highlighted in gray and green, respectively. In this literature review chapter, polymer-based CRFs will be discussed fully.

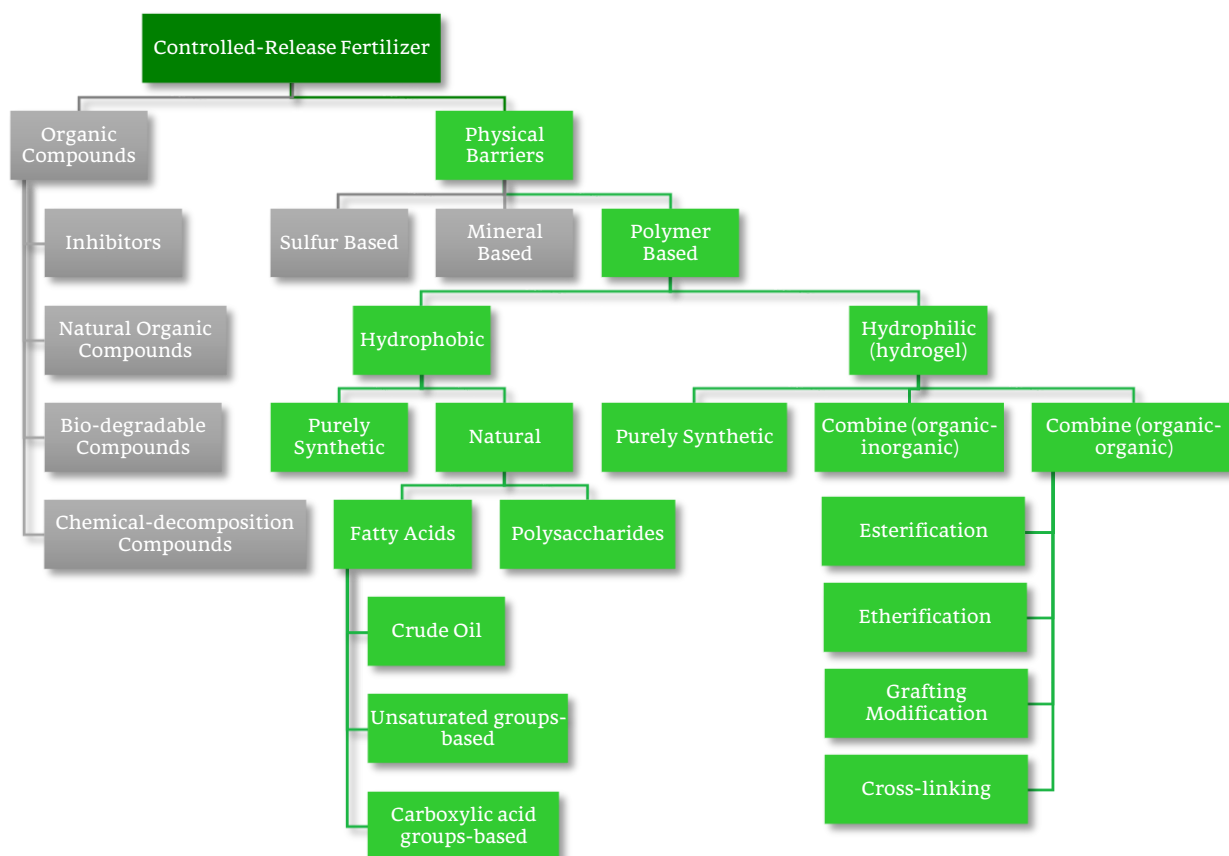


Figure 2.1. Classification of controlled-release fertilizer (CRF) according to the different materials used in the synthesis. Non-polymer and polymer-based materials are highlighted in gray and green, respectively.

2.1.1 Organic compounds (inhibitors, nutrient-rich natural compounds, and urea derivatives)

Organic compounds are subdivided into: i) natural organic compounds, ii) bio-degradable compounds, iii) chemical-degradable compounds, and iv) inhibitors. Natural nitrogen-rich organic compounds can be produced by composting animal manure and plants, sludge, municipal biosolids, and food processing wastes. They can both improve soil health due to increasing the organic matter in the soil and gradually releasing N *through* decomposition of organic matter *via* microbiome-based processes. Chemical and biological synthesis of urea derivations (i.e. urea-formaldehyde, urea acetaldehyde/cyclo diurea, and isobutylidene-diurea) *via* condensation polymerization methods has become one of the most commonly slow-release ureas (SRUs). These urea derivatives further release N into the soil after cracking into simple

molecules such as ammonia and CO₂ [14]. Using urease and nitrification inhibitors is another effective strategy to enhance the nutrient (in this case urea) efficiency in the soil through controlling the hydrolysis rate of urea to ammonium/ammonia and nitrification of ammonia/ammonium to nitrate *via* nitrite, respectively. In this approach, synthetic organic chemicals such as N-(n-Butyl) thiophosphoric triamide (urease inhibitor) and 3,4-Dimethylpyrazole phosphate (nitrification inhibitor) are commonly added to the soil alongside with the urea addition [15-17].

2.1.2 Physical barriers

Physical barriers are materials with the ability to control the release rate of water-soluble nutrients into the surrounding environment. These are typically hydrophobic or hydrophilic barriers on the nutrient granule or a matrix of nutrients containing either hydrophobic or hydrophilic compounds [11, 13]. Over the last two decades, the physical barrier technique has been of great interest to engineers and scientists as by manipulating important factors (i.e. coating thickness, permeability, and wettability) the nutrient dissolution rate can be reasonably controlled. Based on the CRF production method, three types of chemicals are mainly used including sulfur-, mineral-, and polymer-based materials [11].

2.1.3 Sulfur-based CRFs

It is claimed that the synthesis of sulfur-based CRF was the first attempt to control the release rate of N in the agricultural field and was pioneered by Blouin et al. in 1967 [18]. The procedure consisted of two steps: i) immersion of fertilizer into petroleum by-products such as soft wax and motor oil, followed by vacuum drying, and ii) spray coating with a combination of molten sulfur and polyethylene using a rolling drum [18]. Blouin showed that uniformity of the coating plays an important role in controlling the release rate. The uneven coating of the sulfur layer leads to the fissuring of the coating material. Other studies have been completed

by this group to control the release rate using plasticizers and diatomaceous earth to form elastic and uniform coatings [19].

To aid in creating an even and thin layer of sulfur on fertilizer granules, Tsai and Choi have designed a spouted fluidized-bed [20]. The optimized conditions comprised $0.65 \text{ m}^3 \cdot \text{min}^{-1}$ airflow, $80 \text{ }^\circ\text{C}$, and 208 kPa pressurized atomizing air. Under these conditions, the release rate of sulfur-coated urea was 30% after seven days in water at $25 \text{ }^\circ\text{C}$. Detrick and co-workers optimized the fluidized-bed conditions by adding secondary polymer coating [21]. In their study, triethanolamine as the monomer and 4,4-diphenylmethane diisocyanate as the crosslinking agent, reacted with sulfur-coated granules to form an outer-layer polymer coating. In an additional step, excessive sulfur was added as the third layer to increase the thickness, resistance, and mechanical degradations resulting from friction, handling, and storage [22].

Sulfur-based CRFs have been extensively used for decades. Applying sulfur in soil has some advantages as it acts as a fungicide and a secondary nutrient [23]. Besides, due to the acidic nature of sulfur, it may also be used to treat high soil alkalinity through a neutralization process [21]. However, CRF coated with sulfur typically suffers from cracking and significant brittleness due to the crystallinity feature of sulfur [22, 24]. The fracturing of sulfur-coated materials worsens as the coating manufacture temperature increases [20]. The potential mechanism for the release of N from sulfur-based CRF includes the burst release of urea and a continuous release throughout water diffusion [25].

2.1.4 Mineral-based CRFs

Mineral-based CRFs are defined as those requiring a combination with nutrients to form covalent or ionic bonds [26]. Based on the type of minerals used in the system, slightly soluble urea is achieved. Mineral-based CRFs also can be classified into two types, including porous-structure minerals such as zeolites and non-porous structure minerals like

silicon and illites. In this case, nutrients can either load into the porous structure or adsorb onto the surface of minerals. The release rate of the nutrient is mainly determined by the mineral particle size, pH, ionic strength, temperature, and moisture content of the soil [14]. Using minerals in CRFs as a filler may decrease the production cost. Likewise, the hydrophilicity of minerals can increase the water-holding capacity of the soil due to its water absorbency, which is an important factor in arid and semi-arid areas [27].

2.1.4.1 Polymer-based CRFs

Polymers have been widely used for CRFs as coatings on fertilizer granules or through mixing with fertilizer (mostly urea) solutions. Different classifications have been proposed based on polymerization protocols. To date, a wide range of monomers and chemicals, including synthetic and biodegradable materials have been used to utilize polymers for CRF applications. Among polymerization processes (i.e. free-radical polymerization (FRP), polycondensation reactions, atom transfer radical polymerization (ATRP), ring-opening polymerization (ROP), reversible addition-fragmentation chain-transfer polymerization (RAFT)), FRP and polycondensation polymerizations are more feasible methods for the preparation of CRFs due to having a simple process. Moreover, various crosslinking agents are used to synthesize polymers depending on the required properties (i.e. stiffness, wettability, hydrophobicity, and mechanical properties) of polymers for CRFs. Accordingly, the protocol of polymer utilization for CRFs is different based on the type of polymer. For example, the coating method is usually used for coating hydrophobic polymers on urea granules, while loading or mixing of urea solution with hydrophilic polymers is employed to prepare a hydrogel urea-polymer system. Here, polymer-based CRFs are categorized based on the hydrophobicity and hydrophilicity of the polymers (or materials) employed in the CRF preparation.

2.1.4.2 Hydrophobic CRFs

Hydrophobic-based CRFs can be achieved *via* use of three polymer types, including synthetic long alkyl side chain polymers, bio-based polymers, and modification of polymer coatings with hydrophobic chemicals such as fluorinated compounds. The hydrophobic polymers can be synthesized through mixing (blending or loading polymers in fertilizer solution), immersing fertilizer granules in an organic solvent (dip-coating), coating fertilizer granules by fluidized-bed/rotary drum, and spray atomizing in the presence of fertilizer granules. However, as hydrophobic materials (i.e. hydrophobic polymers and additives) are usually dissolved in non-polar and aprotic solvents, and fertilizer is soluble in water, preparing a matrix of these two components through dissolution is difficult. Thus, the coating technique is one of the best options to fabricate hydrophobic CRFs. In the next section, various fabricated hydrophobic-based CRFs are discussed based on their physiochemical properties, and their release profile of fertilizer in either soil or water.

2.1.4.2.1 Fabrication of hydrophobic-based CRFs

Many studies have indicated that synthetic polymers such as polysulfone (PS) [28], polyurethane (PU) [29, 30], polyacrylate (PA) [31], paraffin wax (PW) [32], polyethylene (PE) [33, 34], polystyrene (PS) [35], polyolefin (PO) [36-38] and their modifications can be implemented to fabricate CRFs. In some cases, like polysulfone, the polymer is hydrophobic and no further modification is needed to improve the hydrophobicity and physical properties of the fertilizer coating. However, using a modifier or additive such as grafting agents, crosslinking agents, organic siloxane, fluorinated materials, nanoparticles, long alkyl chain chemicals or surfactants is often necessary to improve the hydrophobicity and thermal stability of water based-polymers.

Pipko et al. in 1990 invented a double-layer coating technique to fabricate a wide range of CRFs [39]. The invention included using a series of hydrophobic organic acid oils and water-insoluble metal salts as the first layer and paraffin wax as the second layer to seal the pores. The cumulative release of coated potassium nitrate granules after 43 days was 36%. Donida et al. in 2002 investigated the release pattern of urea in water when the urea granules were coated with a mixture of methacrylic acid, talc, titanium dioxide, triethyl citrate, polyethylene glycol, and magnesium stearates [40]. They sprayed this solution on the granules *via* a fluidized-bed technique. They showed that higher atomizing air pressure and temperature produced a uniform coating because of the formation of small polymer droplets. However, the system was not effective at pH values higher than 5.5 due to the degradation of the polymer. Mathews et al. in 2010 synthesized a biocompatible and biodegradable dual thermo-pH responsive hydrophobic polymer using a block copolymer of poly (N-isopropyl acrylamide-co-polyurethane) [41]. The polyurethane was synthesized by polyol (Poly (1,4-butylene adipate) diol end-capped) and methylene diphenyl diisocyanate (MDI) and further functionalization was performed by adding amino terminated poly(N-isopropylacrylamide) as a thermal response component. Finally, the urea fertilizer was immersed in molten polymer to coat the polymer onto the urea granules. The release profile of the coated urea investigated at pH 4, 7, and 10 shows that the release rate of urea increased from 20 to 80% after 15 days when the pH increased. Wu et al. in 2012 reported one layer polyurethane coating on urea granules using a rotary drum by mixing the polyol as a substrate and the isocyanate crosslinking agent to synthesize polyurethane [42]. The linear release profile of urea with a 10-15 μm coating thickness was 70% after 30 days. Lubkowski et al. in 2018 fabricated a biodegradable copolymer of poly(butylene succinate)-co-butylene ester of dilinoleic acid (PBS/DA) and coated the polymer on multicomponent (NPK) fertilizer using the immersion method in chloroform [43]. An increase in the layer thickness of the polymer led to a decrease in the rate of nutrient release. Also, the experimental kinetics of the

nutrient release was described by a sigmoidal model equation. Baldanza et al. in 2018 manufactured CRFs through mixing PBS, montmorillonite, and urea [44]. It was assumed that entrapped clay inside the matrix of PBS and urea could control the urea release rate by adjusting the hydrophobicity of the matrix. Increasing the content of clay in the BPS matrix led to a decrease in torque value (the amount of force required to twist materials) by hindering the interaction between the matrix and urea. Moreover, the dispersion of fillers was carried out through melting the matrix resulting in decreasing the dissolution rate of urea. The peak of urea release in water was 31% after 40 h and no further urea release was observed over 120 h. Feng et al. in 2015 synthesized a smart dual temperature-pH responsive behavior controlled-release fertilizer *via* the Atom Transfer Radical Polymerization (ATRP) methodology [45]. Even though ATRP is not particularly new and has been used for many years in the field of polymerization, it is a relatively new method to produce CRFs. For this purpose, a thin layer of dopamine was coated on the surface of ammonium zinc phosphate *via* oxidation of dopamine to polydopamine in dichloromethane. Then, the coating was modified through grafting poly(N, N-dimethylaminoethyl methacrylate) (DMAEMA) to polydopamine using the ATRP methodology. The release rate of the nutrients (ammonium, zinc, and phosphate) in the water was altered by a change in the pH of environment due to the pH-responsive switching behavior of DMAEMA. It was pointed out that the high pH and low-temperature environment accelerated the NH_4^+ release rate. A mussel-inspired controlled-release micronutrient was also synthesized through the ATRP method to achieve a thermosensitive coating [46]. Using the ATRP method for manufacturing CRFs provides many advantages as the fabricated polymer can be further functionalized with a second polymer or grafted to a wide range of functional groups to achieve coatings with desirable physiochemical properties. Lu et al. in 2016 synthesized a series of CRUs by coating a layer of polyurea on the urea granules [47]. The liquified urea first reacted with isocyanate groups to form a polyurea with high mechanical

strength, and then coated on urea granules, and demonstrated excellent film-forming and water resistance properties. The complete dissolution of urea from the fabricated CRUs carried out during 100 days in the soil. Emami et al. in 2017 investigated the effect of Fe_2O_3 magnetic nanoparticles on the release rate of KNO_3 in the nanoparticles/polyethersulfone nanocomposite capsules [48]. The phase inversion and asymmetric ultrafiltration (UF) methods were used to synthesize the nanocomposite CRF. The good interaction between Fe_2O_3 and polyethersulfone resulted in a decrease in the release rate of nitrogen fertilizer in the water. A low fertilizer loading into the capsules *via* either encapsulation or mixing is a big barrier to the commercialization of this method. Boyandin et al. in 2017 synthesized a biodegradable and hydrophobic 3-hydroxybutyrate (PHA) using an enzyme and cold-pressed it with wood flour, ammonium nitrate, and polycaprolactone (PCL) [49], in which 70% of the nitrogen fertilizer dissolved during 80 days in the soil. Synthesis of PHA through a bacterial culture methodology could drop the final product cost [50], which makes it an attractive substrate in agricultural applications, specifically for fabrication of CRFs. Schmücker et al. in 2018 for the first time applied a liquid marble technique to develop CRFs [51]. Liquid marbles are produced by rolling aqueous urea droplets on a mixture of biodegradable polylactic acid (PLA) and PCL followed by solvent vapor treatment with dichloromethane, where the aligned polymer chains in the coating enhanced mechanical and barrier properties [51]. The mechanical resistance of liquid marbles made of PCL showed an elastic behavior, which represents a low resistance to destruction, while PLA took higher compressive loads until 50% deformation [51].

Polyacrylate (latex) can be used to fabricate CRFs. However, its application for preparing coatings is limited due to low mechanical properties of the polymer coating because of the abundant hydrophilic groups in its structure. Du Changwen and his group [31, 52-56] have been investigating the physicochemical properties of polyacrylate using several methods since 2010. In their first study, they used the water-based acrylate latex polymer and aziridine as the

crosslinking agent in a solvent-free system to develop the CRFs by the Wurster-type fluidized-bed [31]. After deposition of 2wt% coating materials on the NPK granules only 40% of the nutrients were released within 9 days. Increasing the content of crosslinking agent could decrease the swelling capacity of the coating followed by an increase in the glass transition temperature (T_g), which could end up to higher mechanical properties of the coating. Further on, this group designed three different emulsion polymerization methods - seeded polymerization, copolymerization, and miniemulsion polymerization (MP) - to synthesize waterborne poly(silicon-co-acrylate) which was then coated onto the NPK granules using the Wurster fluidized-bed equipped with a bottom-spray pneumatic nozzle [54]. The physicochemical properties and water repellency of the microemulsion changed by altering the n-butyl acrylate/methyl methacrylate ratio and organic silicone content, respectively. An increase in the ratio of n-butyl acrylate/methyl methacrylate led to an improvement in the mechanical resistance of the coating, while increasing the organic silicone components provided more hydrophobic coatings [54, 57, 58]. The 30-day cumulative nutrient release was 15% at 25 °C using the microemulsion method. It was shown that the slow-release pattern of NPK can be attributed to the hydrophobic siloxane polymer coating that is applied on the NPK granules. Although polymer coatings using the miniemulsion polymerization showed some advantages over conventional emulsion polymerization (CEP) in decreasing the fertilizer release rate, the influence of miniemulsion or co-stabilizer (hexadecane) alone on the release rate of fertilizers was not demonstrated by any control tests. Thus, by setting a series of experiments they showed that CEP + hexadecane is superior to MP in decreasing the fertilizer release rate as the majority of hexadecane is distributed on the exterior surface resulted in an increase in the hydrophobicity of the external surface of polyacrylate particles [55]. In another study, semi-continuous emulsion polymerization was employed using the organic silicon and crosslinking agent (aziridine) [53]. Although the water resistance and the mechanical properties

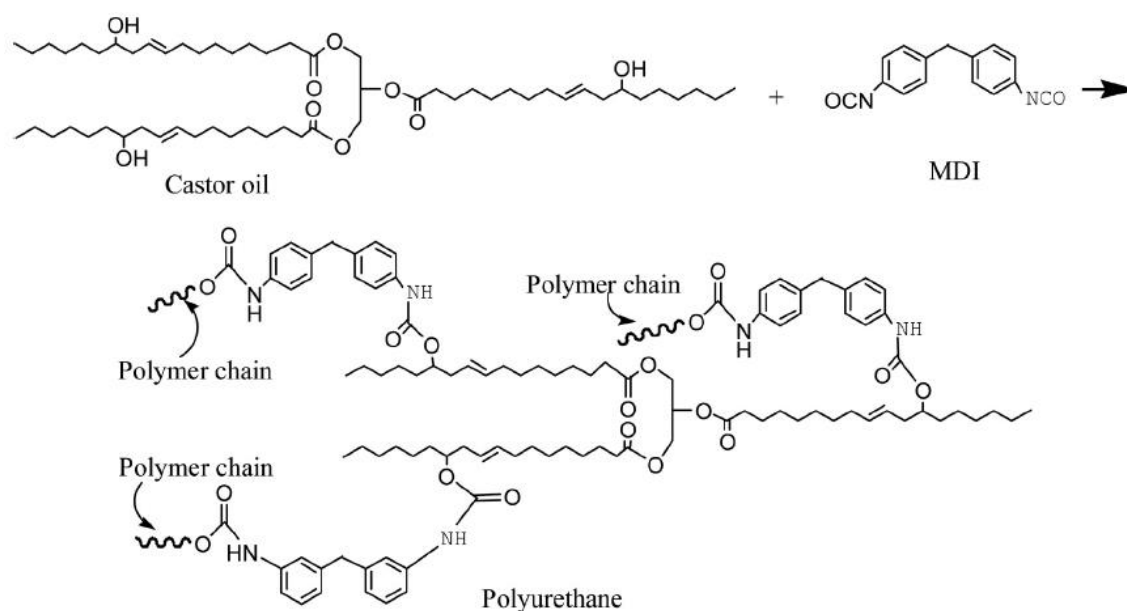
of the coatings significantly improved compared to their previous study, the rate of nutrient release was discovered to be the same. (15% nutrient release after 30 days at 25°C in water). Later on, the effect of thermal treatment on polymer coatings on the urea release rate in water was investigated [56]. In this study, a relatively rigid network of polyacrylate was synthesized by adding aziridine as a cross-linker and spraying this on the urea granules using the Wurster fluidized-bed. It showed that by increasing the temperature through a post-thermal treatment of coated urea from 30 to 80 °C, the nutrient release profile changes from a logarithmic to sigmoidal pattern due to the more compact and smoother membrane surface. The formation of microscale defects in the polymer film and high surface roughness of the membrane were supposed to be the reason for the high nutrient release rate for the materials prepared at 30 °C. Contrary to this, the post-treatment of CRU at 60 and 80 °C showed a slow urea release rate due to a more compact coating and a smoother coating surface.

The development of CRFs using polymers has revealed a high efficiency in controlling the fertilizer release rate. However, using petroleum resources to synthesize polymers does not attract commercial attention due to high industrialization costs and complicated synthesis procedures. Furthermore, the raw materials are non-renewable and have poor degradability, which causes environmental pollution [59]. To reduce the potential side-effects (soil and groundwater pollution) and to decrease the final cost of CRFs, research frontiers have shifted towards developing environmentally friendly materials such as vegetable-extracted bio-oils (fatty acid-based oils), cellulose, starch, and lignin to synthesize polyurethane [7]. Among different types of bio-based resources, bio-oils are receiving great attention for developing polyurethane due to the fabrication of condensed and hydrophobic polyurethane coatings. In brief, three types of fatty acid oils are used for polymer coatings on fertilizers, including those with high degree of polyols, unsaturated fatty acids, and carboxylic functional groups [60]. In all cases, the oils are first modified to make polyols with further polymerization in the presence

of crosslinking agents to produce polyurethanes. Accordingly, the physiochemical properties of coated polyurethane on the fertilizers are changed by varying the oil types.

2.1.4.2.1.1 Crude oils

Some oils such as castor oil have abundant alcohol groups in their structure. Thus, they can be used as a substrate to synthesize polyurethane. The typical procedure consists of dissolving the oil in an appropriate solvent followed by adding a crosslinking agent containing the $-N=C=O$ group. Due to the existence of a long carbon chain in the oil structure, the final product is hydrophobic. Yang et al. in 2012 synthesized polyurethane using castor oil as the polyol substrate and MDI as the crosslinking agent (**Scheme 2.1**) [61]. The polyurethane was sprayed on the urea prills using a fluidized-bed tower. After the optimization of several factors such as the solvent content, the ratio of oil to MDI, and the ratio of additives, a sigmoidal N release with a 28-day lag period in water was achieved, while the complete release rate occurred within 98 days.



Scheme 2.1. Synthesis mechanism of polyurethane using castor oil Adapted with permission from ref 61. Copyright 2012 American Chemical Society.

Zhang et al. in 2019 reported a double-layer coating method to prepare CRUs through coating a bio-based polyurethane derived from castor oil as the first layer [62]. The coated urea granules were later modified within the coordination of lauric acid and copper hydroxide as the second layer in order to increase the hydrophobicity (**Figure 2.2**).

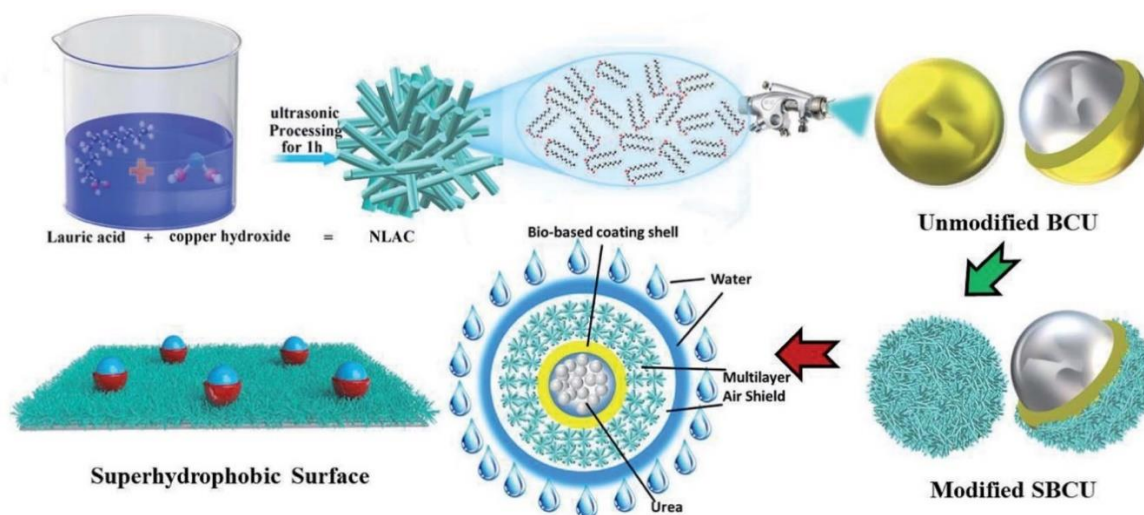


Figure 2.2. Schematic illustration of double layered coating of urea granules using bio-based polyurethane and nano lauric acid copper. Adapted with permission from ref 62. Copyright 2019 Royal Society of Chemistry.

After coating the materials on the urea granules by spraying, the release rate of nitrogen in water was exponential in which the nitrogen cumulative release was almost 80% after 30 days. Zheng et al. (2019) described how the release rate was decreased by adding a nano-crystalline-hydrophobic layer. In fact, an air layer between the aqueous media and the second layer was created, which further controlled the release rate (**Figure 2.3**).

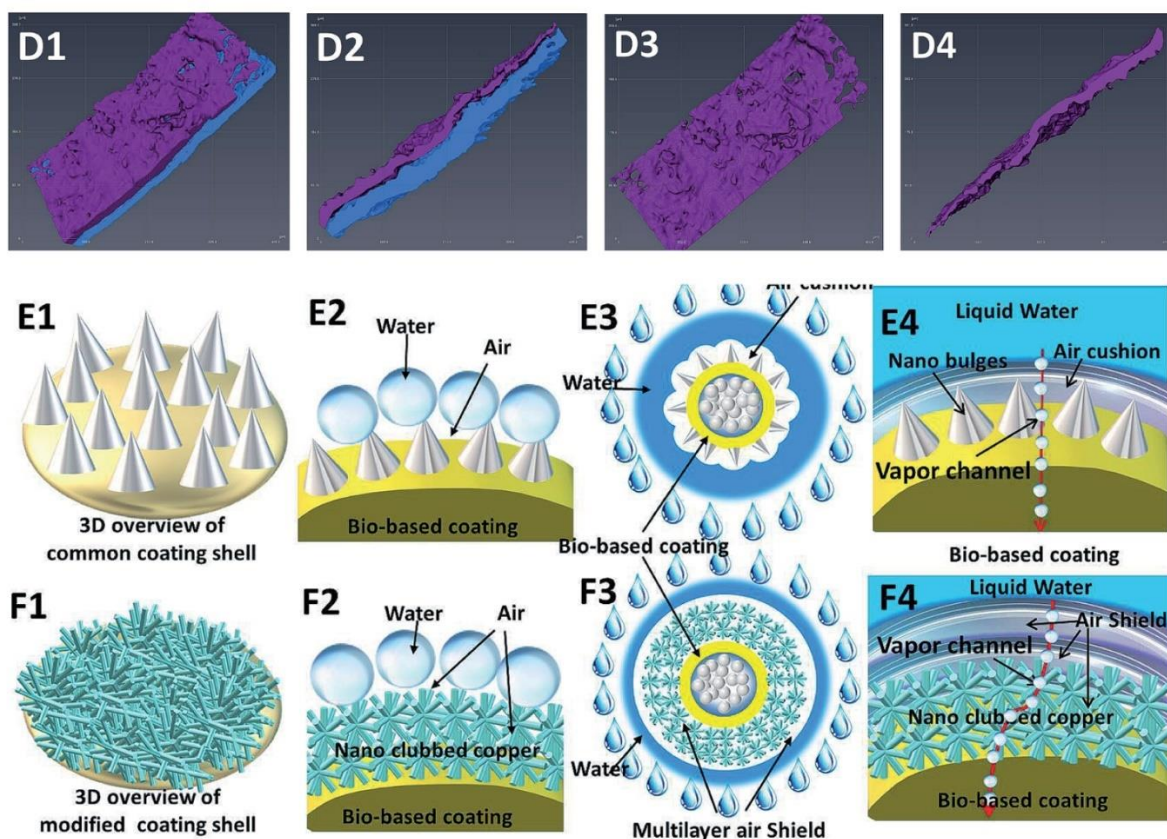
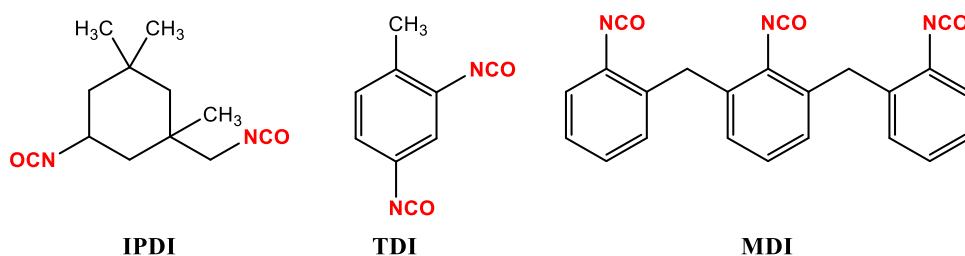


Figure 2.3. 3D reconstruction images and polarization micrograph of modified urea granules (D1 and D2) with the water phase highlighted blue and the air phase highlighted purple. The air phase (purple) is extracted and highlighted (D3 and D4); schematic of common superhydrophobic controlled-release mechanisms (E1–E4), and nano lauric acid copper-modified coated urea granules (F1–F4). Adapted with permission from ref 62. Copyright 2019 Royal Society of Chemistry.

Besides the type of bio-oil, the crosslinking agent has a dominant effect of condensing the polymer by decreasing the polymer's water permeability. Liang et al. in 2019 tailored CRUs using spraying techniques [63]. They used castor oil as a bio-based substrate and polymerized it in the presence of different crosslinking agents including isophorone diisocyanate (IPDI), 2,4-diisocyanatoluene (TDI), and methylene diphenyl diisocyanate (MDI). The urea release rate decreased in the order of IPDI>TDI>MDI because of two main factors. The first factor is associated with aromatic rings, by increasing the number of aromatic rings in the crosslinking agent, the polymerization of polyurethane is more likely to happen, leading to an increase in the density of the polymer; increasing π – π stacking between benzene rings and cyanate groups can stabilize the polymer. In addition, polyurethane prepared by MDI is more hydrophobic than

when TDI or IPDI is used, which leads to a decrease in water diffusion through the coating.

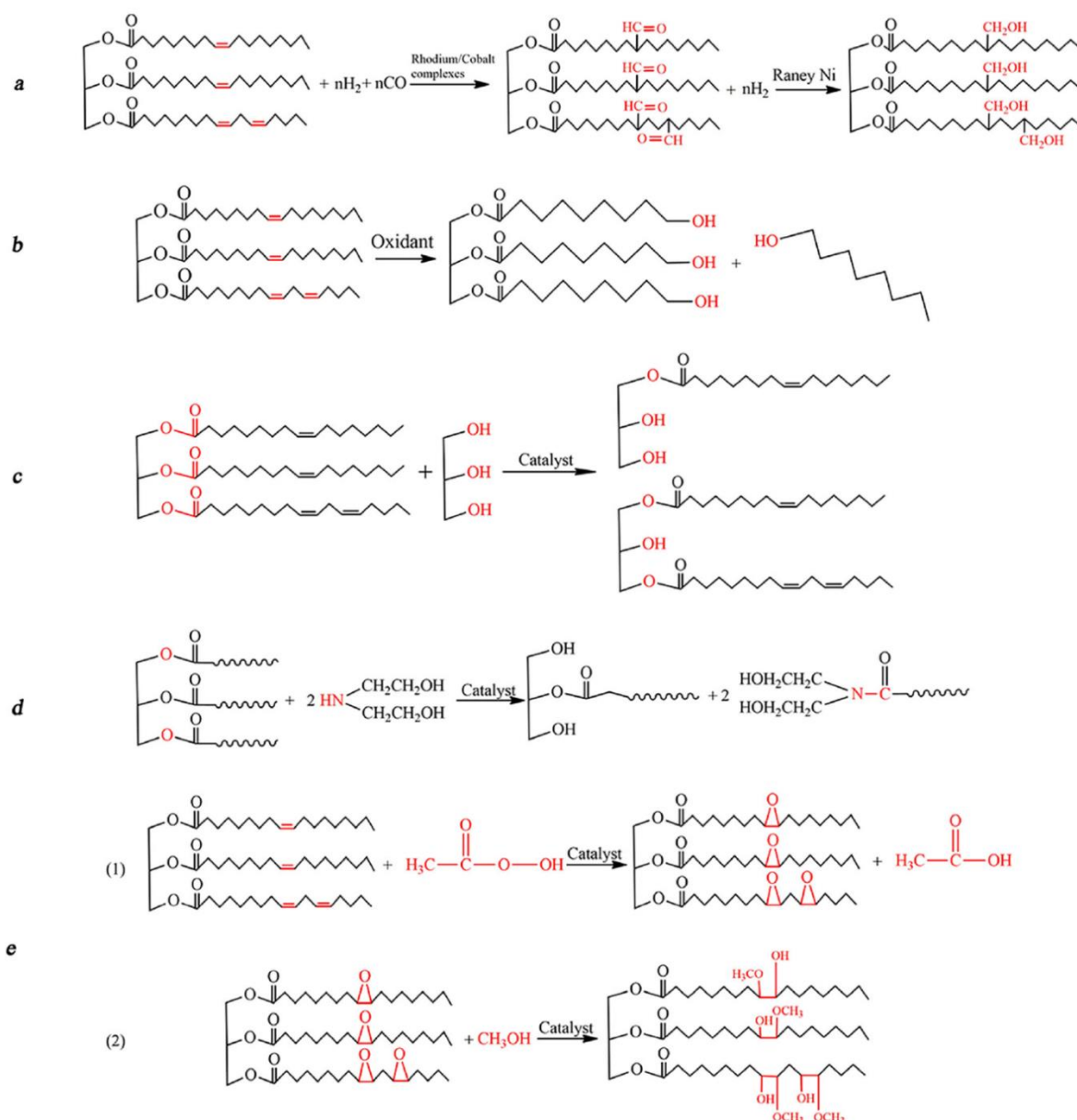
The structure of crosslinking agents is given in **Scheme 2.2**.



Scheme 2.2. The structure of common crosslinking agents used for preparation of polyurethane.

2.1.4.2.1.2 Unsaturated fatty acid-based oils

Biodegradable oils that do not possess hydroxyl groups (-OH) in the molecular chain are required to be modified to be able to start the polyurethane polymerizations. Most of these vegetable oils contain unsaturated fatty acid groups, which can be modified through different pathways, including oxidation, transesterification, aminolysis, epoxy ring-opening, and transition metal-catalyzed carbonylation (**Scheme 2.3**)[7]. The high quantity of hydroxyl groups in the modified vegetable oils can also react with the crosslinking agents for the polyurethane polymerizations.



Scheme 2.3. Modification of vegetable fatty acid oils to polyols by (a) transition metal carbonylation, (b) oxidation method, (c) transesterification reaction, (d) ammonolysis, and (e) epoxy ring-opening method. Adapted with permission from ref 7. Copyright 2022 Elsevier.

Liu et al. in 2017 implemented unsaturated frying oil to prepare CRUs [64]. The procedure included purification of the oil by activated carbon and clay followed by epoxidation of the oil using a catalyst. To make polyol, the epoxidized oil was catalyzed with fluoroboric acid. The schematic of CRU preparation is demonstrated in **Figure 2.4** The CRU was further developed in the presence of MDI and epoxy resin (E44) using a rotary drum. The nitrogen cumulative release after 30 and 80 days was 18% and 85%, respectively. Polymer coatings

have been shown to partially degrade (25%) into small molecules such as CO₂ and methane in the soil after 200 days.

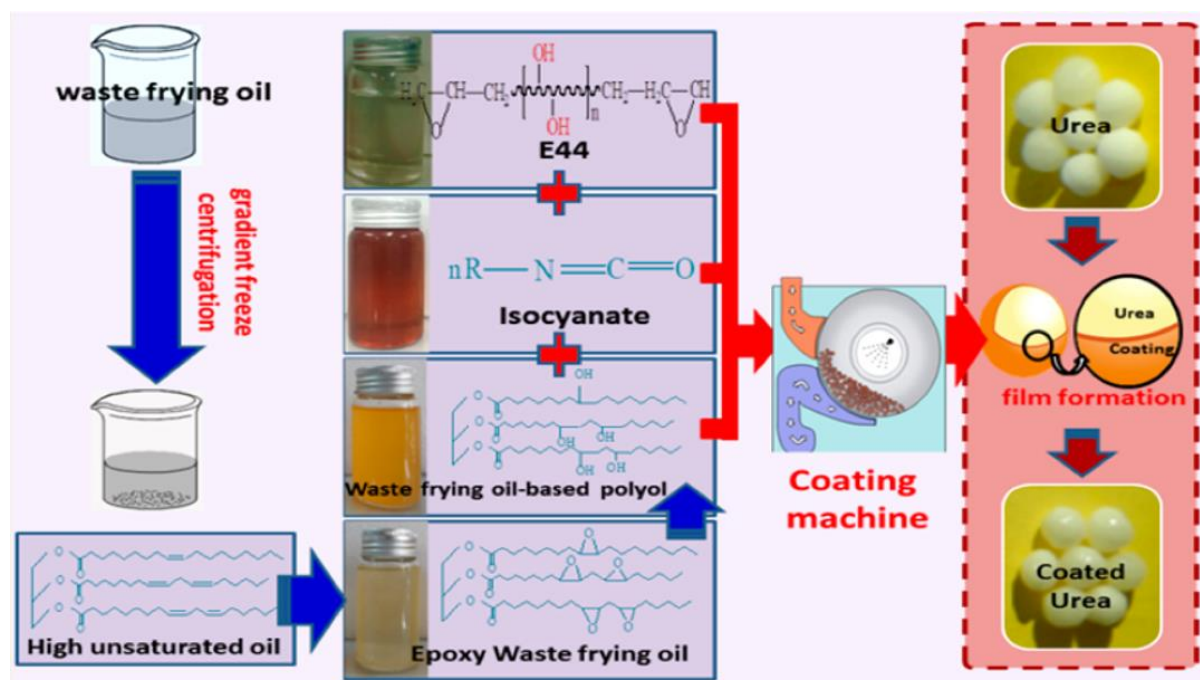
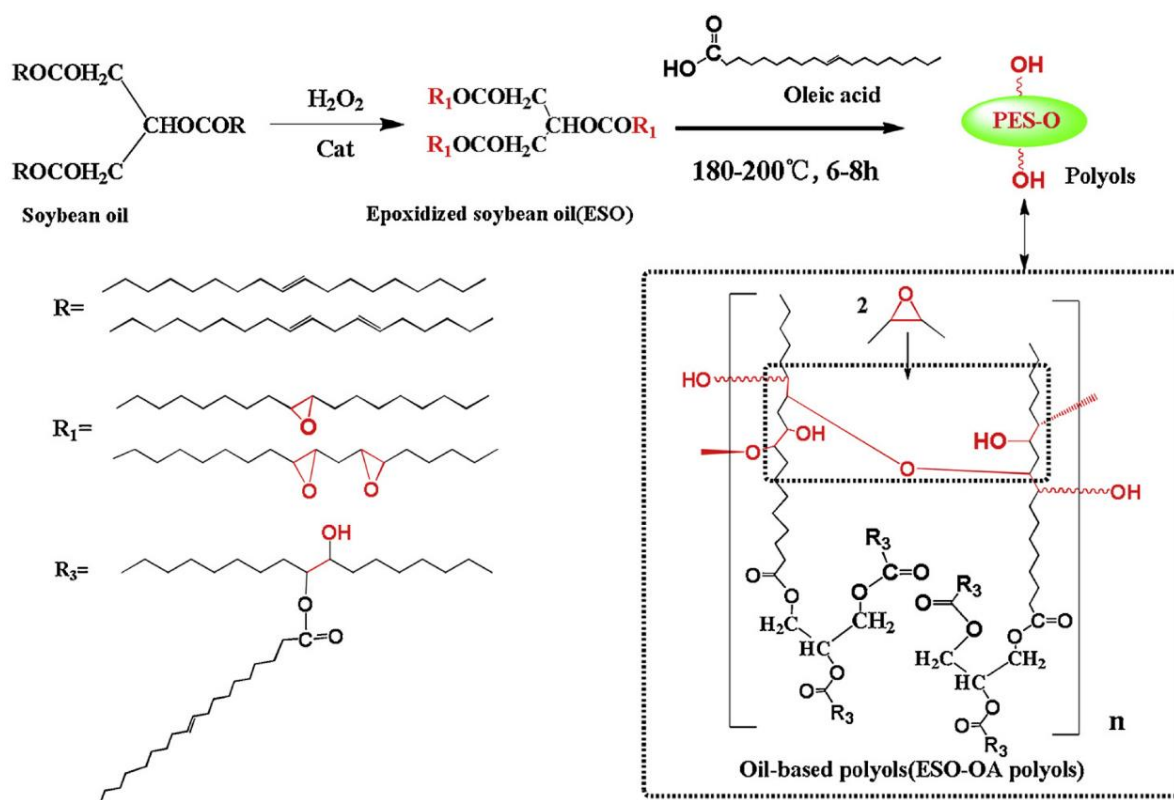


Figure 2.4. Modification of frying oil to produce bio-based polyurethane and coating it on the urea granules. Adapted with permission from ref 64. Copyright 2017 American Chemical Society.

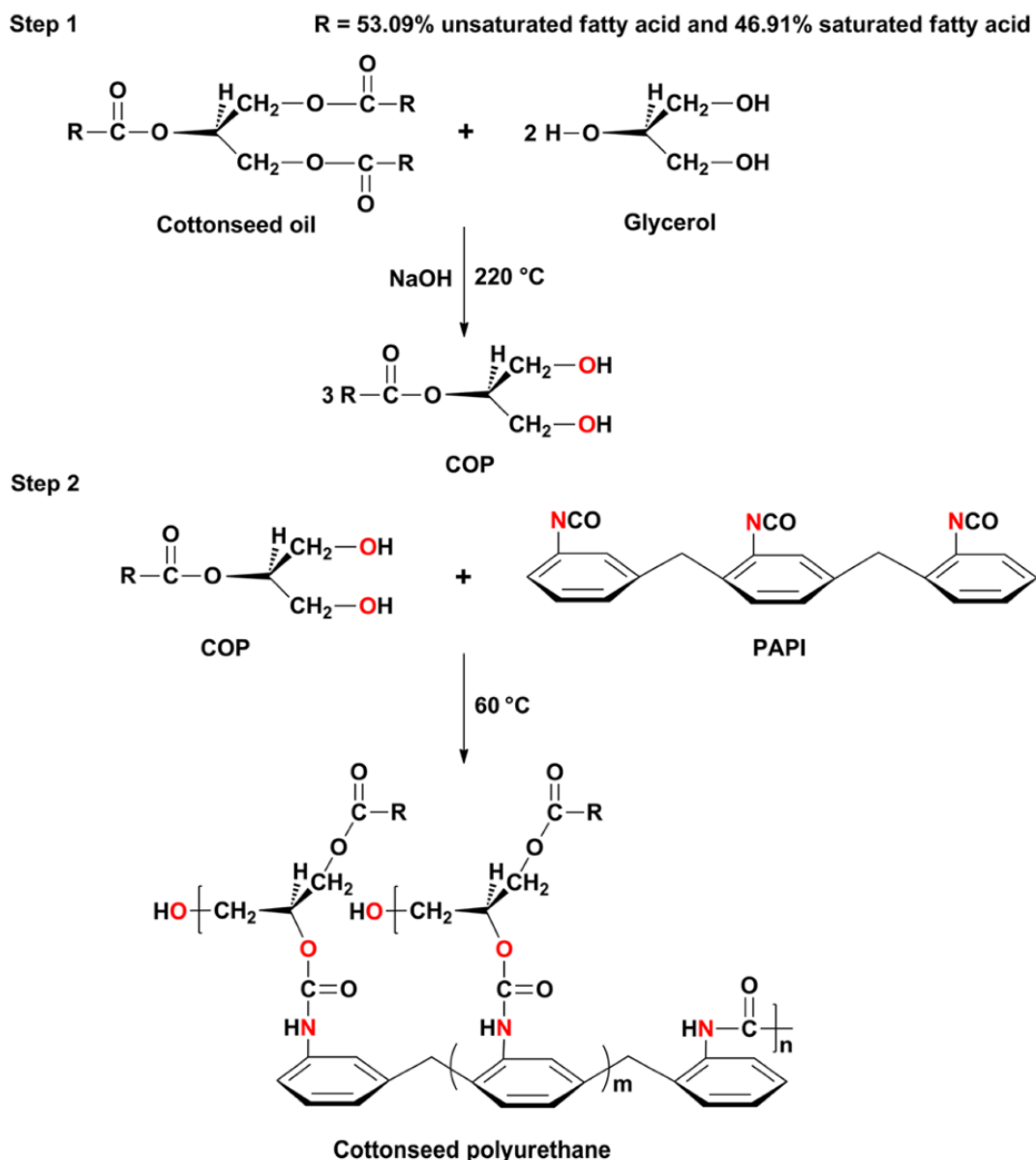
In another study, Feng et al. in 2019 reported a polyurethane-coated urea system in which the polymer was synthesized using soybean oil [65]. The reaction includes the epoxidation of soybean oil in the presence of hydrogen peroxide and tetrabutylammonium chloride as a catalyst following the addition of oleic acid at 200 °C. After the polymerization of polyurethane on the urea granules in the presence of MDI as the crosslinking agent, the mechanical properties of the coating improved by adding attapulgite (**Scheme 2.4**). The complete dissolution of urea in water occurred within 80 days.



Scheme 2.4. Schematic illustration of polyurethane synthesis using soybean oil. Adapted with permission from ref 65. Copyright 2019 Elsevier.

2.1.4.2.1.3 Carboxylic acid-rich bio-based oils

Vegetable oils containing carboxylic acid functional groups can also be used as polyols for polyurethane polymerization after being modified at 220°C . Xie et al. in 2017 proposed a new approach to increase the hydrophobicity of the CRU system [66]. Cottonseed oil, which possesses a high degree of carboxylic acid content, reacted with the hydroxyl groups of glycerol in an alkaline solution at 200°C (**Scheme 2.5**).



Scheme 2.5. The general process for the preparation of cottonseed polyurethane. Adapted with permission from ref 66. Copyright 2017 American Chemical Society.

After coating the polymer on the urea prills as the first layer, SiO_2 and a fluorine compound (1H,1H,2H,2H-Perfluorodecyltrichlorosilane, PFDS) were sprayed on the coated urea prills using a rotating drum (**Figure 2.5**). It was demonstrated that PFDS not only increases the hydrophobicity of the surface but also, upon immersion in water, forms an air pocket between the valley and bulges within coated urea granules, thereby reducing the release rate of urea. The release of urea in water was completed within 70 days with an exponential pattern.

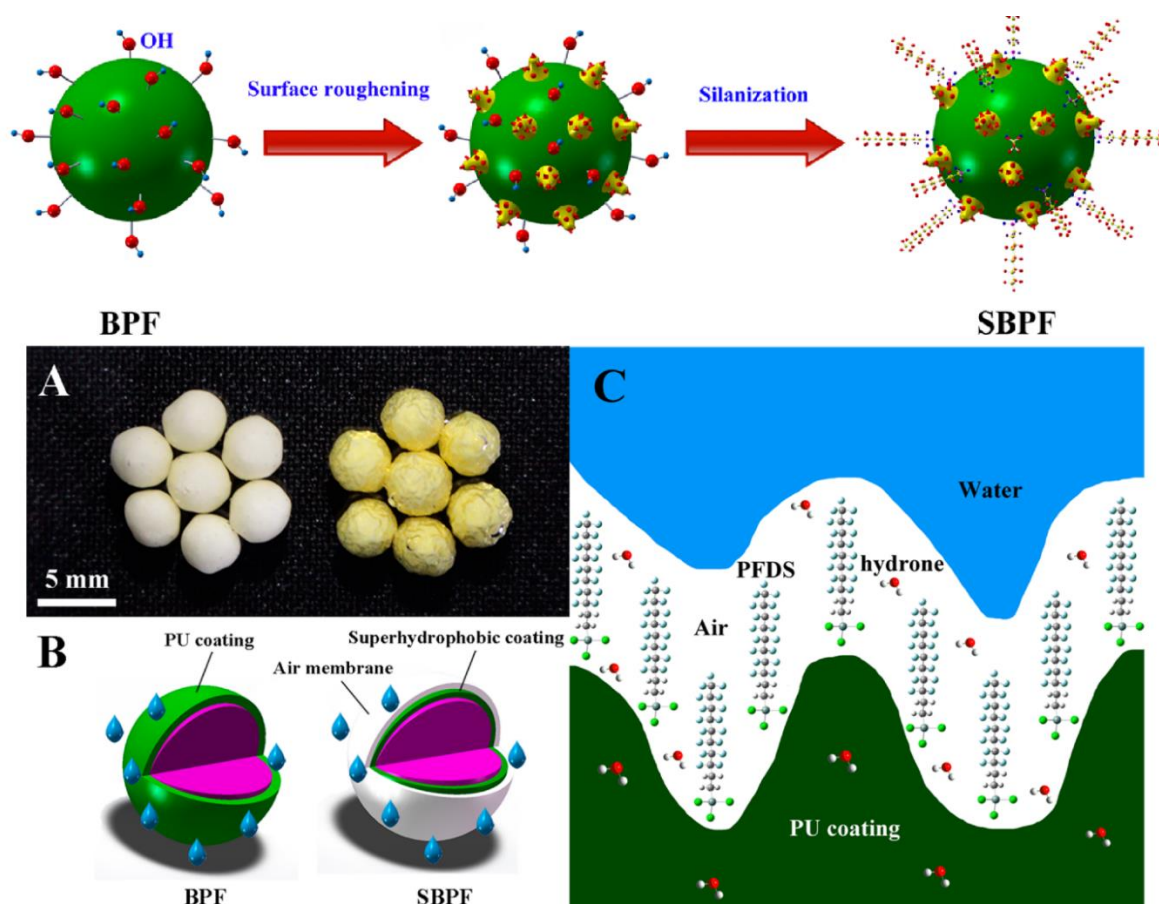


Figure 2.5. (upper) schematic of the CRU formation, (lower) (A) optical image of coated urea granules with polymer before (left) and after (right) fluorine functionalization, (B) model diagram of the CRU, (C) schematic of the CRU after being immersed in water. Adapted with permission from ref 66. Copyright 2017 American Chemical Society.

2.1.4.3 Polysaccharides

Aside from bio-oils, polysaccharides such as starch, cellulose, and lignin are widely used to synthesize polyurethane for the fabrication of CRFs due to the abundance of hydroxylic groups. The preparation mechanism comprised the liquefaction of polysaccharides in an acidic media, followed by the addition of a crosslinking agent to synthesize bio-based polyurethane. Zhang et al. in 2017 mixed ethylene glycol, polyethylene glycol, and wheat straw in acidic media (H_2SO_4) at $150\text{ }^\circ\text{C}$ to convert cellulose into polyols [67]. Then, a mixture of MDI and polyol was sprayed onto the surface of urea prills to prepare the CRFs. Moreover, to increase the surface hydrophobicity, nano-silica and poly(dimethylsiloxane) were sprayed to modify the coated urea prills. The complete linear dissolution of urea prills occurred within 70 days in

water. They claimed that nano-SiO₂ increases the surface roughening of the CRF and subsequently decreases the water contact with the CRF after immersing the CRF in water. The schematic diagram of the fabrication process of the CRF can be seen in **Figure 2.6**.

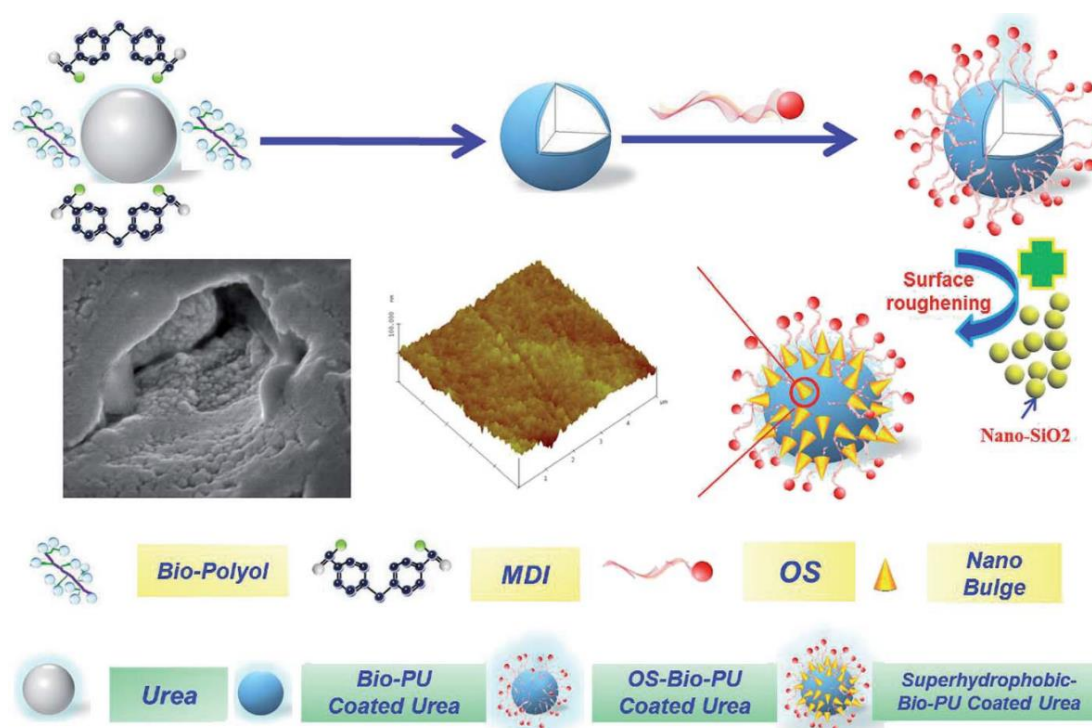


Figure 2.6. Fabrication of CRU using wheat straw as bio-based polysaccharides. Adapted with permission from ref 67. Copyright 2017 Royal Society of Chemistry.

Similarly, Li's group has further published a few papers on using starch as a bio-based polysaccharide to synthesize CRFs [68, 69]. Organosilanes or epoxy resins were used to modify the polysaccharides. The N release rate was faster in polysaccharide-base polyurethane coating compared to the bio-based oil polyurethane due to the lower mechanical strength of the coating.

2.1.4.4 CRFs from Hydrogel Polymers

The nutrient release profile of CRFs is a critical factor for seedling survival and long-term plant growth. In addition, improving the water-holding capacity of the soil in the presence of CRFs is essential to provide favorable conditions for plant growth. Increasing the water-holding capacity of soil also can result in a reduction in the irrigation frequency in arid and

semi-arid areas. Thus, hydrogel materials have attracted research interest because of their ability to absorb a high amount of water and release it over a long period. Combinations of these types of materials can control the fertilizer release rate when designed as CRFs. They can be categorized into three main classes i) purely synthetic polymer, ii) combination of organic-inorganic materials, and iii) combination of organic-organic materials [8].

2.1.4.4.1 Synthesis of CRFs using purely synthetic polymers

The most commonly used monomers to synthesize hydrogel materials are classed as Acrylic Acid (AAc), Acryl Amide (AAM), or their copolymers [70-73]. Due to the compatibility of nitrogen-based fertilizers (mostly urea and ammonium nitrate) with these polymers, they can be either mixed with the nitrogen-based fertilizer or coated as a barrier layer on the granule surface. On a first attempt, the CRU was synthesized using a mixture of AAc and AAM in the presence of urea and N,N methylenebisacrylamide (MBA) as the crosslinking agent by Helaly et al (2005) [73]. Maleic acid was also used to increase the water uptake in the mixture. Generally, the complete urea release rate using these two polymers occurred within four months. Tyliczszak et al. in 2009 reported a biodegradable polyacrylamide base CRU using an Ammonium persulfate initiator (APS) and MBA in an aqueous solution under microwave irradiation [74]. They found that the fertilizer release rate is dependent on the water absorption kinetics. Liu et al. 2007 synthesized CRUs *via* an inverse suspension polymerization by adding AAc, MBA, APS, and urea solution in an oil phase [75]. The complete release of urea occurred within 28 days. To date, different copolymers such as PCL and PLA coupling with polyacrylic acid (PAA) and polyacrylamide (PAAM) have been reported to improve the biodegradability of CRFs *via* coating or mixing methods [76, 77]. However, due to the high cost of monomers and process complexity along with environmental pollution issues, research frontiers shifted

towards developing low-cost, simple fabrication, and environmentally friendly polysaccharide-based materials.

2.1.4.4.2 Synthesis of CRFs using synthetic polymers-inorganic materials

Low mechanical properties and viscosity are the main drawbacks of the hydrogel polymers being used for CRFs [13]. Along with these, hydrogel polymers can be expensive making them impractical for agriculture applications. Thus, the implementation of inorganic materials such as clay minerals (bentonite, kaolinite, montmorillonite, and attapulgite) to increase the mechanical resistance of hydrogel polymers has been widely reported [78-81]. Inorganic materials are also being used as fillers to reduce product costs. It has been proven that involving clays in the hydrogel polymers can improve swelling, mechanical resistance, and thermal properties [78-81]. Moreover, the presence of inorganic materials can facilitate the degradation of polymers in the soil. Liang et al. in 2007 implemented kaolin in PAA/PAAm copolymer system [70]. The hydrogel pores could be blocked within kaolin resulting in a decrease in the release rate of urea.

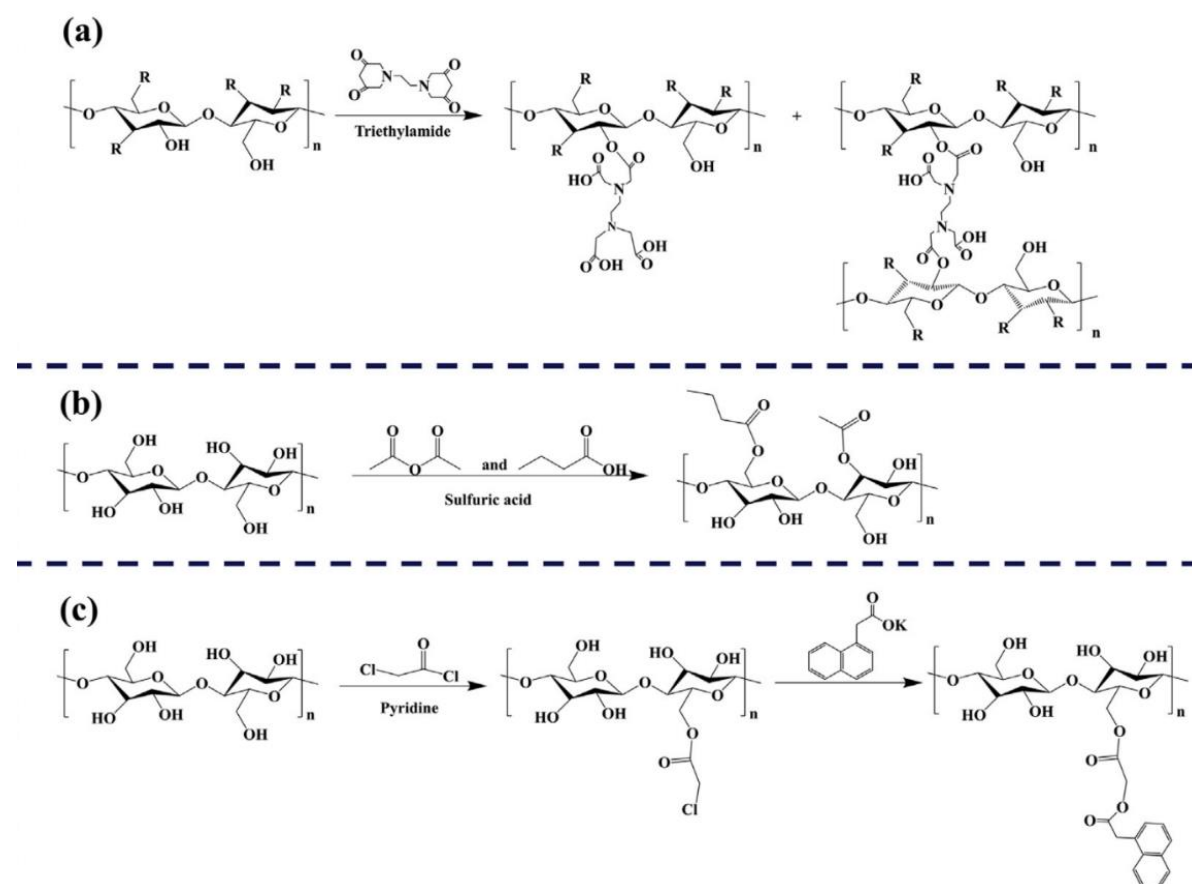
2.1.4.4.3 Synthesis of CRFs using synthetic-natural polymers

Combining synthetic and natural polymers can improve the physical properties and water-holding capacity of CRFs. Natural polymers such as cellulose should be modified through esterification, etherification, or grafting to provide a suitable system for the absorption of fertilizers [8].

Esterification

Esterifying cellulose, such as cellulose acetate and cellulose butyrate, is one of the most useful techniques to improve mechanical strength and hydrophilicity by introducing new functions in the structure of cellulose. Carboxylic acids, carboxylic acid anhydrides,

and acyl halides are frequently used for CRF applications. The schematic illustration of some modifications using the esterification method is shown in **Scheme 2.6**.



Scheme 2.6. Esterification of cellulose using (a) ethylenediaminetetraacetic dianhydride, (b) butyric acid and acetic anhydride, and (c) chloroacetyl chloride. Adapted with permission from ref 8. Copyright 2019 Elsevier.

Senna et al. in 2015 and 2017 esterified cellulose acetate in the presence of ethylenediaminetetraacetic dianhydride (EDTAD) and triethylamine as the catalyst, where EDTAD could increase the water loading of the CRFs because of increasing the polymer entanglement. [82, 83]. Huang et al. in 2018 esterified cellulose acetate butyrate using butyric acid and acetic anhydride in an acidic environment to form CRFs (**Scheme 2.6-b**) [84]. Another method for the esterification of cellulose is using acyl halide derivatives. Martin et al. in 1999 modified the cellulose acetate in two steps i) acylation of cellulose using chloroacetyl chloride, and ii) linking it with 1-naphthylacetic acid [85]. Cellulose

has been esterified via a variety of techniques to improve the mechanical strength of the CRFs, while maintaining a high-water holding capacity [8]. Because of the susceptibility of the ester bonds to hydrolyze, the CRFs are pH-dependent in alkaline or acidic soils.

Etherification

Cellulose ether is another common cellulose derivative used in CRFs. Different etherification studies have been completed to synthesize hydroxyethyl cellulose, ethyl cellulose, and carboxymethyl cellulose. Like esterification, etherification can improve some properties of cellulose for use in CRFs. Generally, chloride or epoxy groups are reacted with hydroxyl groups of cellulose to form ether bonds. **Figure 2.7** shows some examples of etherification using different compounds such as epichlorohydrin [86], β -Cyclodextrine [87], and benzoyl chloride [88]. By modifying the cellulose ether derivatives, the hydrophobicity and hydrophilicity of the compounds can be adjusted based on the type of CRFs. The ether bonds in this type of modified-cellulose are more stable in the alkaline or acidic soil compared to the ester bonds, making them more stable with pH changes.

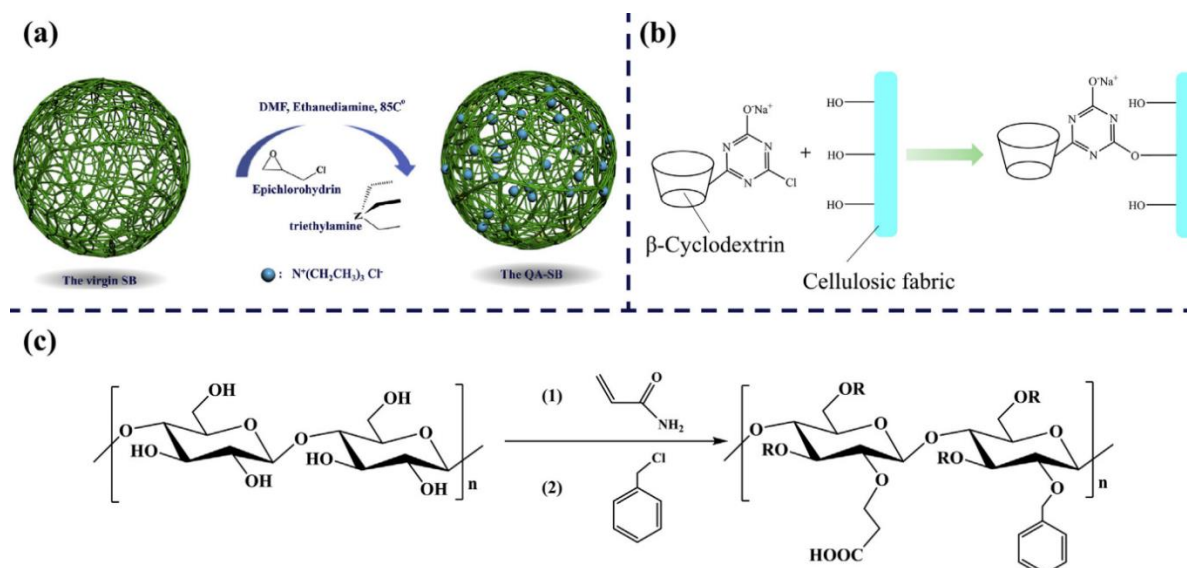
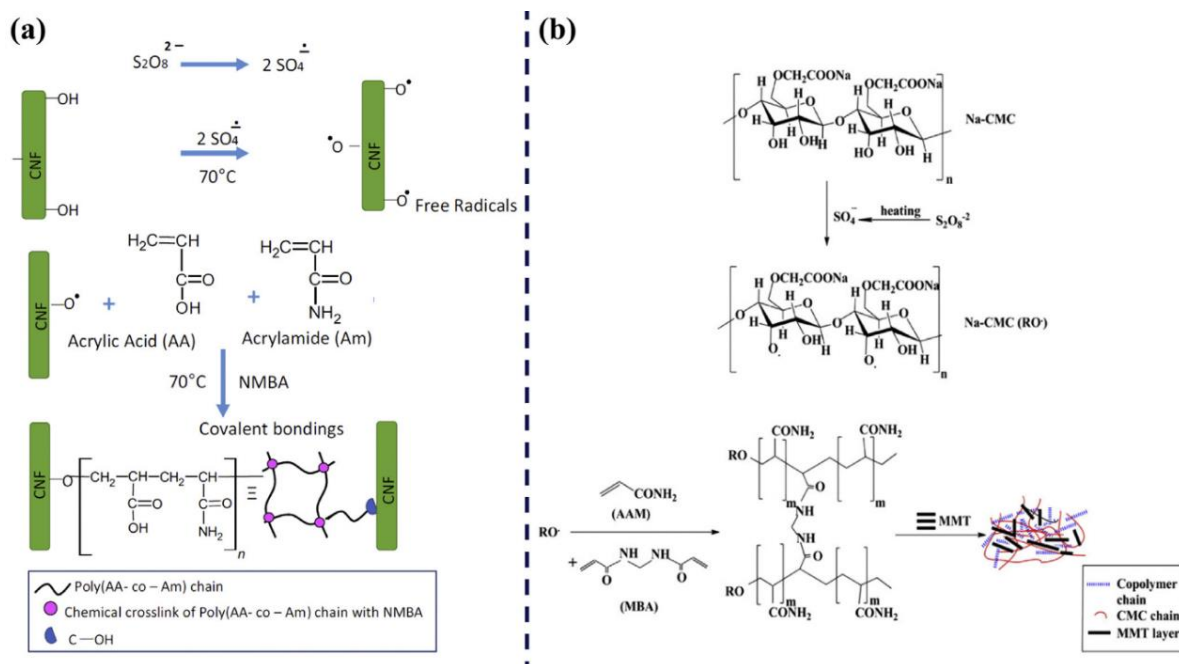


Figure 2.7. Examples of cellulose etherification using etherification agents. (a) epichlorohydrin, (b) monochlorotriazinyl-cyclodextrin, and (c) acrylamide and benzyl chloride. Adapted with permission from ref 8. Copyright 2019 Elsevier.

Grafting Modification

A grafting method is often used to link a polymer with cellulose; this can be classified into two classes “graft from” and “graft to”. In the “grafting to” approach, the synthetic polymer has an end-group, which can be linked to the cellulose backbone. Alternatively, in the “grafting from” method, the radicals are generated through the radicalization of the -OH group of cellulose to -O $\cdot$ by using an initiator (mostly persulfate derivatives such as APS). Then, the radicals initiate free radical polymerization in the presence of a monomer [89, 90]. The “grafting to” approach is mostly used in drug delivery applications since specific functional groups can be added to the polymer, while the “grafting from” approach is more often applied for CRFs. AAc and AAm are common monomers to mix with natural polymers to prepare an interpenetrating polymer network (IPN). Numerous studies have reported fabricating CRFs using this method [91-93]. **Scheme 2.7** shows the schematic of the “grafting from” strategy by using AAc and AAm as the synthetic monomers and the radicalized cellulose acetate as the initiator.



Scheme 2.7. Preparation of the IPN using the “Grafting from” method using cellulose and AAc/AAM monomers. Adapted with permission from ref 8. Copyright 2019 Elsevier

2.2 Fabrication methods of CRFs

The fabrication of CRFs can be conducted through different approaches (**Figure 2.8**), which can be classified into two main pathways, mixing and coating. The mixing method is usually used to fabricate hydrogel materials containing fertilizer, while the coating approach is implemented to provide a physical barrier against water resulting in the controlled-release of fertilizer. While each method has its advantages and drawbacks, they also exhibit different mechanisms of fertilizer release.

2.3 Mixing-type CRFs

Mixing-type CRFs are usually used for hydrogel systems since nutrient molecules can be completely entrapped (encapsulated) in the matrix of chemicals. General speaking, hydrogel polymers along with water-based crosslinking agents are mixed with fertilizers to synthesize CRFs *via* the mixing method, which can be classified into four classes based on the mixing conditions (either in solution or solvent-free condition), including solution

mixing, extruding, ball-mill grinding, and granulation. The solution mixing also can be done in one (in-situ) or two steps [94]. In the one-step technique, all chemicals including monomers, fertilizers, and any modifiers or crosslinking agents are mixed with fertilizers. Here, the fertilizer is entrapped in the matrix during polymerization [93, 95]. The release of fertilizers from the hydrogel systems decreases due to the strong chemical interactions, including hydrogen bonding and electrostatic interactions, between fertilizers and water-based polymers. In the two-step method, the pre-synthesized hydrogel is immersed in a solution of fertilizer followed by absorption of fertilizer and hydrogel drying [96, 97]. The release rate of fertilizers is slower in the two-step method and the resultant side reactions from adding materials are eliminated [98]. However, to make the pre-synthesized polymer, a large amount of crosslinking agents are needed. [99].

A solid-state protocol through fractionation, including extruding, ball-mill grinding, and granulation can be employed to encapsulate fertilizers. The mechanical friction enhances the interaction between nutrients and other materials, resulting in the encapsulation of nano-micro size fertilizers. This method is interesting for both research and industry because it is easy to scale up using a solvent-free protocol and it can be used with a wide range of biodegradable materials.

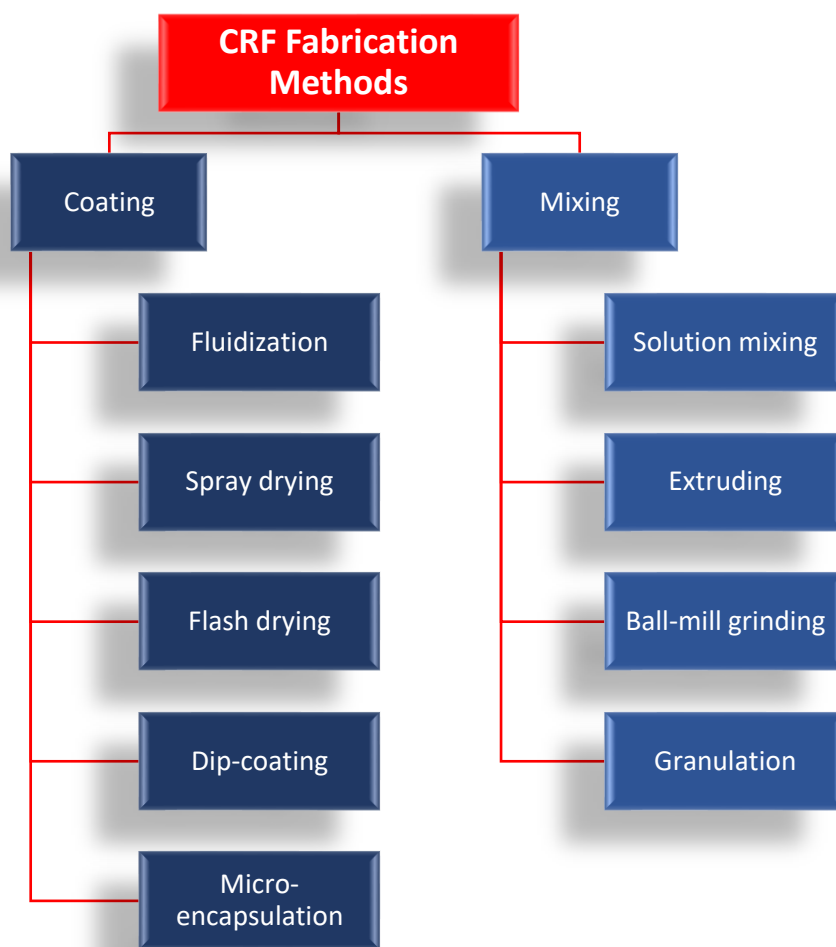


Figure 2.8. The common methods to fabricate CRFs.

2.4 Coated-type CRFs

Coated-type CRFs are fabricated by coating either hydrophobic or hydrophilic materials, dominantly polymers, onto fertilizer to reduce nutrient dissolution. This method is highly dependent on the physical properties of the outer layer such as hydrophobicity, hydrophilicity, wettability, permeability, and thickness. The nutrient release from CRFs prepared by this method is more controlled compared to the mixing method as the rate of water diffusion into the coated fertilizer granules can be adjusted through the physicochemical and mechanical properties of the coating barrier [6, 11]. The coating materials can be either sprayed or assembled on fertilizer granules through different

techniques, including fluidization, spray drying, flash drying, dip coating, and micro-encapsulation. While the coating in the first three techniques mostly depends on the physical phenomenon to attach to the fertilizer granules, the assembly of coating materials in the dip-coating and micro-encapsulation methods relies on the formation of chemical interactions between the surface of fertilizer granules and ingredients.

2.5 The release mechanism of CRFs

The release mechanism of fertilizers from CRFs depends upon several elements such as the inherent nature of the coating material (being hydrophobic or hydrophilic), the procedure used to mix the fertilizer (mixing and coating), agronomic conditions (pH, texture, and moisture of the soil) and the vapor pressure and temperature of the environment.

A possible description of the release mechanism for coated CRFs is the multi-stage diffusion model presented by Shaviv and Liu (**Figure 2.9**) [25]. According to this model, after the application of CRFs to the soil or water, water penetrates the coating to dilute the solid fertilizer core (e.g., urea), followed by partial fertilizer dissolution [11]. Then, as osmotic pressure builds within the capsule, the granule swells and causes two different processes. First, when the osmotic pressure surpasses the threshold of the coating material resistance, the coating ruptures, and the entire core is spontaneously released, which is called “failure mechanism” or “catastrophic release”. Second, if the coating layer resists the pressure, the nutrient may be released slowly by diffusion for which the driving force may be a concentration or pressure gradient, or a combination thereof called the “diffusion mechanism” according to Fick’s 2nd law of diffusion. Overall, fragile coatings such as sulfur and its derivatives show the failure mechanism, while modified polymers exhibit the second mechanism (diffusion mechanism) [75, 100-102].

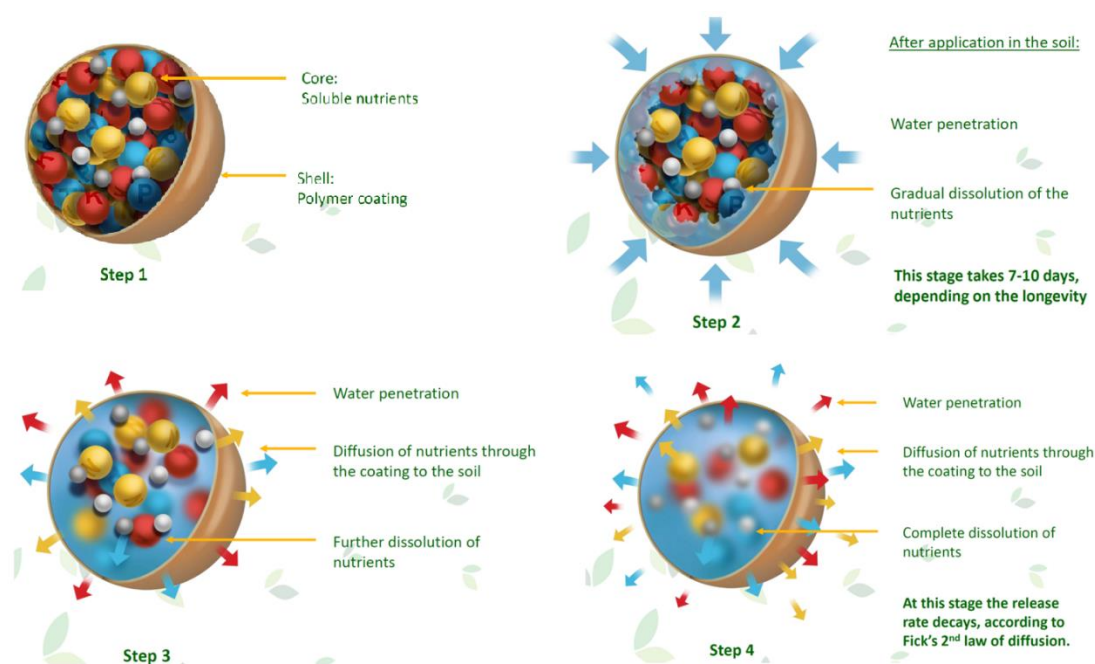


Figure 2.9. Diffusion mechanism of CRFs; (step 1) covering a solid fertilizer using a polymer, (step 2) water penetrating the coating, (step 3) solid fertilizer dissolution and increasing the osmotic pressure inside the coated granules, (step 4) swallowing coating membrane and release the fertilizer [From Haifa slide presentation [103]].

The release of nutrients from the hydrogel CRFs that are made by the mixing-type procedure is predominantly governed by the shrinking or diffusion phenomenon. **Figure 2.10** displays how nutrients can be released from hydrogel systems into the environment [104-106]. In the shrinking pathway, fertilizers only start to release once the water content of the CRFs drops, but in the diffusion mechanism, fertilizers start to release when the osmotic pressure between the CRFs and soil changes.

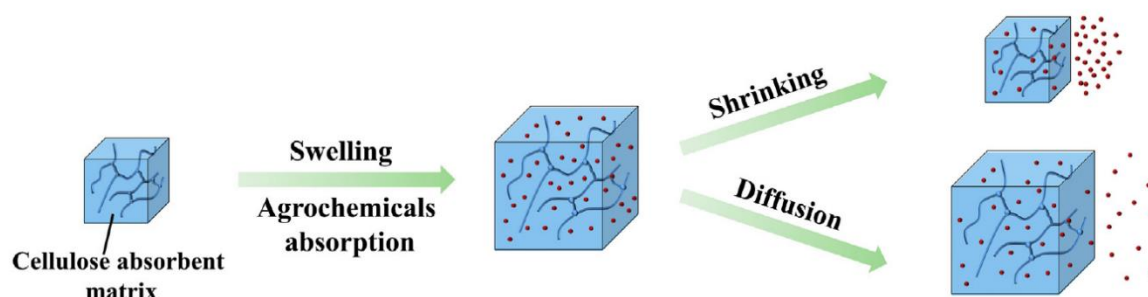


Figure 2.10. The mechanism of nutrient release from hydrogel materials. Adapted with permission from ref 8. Copyright 2019 Elsevier.

2.6 Metal-Phenolic Networks

Simple and facile coating methods are pivotal in CRF applications. Polyphenol coatings have been successfully established for surface coatings [9]. Recently, a simple, rapid, and material-independent surface coating method using metal-phenolic networks (MPNs) was reported [107]. MPNs are a class of dynamic coordination materials that can be synthesized from a wide selection of phenolic ligands and metal ions. They can easily make conformal coatings on a wide range of templates and surfaces due to strong interfacial interactions with substrates [108, 109]. As making MPNs is the main point of this thesis, a broad view of MPNs for CRUs manufacturing is fully covered in the introduction sections of *Chapter 3* and *4*. Please refer to sections 3.2 and 4.2 for more details.

2.7 Conclusion

Based on the literature review conducted, the current CRF technology is limited to using either biodegradable or non-biodegradable polymers. These polymers can be employed using two main techniques, including making a hydrophobic coating on fertilizer granules or preparing a matrix of fertilizer by mixing them with hydrophilic polymers and crosslinking agents. Reducing the fabrication steps of CRFs is another consideration for large-scale production. Thus, the recent efforts move toward using natural resources through a minor modification for CRF applications. With this in mind, the use of metal-phenolic networks (MPNs) for fabrication of CRF may usher in significant changes because natural resource polyphenols are readily available, and the combination of polyphenols with a variety of metals can provide novel tunable coatings for CRF fabrication. Moreover, the quick and straightforward synthesis processes of MPNs make these materials interesting for commercialization. Therefore, in the upcoming research chapters, the synthesis of MPNs for the fabrication of CRFs were considered through both coating (*Chapter 3*) and matrix (*Chapter 4*) approaches. For this

purpose, fundamental insights into the formation of MPNs were first achieved to ensure the compatibility of MPNs with fertilizers. Then, urea fertilizer was chosen as a candidate for the fabrication of CRUs, as around 35% of N application in agriculture occurs as urea fertilizer, while nitrogen loss is the main concern through hydrolysis and nitrification. At the end of each chapter, the release rate of urea from fabricated CRUs was assessed in water (*Chapter 3*) and soil (*Chapter 4*).

CHAPTER 3

Assembly of Metal–Phenolic Networks on Water-Soluble Substrates in Nonaqueous Media

This chapter investigates the formation of metal-phenolic networks in acetonitrile on urea granules and its performance as a controlled-release of urea in water.

The chapter has resulted in the following publication:

O. Mazaheri, M.S. Alivand, A. Zavabeti, S. Spoljaric, S. Pan, D. Chen, F. Caruso, H.C. Suter, and K.A. Mumford, Assembly of Metal–Phenolic Networks on Water-Soluble Substrates in Nonaqueous Media, *Advanced Functional Materials*, **2022**, 32, 2111942.

This Page Intentionally Left Blank

3.1 Abstract

Interfacial modular assemblies of eco-friendly metal–phenolic networks (MPNs) are of interest for surface and materials engineering. To date, most MPNs have been assembled on water-stable substrates; however, the self-assembly of MPNs on highly water-soluble substrates remains unexplored. Herein, a versatile approach is reported to engineer thickness-tunable coatings (2–25 μm) of a water-soluble substrate (i.e., urea) via the self-assembly of MPNs in a non-aqueous solvent (i.e., acetonitrile). The coordination-driven assembly of the MPN coatings in the non-aqueous solvent is distinct from that in aqueous systems, as the assembly is only achieved following the addition of urea granules into the iron–tannin solution. The coating occurs relatively rapidly (5–60 min), generating micrometer-thick coatings from the adsorption of Fe^{III} –TA complexes and micrometer-sized Fe^{III} –TA particles formed in solution. The straightforward nature of the present fabrication method in generating thick and robust coatings with high stability in non-aqueous environments (including at 60 °C) coupled with the broad range of available naturally abundant polyphenol–metal ion combinations expand the applicability of MPNs as coatings for water-soluble materials, thus providing new opportunities for their broader application in a range of industrial processes and applications.

3.2 Introduction

Polyphenol compounds, which are naturally abundant and found in most plant families, possess antibacterial, anticarcinogenic, and antioxidant properties [110]. Tannic acid (TA) is a specific type of tannin with multidentate chelation properties and is inexpensive and highly biocompatible (**Figure 3S 1**) [111]. Its potential to engage in multiple interactions with different types of solid surfaces makes it useful for the formation of coatings via self-assembly [9]. In 2013, Ejima et al. reported a facile assembly method to form metal–phenolic networks

(MPNs) on a range of substrates of nano-to-macroscopic size [107]. In general, the catechol/galloyl groups of TA provide multivalent chelating sites for coordination with various metals [112]. Fundamental studies have shown that the formation kinetics and the physiochemical properties of MPNs on substrates are governed by pH, metal-to-ligand (M:L) ratio, precursor concentration, and the order in which metals and ligands are introduced into aqueous media [113-116].

To date, different MPN assembly methods have been developed, including discrete,[107] multistep [113], precomplex [114], electro-triggered [117, 118], rust-mediated [119, 120], oxidation-mediated [121, 122], and liquid–liquid interfacial growth [123, 124]. Since the introduction of MPNs, there has been a growing interest in their potential applications in areas such as drug delivery [125], theranostics [126], forensics [127], catalysis [128], phototaxis [129], and as conductive materials [130], bioresponsive materials [131, 132], and energy storage devices [133, 134]. In addition, MPN assemblies have been applied as antimicrobial spray coatings for shoe insoles and fruits [135], inks for printing and writing [136], oil–water separation membrane materials [137, 138], and hair dyes [139]. Despite these previous studies, to date MPN coatings have been formed almost exclusively on materials that are stable in aqueous solutions. Assembling MPN coatings on highly water-soluble materials would expand their potential use in a range of fields, including fertilizer and pesticide applications, where often controlled-release of water-soluble materials is required.

Polyphenols provide robust and diverse interactions (i.e., hydrogen bonds, π – π stacking, hydrophobic interactions, metal coordination, electrostatic interactions, and covalent bonds) with substrates, thereby making them suitable for the formation of MPNs on water-soluble substrates in organic solvents. Judicious selection of the organic solvent is important as the pK_a of the solvent affects the availability of potential binding sites between the catechol or galloyl groups and the metal ions for chelation and assembly into mono-, bis-, or tris-complexes [108,

138]. In addition, similar to assembly from aqueous solution, avoiding the polymerization and oxidation of polyphenols, which can alter the MPN coordination structure and subsequent physiochemical properties, is often a key requirement [110, 117, 138]. Furthermore, fundamental studies on the mechanism of MPN formation on water-soluble substrates in non-aqueous media would provide useful insights for potential application in a range of areas.

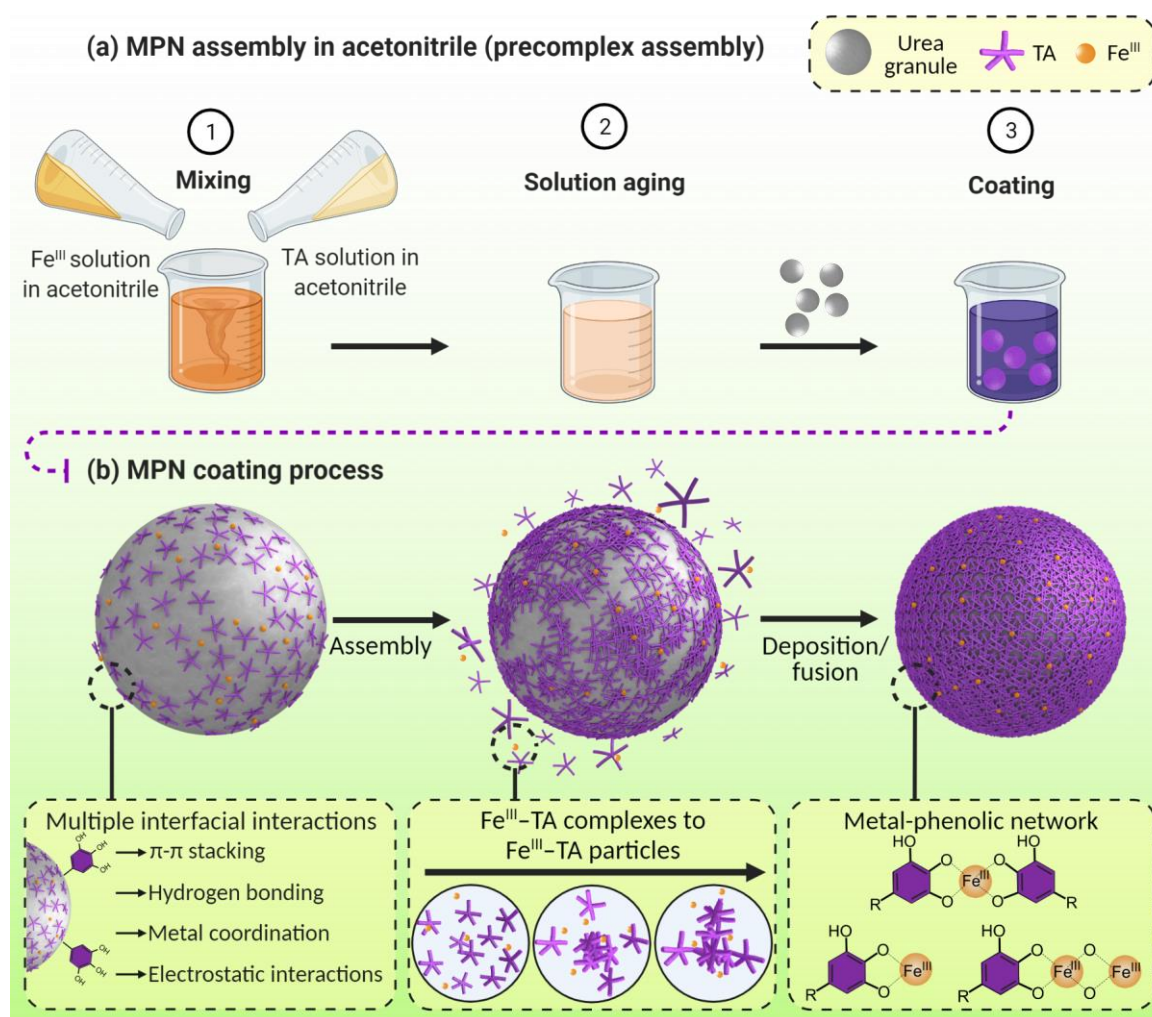
Herein, we report a facile coating strategy for the assembly of Fe^{III}–TA MPNs onto urea granules (i.e., a highly water-soluble substrate) in acetonitrile to engineer a range of coatings with different physicochemical properties (surface roughness, thermal stability, and particle size). Assembly proceeds via a three-step process, as summarized in **Scheme 3.1**. In the first step, Fe^{III} and TA precursor solutions in acetonitrile are mixed and the catechol moiety of TA reacts with Fe^{III} in acetonitrile to form mono-complexes. In the second step, this reaction mixture is allowed to age for a predetermined time (solution aging time). In the third step, urea granules are added to the aged solution, which changes the coordination of the Fe^{III}–TA complexes from mono- to bis-, forming stable MPN films directed by the energetically favorable adsorption of catechol groups onto the substrate, and cross-linking of ligands via covalent and coordination bonding. A real-time particle growth analysis suggests that micrometer-sized Fe^{III}–TA particles are generated in solution only after the addition of urea granules, whereas no Fe^{III}–TA particles are detected in the mixed solution (in the first step) even after solution aging. These observations highlight the key role of substrates with amine functionalities in the formation of MPNs in non-aqueous media. The Fe^{III}–TA complexes and Fe^{III}–TA particles (dynamic building blocks) adsorb on the urea granules. Meanwhile, the Fe^{III}–TA complexes can bridge the micrometer-sized particles, resulting in a driven-diffusion coating process, due to the high binding affinity of the bis-complex building blocks at the surface of the substrate, and fuse into a film (**Scheme 3.1**) with a micrometer-sized thickness (2–25 μm). The present strategy can potentially be extended to different organic ligands and

metal ions for the encapsulation of next-generation water-soluble fertilizers, pharmaceutical compound carriers, and other water-soluble substrates/templates.

3.3 Results and Discussion

3.3.1 MPN Formation in Acetonitrile

The formation of Fe^{III}–TA MPNs on the surface of urea granules in acetonitrile was examined via different assembly approaches, including precomplex, oxidation-mediated coordination, discrete, and spray assembly, as schematically presented in **Scheme 3.1** and **Figure 3S 2**. A summary of the findings obtained are provided in the caption of **Figure 3S 2** and **Table 3S 1**. All methods successfully led to MPN coatings on the urea granules in acetonitrile. However, because the precomplex self-assembly method led to thicker MPN films within a shorter coating timeframe (when compared with the other methods), this method was chosen for further investigation. Briefly, Fe^{III} and TA solutions were mixed in acetonitrile at a stoichiometric ratio of 1.5:1 (the concentration of TA was fixed at 2.3 mM), allowing the formation of Fe^{III}–TA mono-complexes. The solution was allowed to age for 15 min. The urea granules were then immersed into the Fe^{III}–TA aged solution, resulting in the spontaneous formation of Fe^{III}–TA particles in solution, followed by MPN film coating on the surface of the urea granules. UV–vis spectroscopy of a TA solution in acetonitrile confirmed the absence of a quinone intermediate, indicating that further dimerization or oligomerization of TA was unlikely. In addition, mixing Fe^{III} with the TA solution kept the pK_a of the solution low and prevented TA ionization (as discussed in **Figure 3S 3**) [113, 138, 140, 141].



Scheme 3.1. Schematic illustration of the MPN assembly protocol used to coat urea granules (water-soluble substrate) in acetonitrile solution. (a) Overview of the different steps involved in the formation of an MPN coating onto urea granules: step 1, iron and tannic acid solutions are mixed to generate Fe^{III}-TA complexes; step 2, the solution is aged, possibly resulting in the conversion of Fe^{III}-TA complexes into Fe^{III}-acetonitrile complexes; step 3, urea granules are introduced into the aged solution for the MPN coating to proceed. (b) MPN coating proceeds via multiple interfacial interactions between the urea granules and TA, iron, and Fe^{III}-TA complexes; Fe^{III}-TA particle aggregation; and subsequent deposition of the Fe^{III}-TA particles and fusion onto the urea granules.

In aqueous media, typically, Fe^{III}-TA complexes (predominantly bis- and tris-complexes at pH ≥ 3) are formed upon mixing of the metal ion and ligand solutions, as indicated from the dark blue/violet color of the resulting solution [107]. These complexes can then deposit and grow on substrates while MPN nanoparticles can form in solution, and these nanoparticles can also adsorb on the substrates [107, 113]. However, Fe^{III}-TA complex formation in acetonitrile is markedly different to what occurs in aqueous solution. First, bis- and/or tris-complexes of Fe^{III}-

TA do not form upon mixing of the metal ion and ligand solutions, as confirmed by the absence of a ligand-to-metal charge transfer (LMCT) band at 565 nm (**Figure 3S 4**) and the lack of a solution color change to blue/violet in the mixing and solution aging steps. Second, the bis-complexes due to Fe^{III} -TA coordination form only after the addition of urea granules (as discussed in detail below). Third, micrometer-sized Fe^{III} -TA particles are generated in solution after the addition of the urea granules and coated the urea granules (as discussed in detail below). During the formation of MPNs in aqueous media, the presence of water molecules may be necessary to form Fe^{III} -TA bonds through the formation of different iron species, including monomeric, dimeric, and trimeric ferric aqua hydroxo complexes. Therefore, under these conditions, pH adjustment of the prepared Fe^{III} solution is important, as FeCl_3 is highly prone to hydrolyzation (solubility product constant, $K_{\text{sp}} = 6 \times 10^{-39}$), leading to the formation of insoluble $\text{Fe}(\text{OH})_3$ [113].

From the findings discussed above, to further examine the formation of Fe^{III} -TA coordination complexes in acetonitrile solution prior to the addition of the urea granules, the solution aging time was varied. As the aging time was increased from 1 to 180 min, the originally amber-colored solution became lighter (**Figure 3.1a**). The UV-vis absorption spectra of the solution at different aging times featured an absorption band within the range ~ 450 – 650 nm with λ_{max} of 475 nm in line with the formation of mono Fe^{III} -TA complexes (**Figure 3.1b**). The absorption intensity of the peak within the range of ~ 450 – 650 nm decreased as the aging time increased. As no precipitation was detected, as determined by dynamic light scattering (data not shown), the reduction in peak intensity with increasing aging time can be attributed to a change in the Fe^{III} -TA coordination complexes via a reversible reaction. (**Figure 3.1c**). Acetonitrile with high electron-donor strength can be partially replaced by TA in the Fe^{III} -TA complexes to form $2\text{FeCl}_3 \cdot \text{FeCl}_2 \cdot x\text{CH}_3\text{CN} \cdot y\text{H}_2\text{O}$ through the reduction of Fe^{III} to Fe^{II} [142-144], leading to the dissociation of mono Fe^{III} -TA complexes [121, 145]. The lower reactivity

and stability of Fe^{II} -TA owing to the dynamic nature of the coordination bond causes this dissociation and the formation of H_2O - Fe^{II} complexes over time (**Figure 3S 5**) [121, 122, 146]. To monitor the formation of Fe^{II} and acetonitrile- Fe^{II} interactions in solution after mixing the ligand and metal, 1,10-phenanthroline indicator was added to the Fe^{III} -TA solution, and the solution was analyzed via UV-vis spectroscopy (**Figure 3.1d**). An absorption band within the range of ~ 400 – 600 nm with λ_{max} at 512 nm was observed, which is attributed to the formation of Fe^{II} -1,10-phenanthroline complexes [147]. The absorption intensity of this band increased with aging time, confirming that Fe^{III} partially converted into Fe^{II} during aging of the Fe^{III} -TA solution.

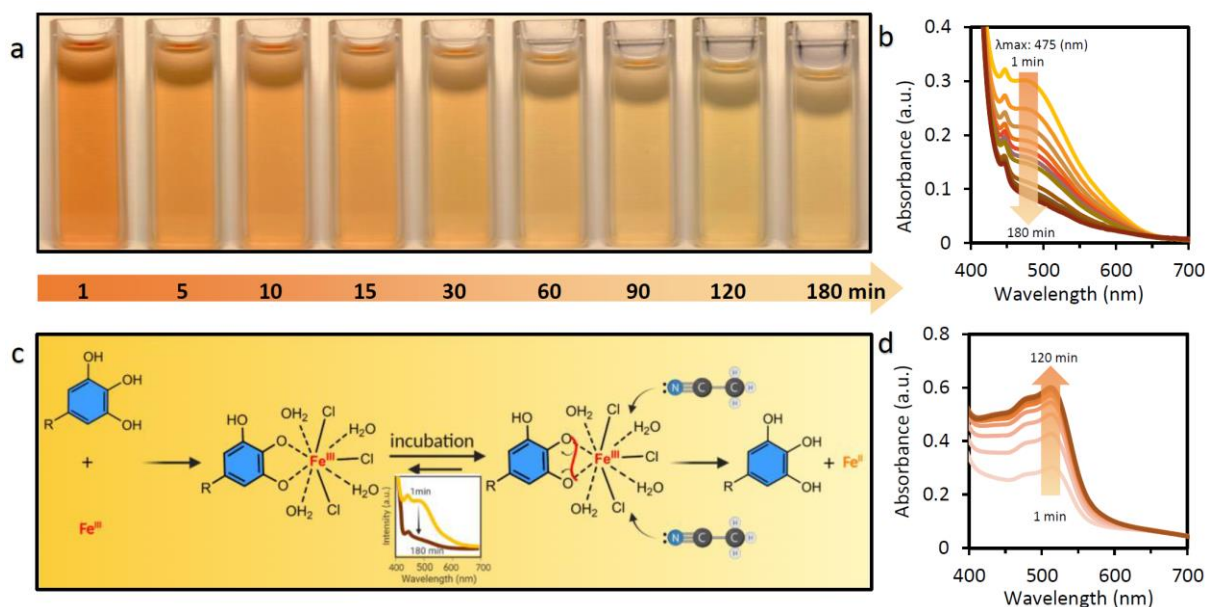


Figure 3.1. Influence of solution aging time on Fe^{III} -TA complex formation in acetonitrile before the addition of urea granules. (a) Photograph of Fe^{III} -TA solutions showing solution color changes as a function of solution aging time. (b) UV-Vis spectra of Fe^{III} -TA solutions at different solution aging times. (c) Schematic illustration of the formation of Fe^{III} -TA complexes in acetonitrile solution at different solution aging times. (d) UV-vis spectra of Fe -TA solution at different solution aging times after addition of 1,10-phenanthroline indicator. All data are for systems prepared with a final concentration of 2.3 mM TA and an M:L molar ratio of 1.5:1 at 25 °C.

An aging time of 15 min was selected to subsequently evaluate the formation of Fe^{III} -TA particles upon addition of the urea granules in the aged solution using UV-vis spectroscopy. Analysis of the Fe^{III} -TA solution after the addition of urea granules revealed a characteristic

LMCT band at ~565 nm (**Figure 3.2a**), confirming the formation of Fe^{III}–TA complexes [148]. The analytical data suggest that several factors contribute to Fe^{III}–TA particle formation in acetonitrile following the addition of urea granules. First, the amine group of dissolved urea (–NH₂) in acetonitrile (the solubility of urea in acetonitrile is ~4 g L⁻¹ at room temperature) can play a role in the formation of intermediates between the hydroxyl groups of TA and water molecules of FeCl₃·6H₂O via hydrogen bonding. This approach further facilitates the formation of Fe^{III}–TA complexes (similar to the role of H₂O in aqueous solution) (**Figure 3S 6a**) [149]. Control experiments were conducted to investigate this process. Water droplets were added to the aged solution in acetonitrile, resulting in an immediate dark blue solution. Also, protic organic solvents, such as methanol, ethanol, and butanol, were added to the aged solution—an LMCT band at $\lambda_{\text{max}} = 565$ nm, typical for Fe^{III}–TA bis-complexes, and a dark blue solution were obtained, highlighting the role of solvent-present hydroxyl groups for adsorbing Fe^{III} species and binding to TA through the provision of hydrogen bonds. The absence of water in the urea granules was confirmed by thermogravimetric analysis (TGA) (**Figure 3S 7**). Second, the –NH₂ groups of urea can deprotonate the catechol groups of TA and initiate the formation of coordination complexes (**Figure 3S 6b**). Third, after the formation of an acetonitrile solvation shell around the iron complexes, the acetonitrile can replace the H₂O and Cl⁻ ligands of FeCl₃·6H₂O, releasing water and chlorine, thereby providing suitable conditions for the hydrolysis of urea to ammonia [142]. The generated NH₃ can facilitate further deprotonation of catechol groups and subsequent Fe^{III}–TA particle formation (**Figure 3S 6c**).

Fourier transform infrared spectroscopy and energy-dispersive X-ray spectroscopy (EDX) analyses revealed the presence of amide bonds and nitrogen atoms in the Fe^{III}–TA films (following removal from solution and washing with water) (**Figure 3S 8a,b**). Furthermore, the presence of N–Fe bonds was detected via X-ray photoelectron spectroscopy (XPS), confirming coordination bonding between urea and Fe^{III} (**Figure 3S 8c**). No urea–TA bonding interactions

were detected in the XPS spectrum of Fe^{III}–TA MPNs following removal of the urea granules. Moreover, the role of urea in cross-linking via Michael addition and/or Schiff-base reactions among TA molecules can be ruled out, as investigated by matrix-assisted laser desorption ionization–time-of-flight (MALDI-ToF) mass spectrometry, most likely due to the weak nucleophilicity of urea (**Figure 3S 8d**) [150-152]. Thus, the formation of dipolar bonds between the lone pair of electrons on the nitrogen atoms of urea and Fe^{III} (**Figure 3S 8e**) is likely to cause the color change of Fe^{III} solution from yellow to transparent and the immediate formation of Fe^{III}–TA particles after the addition of urea granules [153-156].

Using the same solution aging time of 15 min, the subsequent formation of the MPN coating on the urea granules (urea granules@MPN) from the adsorption of the Fe^{III}–TA complexes and particles was investigated. The broad band at 500–650 cm⁻¹ observed in the Raman spectroscopy pattern of the MPN film was attributed to Fe–O vibrations arising from Fe^{III}–galloyl coordination (**Figure 3.2b**) [133]. In addition, the presence of bands at 1430 cm⁻¹ (symmetric) and 1575 cm⁻¹ (asymmetric), and the difference between these two bands of 145 cm⁻¹ is attributed to the bridging carboxylate functionality [157]. The absence of a peak in the range of 385–410 cm⁻¹ suggests that the μ -catecholate bridging mode, which is assigned to $\nu_{\text{Fe-O}}$, is not dominant in the Fe^{III}–TA complexes [157]. This is likely due to the local environment, i.e., acetonitrile, and the existence of dissolved urea, around the Fe^{III} center. The XPS pattern of the MPN capsules featured Fe 2p_{3/2} and 2p_{1/2} signals at 712 and 726 eV with a separation of ~14 eV, indicating that the dominant iron species in the MPN film was Fe^{III} (**Figure 3.2 c**) [118, 158, 159]. This finding was consistent with the EDX images of the cross-section of urea granules@MPN, which confirmed the presence of elemental iron in the coating (**Figure 3S 9**). The MPN coating process was also monitored by scanning electron microscopy (SEM). **Figure 3.2d–g** shows SEM images of the surface of urea granules@MPN as the coating proceeded (15, 30, and 45 min) while the solution aging time was fixed at 15 min. The changes observed

in the morphology and surface roughness as a function of coating time indicated the occurrence of a diffusion-driven process. In addition, the observed depletion of the Fe^{III} -TA particles generated in solution through adsorption onto the urea granules (**Figure 3S 10**) confirms the formation of an MPN coating. The MPN film thickness of urea granules@MPN (obtained after coating for 45 min) was $\sim 10\text{--}14\ \mu\text{m}$, as evaluated by optical profiling, height profiling of the film/capsule (after urea granules were removed from the core-shell structure), and cross-section SEM imaging (**Figure 3S 11** and **Figure 3.2g** inset). It is noteworthy to mention that the dynamic nature of MPN assembly in acetonitrile facilitates the adsorption of different types of species on the urea granules. For example, both Fe^{III} -TA complexes and micrometer-sized particles adsorb on the urea granules throughout the coating process, as well as Fe^{III} -TA complex-bridged micrometer-sized Fe^{III} -TA particles. Furthermore, SEM images confirmed that MPNs could be coated onto urea granules in acetonitrile when anhydrous FeCl_3 precursor was used instead of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (**Figure 3S 12**). The surface morphology of urea granules@MPN prepared with anhydrous FeCl_3 was similar to that prepared with $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$. To highlight the versatility of this coating method, various nitrogen-rich, water-soluble substrates (i.e., calcium ammonium nitrate, sodium nitrate, and potassium nitrate) were coated with MPN films in acetonitrile media (**Figure 3S 13**). After coating, the color of calcium ammonium nitrate and potassium nitrate changed from white to blue-violet, whereas the color of sodium nitrate changed from white to brown. The presence of LMCT bands at $\sim 400\text{--}800\ \text{nm}$ in the UV-vis spectra of the Fe^{III} -TA solutions following addition of the substrates confirmed the formation of Fe^{III} -TA complexes. Fe^{III} -TA complex formation and MPN coating of urea granules were also successfully achieved in a range of other different solvents (i.e., isopropanol, tetrahydrofuran, ethyl acetate, and 1,4-dioxane) (**Figure 3S 14**), further confirming the versatility of this coating method.

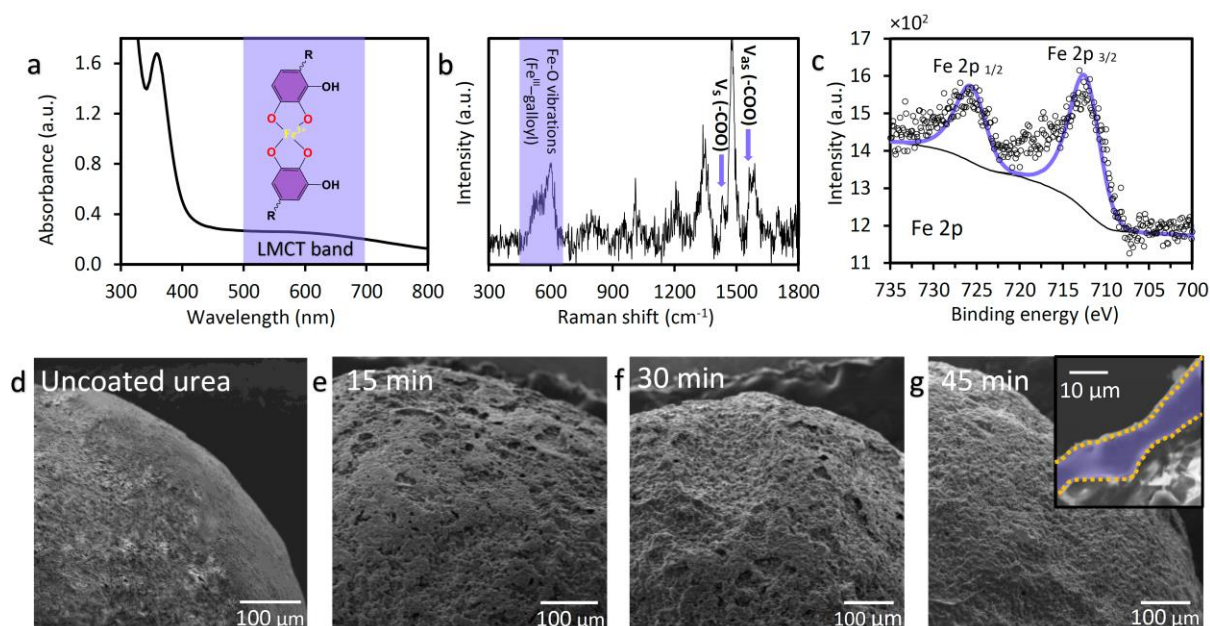


Figure 3.2. Formation of MPN film on urea granules. (a) UV–Vis spectrum of Fe^{III}–TA solution in acetonitrile after immersion of urea granules; the highlighted area (500–665 nm) corresponds to the LMCT band of the Fe^{III}–TA complexes. (b) Raman spectrum of the MPN film deposited on the urea granules. (c) XPS pattern of the MPN film deposited on the urea granules (Fe 2p area). (d–g) SEM images of the surfaces of urea granules@MPN showing the time-dependent growth of an MPN film on urea granules following immersion of the urea granules in the Fe^{III}–TA solution: 0 min (uncoated urea granule) (d); 15 min (e); 30 min (f); and 45 min (g). The inset in (g) shows an SEM cross-section image of urea granules@MPN. All data are for systems prepared with a final concentration of 2.3 mM TA, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min at 25 °C.

3.4 Factors Influencing MPN Formation and Growth

3.4.1 Effect of Solution Aging Time

To investigate the effect of solution aging time on Fe^{III}–TA particle formation and morphology of the MPN films, urea granules were added to TA and Fe^{III} solutions that were aged at different times (1, 15, and 60 min). A real-time focused beam reflectance measurement (FBRM) technique was employed to assess the effect of solution aging time on the Fe^{III}–TA particle growth and the coating time using population distribution measurements of generated Fe^{III}–TA particles in the form of chord length [160, 161]. As observed in **Figure 3.3a, b**, the MPN coating process was complete within 35 min when a solution aging time of 1 min was used, whereas a longer coating process of 55 min was observed when a longer solution aging time

of 60 min was used. These results reflect the role of Fe^{II} on the kinetics of MPN formation. SEM analysis of the coated urea granules revealed that the morphology of the MPN films was smoother when the films were formed from solutions with longer solution aging times (**Figure 3.2g** and **Figure 3.3c, d**). The longer solution aging times, as discussed above, resulted in higher $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ ratios in the solution. The assembly kinetics can strongly influence the mode of molecular packing. Thus, the gradual conversion of $\text{Fe}^{\text{II}}\text{-TA}$ into $\text{Fe}^{\text{III}}\text{-TA}$ via oxidation of iron provides additional opportunities for conformational rearrangement and results in the formation of smaller building blocks of $\text{Fe}^{\text{III}}\text{-TA}$ complexes [121, 122].

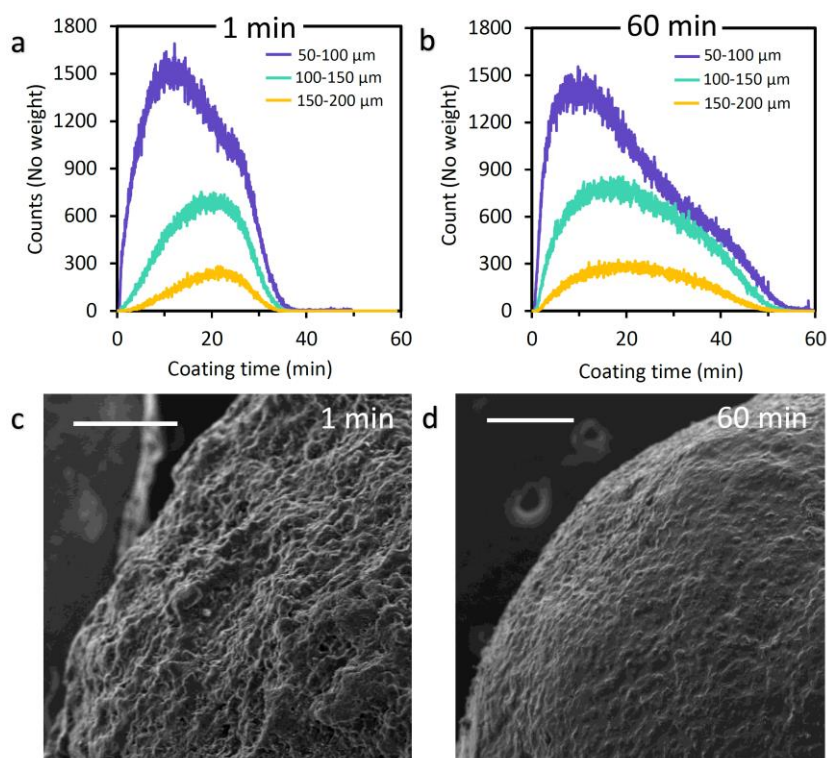


Figure 3.3. Influence of solution aging time on $\text{Fe}^{\text{III}}\text{-TA}$ particle formation in acetonitrile after the addition of urea granules into the $\text{Fe}^{\text{III}}\text{-TA}$ solution. (a, b) $\text{Fe}^{\text{III}}\text{-TA}$ particle growth and population distribution (number weight) using solution aging times of 1 and 60 min, as measured by FBRM. (c, d) SEM images of the surface of MPN films coated on urea granules prepared using solution aging times of 1 and 60 min. Scale bars are 250 μm . All data are for systems prepared with a final concentration of 2.3 mM TA and an M:L molar ratio of 1.5:1 at 25 $^{\circ}\text{C}$.

3.4.2 Effect of Precursor Ratio

The effect of the M:L molar ratio on the assembly of the MPN coating after the addition of urea granules into the aged solution was explored by changing the concentration of the iron solution from 1.1 to 7.0 mM, while the concentration of TA, solution aging time, and coating process temperature were kept constant at 2.3 mM, 15 min, and 25 °C, respectively. As observed from the FBRM results in **Figure 3S 15**, the coating time increased from 35 to 60 min with an increasing M:L ratio from 0.5:1 to 3:1. Likewise, the number of particles formed in acetonitrile solution increased with an increase in the M:L ratio. It is likely that increasing the concentration of Fe^{III} , as the cross-linking agent, led to an increased degree of Fe^{III} -TA complex formation and facilitated MPN nucleation in solution. Accordingly, a longer coating time can be expected at higher M:L ratios owing to the higher number of particles formed in Fe^{III} -TA solution at the higher M:L ratios. Interestingly, the particle count in the range of 150–200 μm showed negligible increases as the M:L ratio was increased from 0.5:1 to 3:1 compared with the particle count in the range of 50–100 and 100–150 μm . The Fe^{III} -TA particle growth in acetonitrile was likely complete for particles smaller than 150 μm . The higher content of Fe^{III} could induce enhanced deprotonation of the ligands, leading to electrostatic repulsion among TA molecules and the separation of larger complexes into smaller fragments[162]. The influence of the M:L molar ratio on the surface morphology is shown schematically in **Figure 3S 16a**. SEM (**Figure 3.4a** inset and **Figure 3S 16b–e**) and atomic force microscopy (AFM) (**Figure 3.4a** and **Figure 3S 17**) images show that the surface roughness increased considerably with increasing M:L ratios, as determined from the root-mean-square value that increased from 13.4 to 74.0 nm as the M:L ratio increased from 0.5:1 to 3:1. The binding of the 100–200 μm particles to the MPN film surface followed by fusion onto the film led to an increase in the surface roughness [121]. The increased surface roughness at the higher M:L ratio may be attributed to the generation of a large variety of complexes such as μ -carboxylate bridging and

μ -oxo bridging in multinuclear Fe^{III} species (**Figure 3S 18a**). The thickness of the MPN coatings increased from ~ 5 to ~ 20 μm with increasing M:L molar ratio (**Figure 3.4 4b** and **Figure 3S 18b–i**). Accordingly, the total MPN content in the prepared urea granules@MPN increased from 0.27 to 1.54 wt% with an increase in the M:L molar ratio from 0.5:1 to 3:1 owing to an increase in the total count of particles generated at higher Fe^{III} concentrations (**Equation S1**, **Figure 3S 19**, and **Table 3S 2**).

The proportion of bis-type complexes formed following immersion of urea granules into the aged solution increased with increasing M:L molar ratio, as indicated by the increased intensity of the absorbance band at 565 nm (**Figure 3S 20**). TGA/differential thermogravimetry (DTG) analysis of the MPN capsules was conducted to evaluate the MPN formation mechanism at different M:L ratios. About 10 wt% MPN film loss occurred below 150 $^{\circ}\text{C}$, which is due to water evaporation (**Figure 3.4c** and **Figure 3S 21**). The two major mass losses (75 wt% loss in total) occurring above 200 $^{\circ}\text{C}$ is attributed to the degradation of TA. MPN films prepared with a higher concentration of Fe^{III} experienced a higher resistance to TA decomposition, as indicated by the two mass loss steps shifting to higher temperatures and the smaller reduction in mass observed after 350 $^{\circ}\text{C}$. This can be attributed to the increased likelihood of cross-link formation with increased iron concentration, resulting in a higher activation energy required to break Fe^{III} –TA complexes and a subsequent increase in thermal stability [163]. Interestingly, the DTG results revealed that increasing the M:L molar ratio from 0.5:1 to 3:1 in the bulk solution linearly altered the maximum rate of degradation for the two mass loss events at 250 and 320 $^{\circ}\text{C}$ —the extent of degradation at 250 $^{\circ}\text{C}$ decreased, whereas that at 320 $^{\circ}\text{C}$ increased as the M:L ratio increased (**Figure 3S 21**). The degradation at 250 $^{\circ}\text{C}$ is attributed to the decomposition of 1,2,3-benzene triol and the ester groups between two aromatic rings in the outer layer of TA (**Figure 3.4d**), whereas the degradation at 320 $^{\circ}\text{C}$ corresponds to the decomposition of benzene diol and the ester groups connected to glucose [164, 165]. It is

proposed that Fe^{III} mostly interacts with the outer layer of TA at low M:L molar ratios, whereas at increased M:L molar ratios, the metals diffuse inside the TA molecules and cross-link with the inner layer (through μ -carboxylate interactions) (**Figure 3.4d**), leading to rougher films. The stoichiometry of Fe^{III} and TA in the film was determined by XPS and compared with the theoretical M:L molar ratio used during MPN fabrication (**Figure 3.4e** and **Figure 3S 22**). The atomic composition of the MPN films was calculated by integrating the peaks with reference to their relative sensitivity factor. Fe^{III} :TA ratios of $\sim 1.9:1$, $\sim 2.3:1$, and $\sim 2.9:1$ were achieved for the films assembled at M:L molar ratios of 0.5:1, 1.5:1, and 3:1, respectively. The XPS results were consistent with the inductively coupled plasma atomic emission spectroscopy (ICP-AES) results, which confirmed that the iron content in the films increased from 6.82 to 9.36 wt% with increasing iron concentration (**Figure 3.4e**).

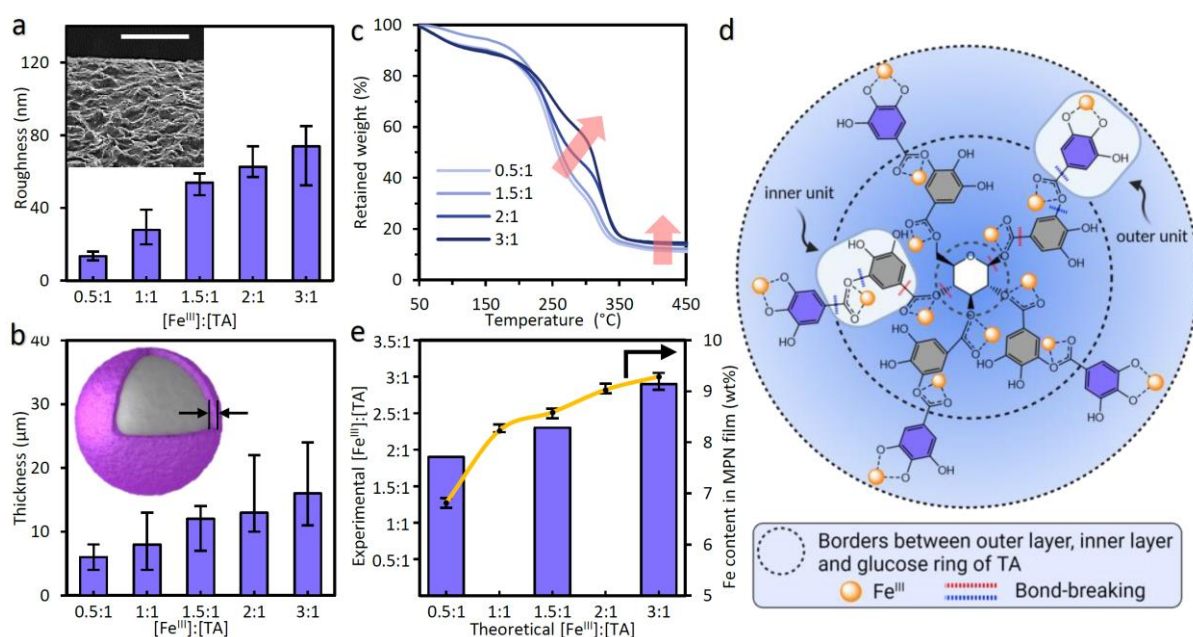


Figure 3.4. Influence of precursor ratio on MPN film formation after addition of urea granules into the aged solution. (a) Surface roughness of the MPN films prepared at different M:L molar ratios, as measured by AFM (the inset shows a representative SEM image of the external surface of an MPN film on urea granules prepared at an M:L ratio of 1.5:1; scale bar is 100 μm). (b) Corresponding thickness profiles of MPN films prepared at different M:L ratios, as measured from the cross-section SEM images. Inset shows a schematic representation of the film thickness. (c) Thermograms of MPN films prepared at different M:L molar ratios. (d) Schematic representation of the interactions of gallic acid units of TA with Fe^{III} and different types of bond breakage during heating of the MPN film. (e) M:L molar ratio profiles of the MPN films measured by XPS (bar graph) and Fe content in the MPN films measured by ICP-AES (yellow line) as a function of the theoretical M:L molar ratio in mixed solutions. All data

are for systems prepared with a final concentration of 2.3 mM TA and a solution aging time of 15 min at 25 °C.

3.4.3 Effect of Precursor Concentration

The influence of the concentrations of TA and iron on the formation of MPN coatings on urea granules was investigated by changing the TA concentration from 1.1 to 23.5 mM, while fixing the Fe^{III}:TA ratio at 1.5:1, and the solution aging time and coating process temperature to 15 min and 25 °C, respectively. FBRM results highlighted that the formation of Fe^{III}–TA particles at the lower TA concentration of 1.1 mM was slower than that at the higher TA concentrations of 4.7 and 23.5 mM (**Figure 3.5a–c**), and most of the Fe^{III}–TA particles did not adsorb onto the urea granules. The TA molecules in the low-concentration bulk solution are most likely widely spaced apart and unable to approach the metal ions to form bis-type complexes. Furthermore, the lack of sufficient cross-linking significantly reduced the adsorption properties of the formed particles and many of the urea granules remained uncoated even after 10 h following addition of urea granules (data not shown). Although the total count of generated particles for all particle size ranges and the coating process times increased with increasing TA concentration from 1.1 to 4.7 mM, further increases in the TA precursor concentration (>4.7 mM) resulted in a sharp decrease in the total number of generated particles within the 100–200 µm size range (**Figure 3.5c, d**). This can be attributed to the saturation of TA in acetonitrile at very high concentrations, which can terminate particle growth.

The surface roughness of the MPN films increased with increasing TA and iron precursor concentrations (**Figure 3.5a–c**, insets) due to the increased degree of adsorption within the film, which occurs at higher precursor concentrations. Moreover, excess Fe^{III} induced aggregation of the complexes, resulting in increased roughness [107]. The film thickness initially increased as the concentration of TA increased, reaching a maximum of ~18 µm at 4.7 mM before decreasing with further increases in TA concentration (**Figure 3.5e**, **Figure 3S 23**).

At high TA concentrations (>4.7 mM), the affinity of the Fe^{III} –TA particles to adsorb at the interface of a previously adsorbed MPN layer decreased as a result of steric hindrance among preformed Fe^{III} –TA particles in solution [113]. The trend in the total MPN content in the urea granules@MPN samples prepared at different TA concentrations is consistent with the trend observed in the MPN film thickness; a maximum MPN content of 2.3% was obtained at 4.7 mM of TA, which coincides with the maximum MPN film thickness obtained (**Figure 3.5f**).

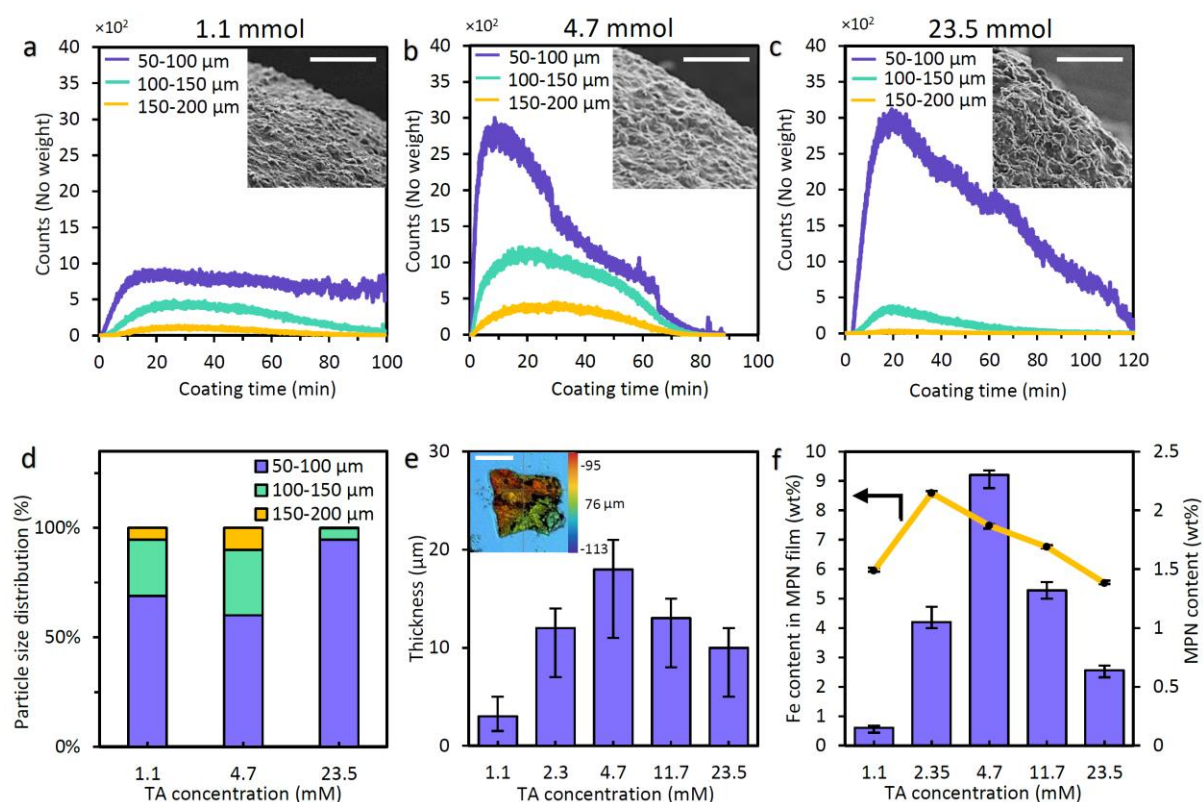


Figure 3.5. Influence of precursor concentration on MPN film formation. (a–c) FBRM analysis of growth of Fe^{III} –TA particles and their population distribution in Fe^{III} –TA solutions of varying TA concentrations (insets show the corresponding SEM images of the surface morphology of the MPN films coated on urea granules (scale bars are 100 μm)). (d) Size distribution of Fe^{III} –TA particles formed in Fe^{III} –TA solutions of varying TA concentrations. (e) Corresponding thickness profiles of the MPN films prepared using Fe^{III} –TA solutions of varying TA concentrations, as measured from the cross-section SEM and optical profiler images (inset shows an optical profiler image of an MPN film prepared with 4.7 mM TA) (scale bar is 50 μm). (f) MPN content in urea granules@MPN prepared using Fe^{III} –TA solutions of varying TA concentrations and Fe content in MPN films obtained using Fe^{III} –TA solutions of varying TA concentrations, followed by removal of urea granules. All data are for systems prepared using an M:L molar ratio of 1.5:1 and a solution aging time of 15 min at 25 $^{\circ}\text{C}$.

3.4.4 Effect of MPN Deposition Cycles

X-ray micro-computed tomography (micro-CT) was used to obtain cross-section images and three-dimensional images of the external surface of urea granules@MPN after 1 and 10 MPN deposition cycles and to measure the volume fraction of the MPN film, urea granule, and urea granule porosity (**Figure 3.6a–f**). The cross-section images (**Figure 3.6c,d**) and computed analysis (**Figure 3.6e,f** and **Table 3S 3**) show that repeated film deposition processes increased the film thickness from $\sim 14\ \mu\text{m}$ (1^{st} deposition) to $\sim 40\ \mu\text{m}$ after the 10^{th} deposition cycle. These results were consistent with the film thickness measured from the SEM cross-section images (**Figure 3S 24**). It is worth noting that the self-assembly coating provides a uniform coating without generating voids between the coating and granule, which is important in coating applications [166-168].

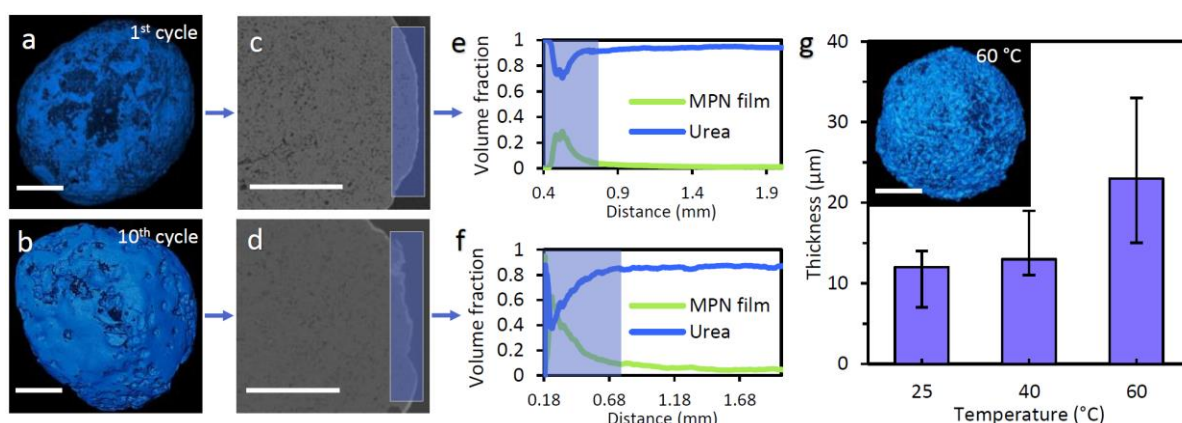


Figure 3.6. Effect of deposition cycle and temperature on MPN film formation. (a, b) Micro-CT images of an MPN film on a urea granule after the 1^{st} and 10^{th} MPN film deposition cycles, and (c, d) corresponding cross-section images of urea granules@MPN sectioned in half and (e, f) volume reconstruction of the micro-CT data from approximately 1500 scan projections. (g) Thickness profiles of MPN films prepared at different temperatures, as measured from the cross-section SEM images and optical profiler images (inset shows a micro-CT image of a sample prepared at $60\ ^{\circ}\text{C}$). Scale bars in all micro-CT images are 1 mm. All data are for systems prepared with a final TA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min.

3.4.5 Effect of Temperature

In contrast to the formation of MPNs in aqueous media, whereby temperature has minimal impact [114], elevating the temperature to $60\ ^{\circ}\text{C}$ for non-aqueous media had a large impact on

the coating time, and the surface morphology and thickness of the film. This temperature (60 °C) was chosen as the highest operational temperature to avoid significant solvent evaporation and coating inconsistencies (the boiling point of acetonitrile is ~82 °C). Increasing the temperature from 25 to 60 °C resulted in an increase in the film thickness from 12 to 23 µm (**Figure 3.6g** and **Figure 3S 25**) and a reduction in the MPN coating time from 40 to 5 min (**Figure 3S 15b** and **Figure 3S 26a,b**). The higher solid–liquid interface affinity at the higher coating temperature can increase the kinetics of the coating process (**Figure 3S 26a,b**). The formation of fewer Fe^{III}–TA particles at higher temperatures can be attributed to an increase in TA solubility. Some microscale indentations appeared on the film surface of specimens prepared at ≥40 °C, most likely due to changes in the building block configuration of MPN during its initial formation stage (**Figure 3S 26c,d**). TGA–DTG analysis of MPN capsules formed at different coating temperatures revealed the same pattern as that observed when the molar ratio was increased—the intensity of decomposition peak related to the mass loss at 250 °C decreased, whereas that of the peak related to the mass loss at 320 °C increased (**Figure 3S 26e,f**). The mass of residual materials after 400 °C (attributed to iron metal) increased slightly (**Figure 3S 26f**) due to increased solubility of iron in acetonitrile at >25 °C.

3.5 Release Profile of Urea from Urea Granules@MPN Samples

The release profiles of urea from the urea granules@MPN samples in water (**Figure 3.7** and **Figure 3S 27**) were estimated via the colorimetric method (**Scheme 3S 1**) by calculating the cumulative dissolution of urea granules versus time (**Equation S2**). The urea granules@MPN samples prepared using mixed precursor solutions that were aged for different times (1, 15, and 60 min) showed similar urea release profiles, with ~100% release achieved within 180 min (**Figure 3S 27a**). The time taken for complete release of urea from samples prepared with different M:L ratios initially increased as the molar ratio increased, reaching a maximum of

180 min at 1.5:1 before decreasing with further increases in the molar ratio (**Figure 3S 27b**). An increase in the time required for complete urea release was expected with an increase in the M:L molar ratio and film thickness. However, it is likely that increasing the metal content in the MPN coating increased the number of hydrogen bond interactions between the metal ions and water molecules, which facilitated water diffusion throughout the film. Increasing the concentration of TA solution to 4.7 mM led to a slower release of urea, with the release time prolonging to 240 min. Further increases in the TA concentration to 11.7 and 23.5 mM led to a faster urea release that was complete within 180 and 120 min, respectively (**Figure 3S 27c**). These results may likely be due to the reduced thickness of the films prepared at 11.7 and 23.5 mM.

The MPN deposition cycle also influenced the release profile of the urea granules@MPN samples. As observed from **Figure 3.7a**, the timeframe within which complete urea release occurred increased from 210 to 240 min as the MPN deposition cycle number increased from 1 to 10 due to the increased film thickness. The coating temperature had a significant effect on the cumulative release rate of urea from the urea granules@MPN samples: complete urea release from the urea granules@MPN sample prepared at 60 °C occurred within 330 min, whereas the release of urea from urea granules@MPN samples prepared at lower temperatures occurred within a shorter timeframe of 180 min (**Figure 3.7b**). From the SEM, micro-CT, and water contact angle images of urea granules@MPN, and optical microscopy images of the urea granules@MPNs following immersion in water (**Figure 3S 26d**, **Figure 3.6g** inset, and **Figure 3S 28**), the “spikes” that form on the external surface of the film may provide an air cushion between the micro-dents and water molecules (similar to what occurs in hydrophobic surface materials) [169]. Recent studies have shown that air pockets are trapped underneath the water in the valleys between the bulges (**Figure 3S 25d** and as discussed in **Figure 3S 28**); this reduces the contact area between water molecules and the external surface of the film, reducing

water permeation [62, 67, 170]. Furthermore, the increased thickness of the present films prepared at higher temperatures impeded water diffusion inside the urea granules@MPN sample.

Taking advantage of the pH dependency of MPN films, the effect of varying the solution pH from 4 to 9 was investigated (**Figure 3S 27d**). When the pH was reduced from 7 to 4, complete urea release was accomplished within 120 min, whereas the release pattern was prolonged when the pH was increased to 9. At low pH, the catechol groups of TA are protonated, which leads to a more positively charged Fe^{III} -TA film [116]. Thus, the enhanced electrostatic repulsion among TA molecules leads to loosening of the internal molecular packing and reduced stability of the Fe^{III} -TA complexes, followed by an increase in water diffusion inside the film [162]. The stability of the coated MPN films following immersion of the urea granules@MPN samples in water at different pH (4 and 7) was investigated using optical microscopy (**Figure 3S 29a–c**). The images show the formation of a sponge-like surface morphology, most prominently for urea granules@MPN immersed in pH 4 solution. This is most likely due to disassembly of part of the MPN coating in the acidic environment. However, the MPN capsules remained intact even after the complete dissolution of the urea granule (**Figure 3S 29d–e**). It should be noted that the release profile of urea in water provides an extreme/maximum release rate; urea release within soil is expected to be significantly slower and is influenced by numerous factors including soil composition, pH, temperature, and moisture levels. The release of urea in various soil environments will be detailed in a future publication.

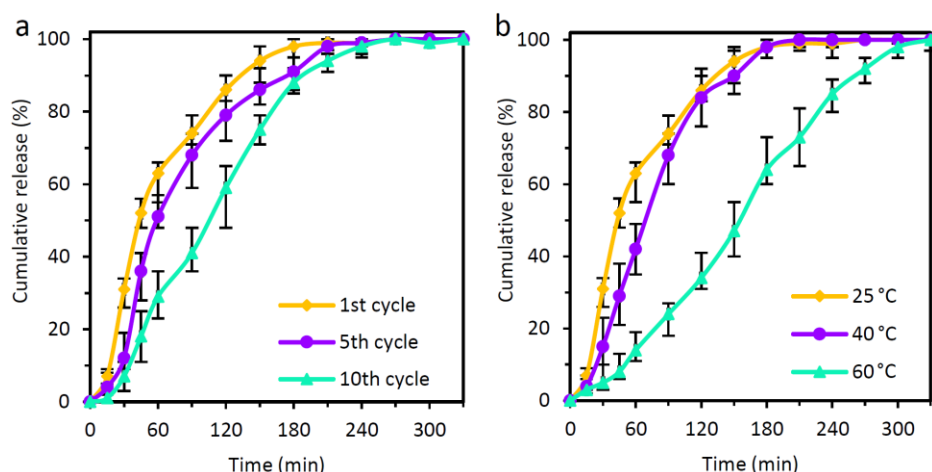


Figure 3.7. Cumulative release rate of urea in water at 25 °C, measured by colorimetric method, from urea granules@MPN samples prepared (a) using different MPN deposition cycles and (b) at different solution temperatures. Samples were prepared at a TA concentration of 2.3 mM, M:L molar ratio of 1.5:1, and a solution aging time of 15 min. The temperature used for the samples examined in **Figure 3.7a** was 25 °C.

3.6 Conclusion

We have reported a strategy for the self-assembly of MPNs on water-soluble urea granules in acetonitrile, thereby demonstrating the robustness and versatility of MPN self-assembly and expanding the conditions and environments in which MPNs can be synthesized and used for coating water-soluble substrates. We showed that the formation mechanism of MPN and the coating process in acetonitrile is different from that in aqueous media, resulting in the formation of micrometer-sized Fe^{III} -TA particles that can adsorb onto the substrate, and the formation of highly stable and thick MPN films (2–25 μm). In addition, we showed that the coating time could be varied by changing the assembly parameters, which subsequently influenced the surface morphology of the MPN film. Specifically, parameters, including MPN self-assembly method, solution aging time, metal-to-ligand molar ratio, precursor concentration, and processing temperature all influenced the formation kinetics, thickness, and surface roughness of the films. The MPN-coated platform was examined as a controlled-release system. The release rate of urea in water was controlled via the pH-dependent behavior of the self-assembled MPN. Overall, our results provide insights into MPN coating in non-aqueous

solvents for the controlled-release of water-soluble urea, which is specifically relevant for agricultural applications. We are currently extending our evaluation to other factors (e.g., ligand modification) that can further influence the release pattern of a range of fertilizers.

3.7 Supplementary Information

3.7.1 Experimental Section

3.7.1.1 Materials

Tannic acid (TA, ACS reagent), gallic acid (GA, ACS reagent, 97.5–102.5%), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%), iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99%), urea granules (ACS reagent, 99–100.5%) for elemental analysis calibration usage, acetonitrile (ACN, HPLC grade, 99.9%), nitric acid (ACS reagent, 70%), 2,5-dihydroxybenzoic acid (DHB, 98%), sodium trifluoroacetate (NaTFA, 98%), ethanol (HPLC grade, 99.9%), trichloroacetic acid (TCA, ACS reagent, 99%), 4-(dimethylamino)benzaldehyde (*p*-DMAB, 99%), ethanol (98%), 3-(*N*-morpholino)propanesulfonic acid (MOPS, 99.5%), hydrochloric acid (HCl, ACS reagent, 37%), 1,4-dioxane (ACS reagent, 99.5%), tetrahydrofuran (ACS reagent, 99%), ethyl acetate (ACS reagent, 99.5%), and isopropanol (ACS reagent, 99.5%) were purchased from Sigma-Aldrich. Sulfuric acid (H_2SO_4 , 98%), hydrogen peroxide (H_2O_2 , 30%), potassium nitrate (99%), and sodium nitrate (98%) were purchased from Chem-Supply. Industrial urea granules and calcium ammonium nitrate granules (comprised of 80% ammonium nitrate and 20% calcium carbonate) were received from Incitec Pivot Ltd. (Melbourne, Australia) with a N content of 46 wt%. High-purity (Milli-Q) H_2O with a resistivity of 18.2 $\text{M}\Omega \text{ cm}$ was obtained from an inline Millipore RiOs/Origin H_2O purification system. All solutions were freshly prepared for immediate use for each experiment. Mica discs (9.5 mm diameter) were obtained from ProSciTech Pty. Ltd. (Australia). Dialysis bag (molecular weight cutoff 3500 Da) with a wall thickness of 25 μm (CelluSep T1) was prepared from Membrane Filtration Product, Inc.

3.7.1.2 Methods

Preparation of urea granules@MPN

Four coating strategies were examined for the preparation of metal–phenolic network (MPN) films on urea granules in non-aqueous media as described below and schematically shown in **Figure 3S 2**. All solutions were freshly prepared for immediate use. All glassware was precleaned with piranha solution (30% H_2O_2 /98% H_2SO_4 , 1:3 v/v) for 10 min, rinsed with copious amounts of Milli-Q water, and dried under a stream of air. *Caution! Piranha solution reacts violently with organic materials and should be handled carefully.* All prepared urea granules@MPN samples were dried at atmospheric temperature for 5–10 min. The high vapor pressure of acetonitrile at 25 °C (11.8 kPa) facilitates the drying process.

Preparation of urea granules@MPN via Precomplex Assembly. In a typical synthesis, aliquots (250 mL) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in ACN (3.7 mM) and TA in ACN (2.35 mM) (M:L of 1.5:1) were mixed using a glass spatula for 15 s in a 1 L glass vessel until a transparent amber color solution was obtained. This reaction vessel was then placed in an OptiMax TM workstation 1001 (Mettler Toledo) to monitor the particle size distribution throughout the formation of an MPN. After aging the solution for 15 min at room temperature, urea granules (50 g, 3–4 mm in diameter) were added to the solution while stirring (200 rpm) until a dark blue solution was obtained. After the coating process was complete (~45 min), the MPN-coated urea granules were removed from the solution (the color of the solution became transparent after coating). The MPN-coated urea granules were then rinsed with fresh ACN to remove unattached MPN from the urea granules and dried under a stream of air to obtain urea granules@MPN.

Variables influencing the growth of the MPN film on the urea granules including solution aging time (1, 15, or 60 min), metal-to-ligand (M:L) ratio (0.5:1, 1:1, 1.5:1, 2:1, or 3:1), precursor concentration (1.1, 2.3, 4.7, 11.7, or 23.5 mM of TA), temperature (25, 40, or 60 °C), deposition cycle (1, 5, or 10), substrate type, and solvent type were examined. A schematic illustration of the MPN coating process is shown in **Figure 3S 2a**.

Preparation of urea granules@MPN via Oxidation-Mediated Coordination (OMC)

Assembly. Aliquots (250 mL) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in ACN (3.7 mM) and TA in ACN (2.35 mM) were mixed with a glass spatula for 15 s in a 1 L glass vessel until a transparent amber color was obtained. The reaction vessel was subsequently placed in an OptiMax TM workstation 1001 (Mettler Toledo). After aging the solution for 15 min at room temperature, urea granules (50 g, 3–4 mm in diameter) were added to the solution while the solution was stirred at 200 rpm. The color of the solution gradually changed to dark blue. After the coating process was complete, as monitored using the focused beam reflectance measurement (FBRM) technique, the MPN-coated urea granules were withdrawn from the solution (the color of the solution became transparent after the coating). The MPN-coated urea granules were then rinsed with fresh ACN to remove weakly coated MPN on the urea granules and dried under a stream of air to obtain urea granules@MPN. A schematic illustration of the MPN coating process is shown in **Figure 3S 2b**.

Preparation of urea granules@MPN via Discrete Assembly. To investigate the effect of the addition sequence of reagents (ligand precursor solution and metal precursor solution), the following procedure was employed. In the first coating process, the urea granules (50 g) were added to the TA solution in ACN (250 mL, 2.35 mM) in a 1 L glass vessel placed in an OptiMax TM workstation 1001 (Mettler Toledo). The solution color remained light yellow. After 15 min of gentle mixing, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution in ACN (250 mL, 3.7 mM) was added to the TA solution (the solution changed to dark blue), while the coating process at room temperature was monitored by the FBRM probe. Upon completion of the coating process, the MPN-coated urea granules were removed from the solution (the color of the solution became transparent after coating) and rinsed with fresh ACN to remove weakly coated MPN on the urea granules and dried under a stream of air to obtain urea granules@MPN. In the second coating process, the order of addition of the TA and metal solutions was reversed. Urea granules were added to the metal solution (the color of solution after addition of urea granules changed from an amber

color to transparent) before addition of the TA solution. Interestingly, in this coating process, the originally coated MPN film on the urea granules detached from the urea granules following rinsing of the MPN-coated urea granules in fresh ACN. A schematic illustration of the MPN coating process is shown in **Figure 3S 2c**.

Preparation of urea granules@MPN through Spray Assembly. Aliquots (100 mL) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in ACN (3.7 mM) and TA in ACN (2.35 mM) in glass bottles were sequentially deposited for 10 s on the urea granules using spray guns connected to an air compressor pump for each sequence. The distance between the spray nozzle and the urea granules was adjusted to 15 cm. Spraying was performed with the nozzle positioned perpendicularly to the plane of the granules. Specifically, the TA solution was first sprayed onto the granules for 10 s, followed by spraying of the metal solution for another 10 s. After each spraying step, the sprayed granules were allowed to stand for 30 s. The excess sprayed solution was washed with ACN, and the coated granules were dried under a stream of air. This procedure is referred to as one cycle of spray coating (**Figure 3S 2d**).

Variables Influencing the Growth of MPN Film on Urea Granules via Precomplex Assembly

Solution Aging Time. Aliquots (250 mL) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in ACN (3.7 mM) and TA in ACN (2.35 mM) (M:L = 1.5:1) were added and mixed using a glass spatula for 15 s in a 1 L glass vessel placed in an OptiMax TM workstation 1001 (Mettler Toledo) until a transparent amber color solution formed. After aging of the solution at different times (1, 15, or 60 min) at room temperature, urea granules (50 g, 3–4 mm in diameter) were added to the solution under stirring (200 rpm) to yield a dark blue solution. After the coating process was complete, as monitored by the FBRM probe, the MPN-coated urea granules were removed from the solution (the color of the solution became transparent after coating) and rinsed with fresh ACN to remove weakly coated MPN on the urea granules and dried under a stream of air, yielding urea granules@MPN.

Metal-to-Ligand Molar Ratio. Aliquots (250 mL) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in ACN (1.175, 2.35, 3.7, 4.7, or 7 mM) and TA in ACN (2.35 mM) were mixed with a glass spatula for 15 s in a 1 L glass

vessel placed in an OptiMax TM workstation 1001 (Mettler Toledo) until the solution became transparent/amber in color. The final M:L molar ratios were 0.5:1, 1:1, 1.5:1, 2:1, and 3:1. After aging of the solution for 15 min at room temperature, the urea granules (50 g, 3–4 mm in diameter) were added to the solution under stirring (200 rpm) until a dark blue solution formed. After the coating process was complete, as monitored by the FBRM probe, the MPN-coated urea granules were removed from the solution (the solution became transparent after coating) and rinsed with fresh ACN to remove weakly coated MPN on the urea granules and dried under a stream of air, yielding urea granules@MPN.

Concentration. Aliquots (250 mL) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in ACN (2.76, 3.7, 7.4, 18.5, and 37 mM) and TA in ACN (1.75, 2.35, 4.7, 11.75, and 23.5 mM) were mixed with a glass spatula for 15 s in a 1 L glass vessel placed in an OptiMax TM workstation 1001 (Mettler Toledo) until the solution became transparent/amber in color. The ratio of M:L was fixed at 1.5:1. After aging of the solution for 15 min at room temperature, urea granules (50 g, 3–4 mm in diameter) were added to the solution under stirring (200 rpm) until a dark blue solution formed. After the coating process was complete, as monitored by the FBRM probe, the MPN-coated urea granules were removed from the solution (the solution turned transparent after coating) and rinsed with fresh ACN to remove weakly coated MPN on the urea granules and dried under a stream of air, yielding urea granules@MPN.

Temperature. Aliquots (250 mL) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in ACN (3.7 mM) and TA in ACN (2.35 mM) (M:L = 1.5:1) were mixed with a glass spatula for 15 s in a 1 L glass vessel placed in an OptiMax TM workstation 1001 (Mettler Toledo) until the solution turned transparent/amber in color. After aging of the solution for 15 min, the temperature was adjusted to 25, 40, or 60 °C using a highly accurate temperature controller covered by a jacketed vessel for stringent heat transfer. While the solution was stirring at 200 rpm, the urea granules (50 g) were added causing the solution to become dark blue. After the coating process was complete, as monitored by the FBRM probe, the MPN-coated urea granules were removed from the solution (the solution

turned transparent after coating). The MPN-coated urea granules were then rinsed with fresh ACN to remove weakly coated MPN on the urea granules and dried under a stream of air.

Caution! Short exposure to hot acetonitrile could cause serious temporary or moderate residual injury to the respiratory system and should be handled carefully by wearing a proper mask.

Substrate type. Aliquots (250 mL) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in ACN (3.7 mM) and TA in ACN (2.35 mM) were mixed with a glass spatula for 15 s in a 1 L glass vessel placed in an OptiMax™ workstation 1001 (Mettler Toledo) until the solution became transparent and amber in color. The molar ratio of M:L was fixed at 1.5:1. After aging of the solution for 15 min at room temperature, calcium ammonium nitrate, potassium nitrate, or sodium nitrate (50 g), which was used as an alternative substrate to urea granules, was added to the solution under stirring (200 rpm). After the coating process was complete, the MPN-coated substrates were removed from the solution and rinsed with fresh ACN to remove weakly coated MPN from the substrates and dried under a stream of air, yielding calcium ammonium nitrate@MPN, potassium nitrate@MPN, and sodium nitrate@MPN.

Solvent type. Aliquots (250 mL) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in different types of solvents including 1,4-dioxane, ethyl acetate, isopropanol, or tetrahydrofuran (3.7 mM) and TA in ACN (2.35 mM) were mixed with a glass spatula for 15 s in a 1 L glass vessel placed in an OptiMax™ workstation 1001 (Mettler Toledo). The molar ratio of M:L was fixed at 1.5:1. After aging of the solution for 15 min at room temperature, urea granules (50 g) were added to the solution under stirring (200 rpm). After the coating process was complete, the MPN-coated urea granules were removed from the solution and rinsed with fresh corresponding solvent to remove weakly coated MPN from the urea granules and dried under a stream of air, yielding urea granules@MPN.

Measurement of the MPN Coating Content

The MPN coating content (mass%) was measured according to Equation S1, where w_1 is the weight of the coated granules (urea granule + MPN coating) and w_2 is the weight of the dried MPN film (after removing urea granule) at 110 °C, as follows:

$$\text{mass\%} = \frac{w_2}{w_1} \times 100 \quad (\text{S1})$$

Urea Release Characteristics of the urea granules@MPN Samples

To investigate the urea release profiles of the urea granules@MPN samples, the MPN-coated urea granules (~0.4 g) were placed in a dialysis bag that was sealed at both ends. The bag was then placed in a glass bottle containing deionized water (200 mL) and kept in an incubator at 25 ± 0.5 °C. At different time intervals, aliquots (1 mL) of the solution were sampled to measure the urea content using the colorimetric method (described in *Urea Release Evaluated by Colorimetric Analysis*). To keep the amount of solvent constant, deionized water (1 mL) was added to the bottle. The urea release experiments were conducted with three replicates. Equation S2 was used to determine the cumulative release rate of urea as follows:

$$C_r(\% \frac{W}{W}) = \frac{V_E \sum_{i=1}^{n-1} C_i + V_0 C_n}{M_0} \times 100 \quad (\text{S2})$$

where C_r is the cumulative release rate of urea from the coated granules (%), V_E and V_0 are the samplings and initial volume of the medium, respectively, C_i and C_n are the urea concentrations in the last sample and the extraction samples (mg mL^{-1}) obtained from UV-vis (UV-Visible) analysis. M_0 is the total mass of the coated urea granules. The weight of coated materials (MPN shell) was deducted from the urea granules@MPN samples.

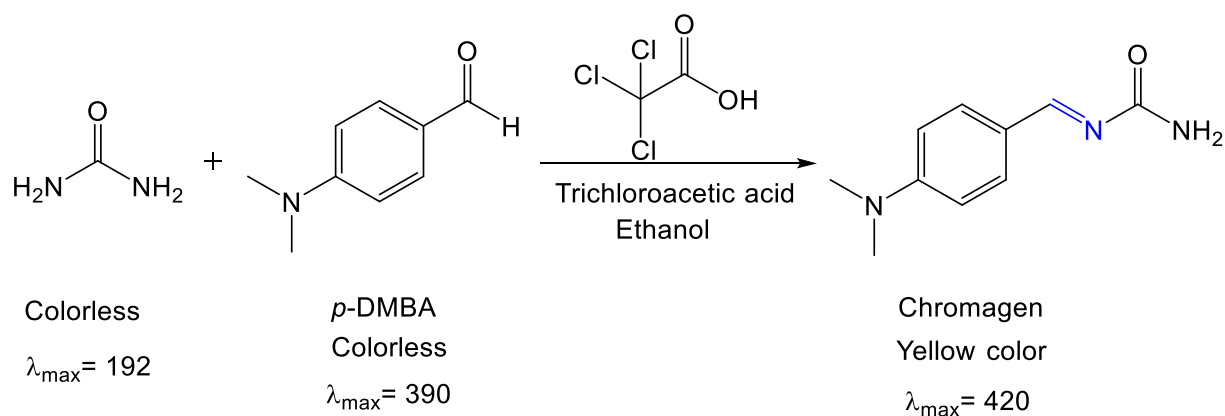
Influence of Solution pH on the Urea Release Characteristics

To investigate the effect of pH on the release rate of urea from the urea granules@MPN samples, the coated urea granules (~0.4 g) were placed in a dialysis bag and sealed at both ends with clips. The dialysis bag was then immersed in Mili-Q water (200 mL) at different pH (4.0, 7.0, or 9.0) adjusted by HCl or NaOH in the presence of citric acid-sodium acetate or MOPS

buffers, respectively and incubated at 25 ± 0.5 °C. At different time intervals, aliquots (1 mL) of the solution were sampled to measure the urea content using a colorimetric method. To keep the amount of solvent constant, deionized water (1 mL) was added to solution.

Urea Release Evaluated by Colorimetric Analysis

The concentration of urea was determined by UV–vis spectroscopy according to the methodology established by With et al. in 1961 (Scheme S1) [171]. In brief, an Ehrlich reagent was prepared by dissolving *p*-DMAB (5 g) in HCl (37%, 20 mL) and diluted with ethanol in a 100 mL volumetric flask. To analyze the concentration of urea, the sample (0.5 mL; either standard or unknown urea concentration solutions) was mixed with Ehrlich reagent (0.5 mL) in a cuvette. Then, TCA (2 mL, 10% in water) was added to the cuvette. *Caution! Trichloroacetic acid is corrosive and toxic to some organs and should be handled carefully.* A curve of urea concentration (30–1000 ppm) in solution versus absorbance at $\lambda = 420$ nm was obtained as a function of release time with $R^2 = 0.9994$.



Scheme 3S 1. Determination of urea concentration by colorimetric analysis using the Ehrlich reagent.

3.7.1.3 Characterization

Scanning Electron Microscopy (SEM)

The morphology of the coated urea granules was studied by SEM (Hitachi FlexSEM 1000) using the secondary electron detector and an accelerating voltage of 15 kV. For SEM imaging of the cross-sections of the coated granules, the granules were first introduced into a 5 mL vial with the cap closed, and the vial was stored in liquid nitrogen for 10 min (to minimize shear effects) before the granules were sectioned in half using a razor blade. The surface of the granules was then coated with 10-nm gold using an ionization chamber sputter coater (Quorum K575X) before SEM imaging. For better differentiation between the MPN film and the urea granule, the backscattered electron detector was used. For each coated urea granule specimen prepared, three granules were randomly chosen for imaging.

To validate the thickness measurements of the coatings, 20 measurements of different areas on each granule were performed. Digimizer software was used for image analysis and coating thickness measurement via the drawing option. Energy-dispersive X-ray spectroscopy (EDX) line scanning and mapping was performed at 15 kV using a Bruker Quantax 80 EDX unit attached to the SEM instrument.

Surface Optical Profiling

A white light interferometer surface optical profiler (ContourGT, Bruker) was used to characterize the thickness of the MPN films using the following procedure. The MPN-coated urea granules were first placed in a dish containing water to dissolve the urea granule. Then, the residual MPN film was washed several times with water to remove all dissolved urea. Small fragments of the MPN film were transferred onto a mica disc using a 5-mL micropipette and dried at room temperature. As the fragmented MPN film is black, a thin layer of gold (5 nm) was coated on the disc to increase the light reflection. Five different fragments of the film were analyzed for each urea granules@MPN sample prepared and the average coating thickness was reported.

Micro-Computed Tomography (Micro-CT)

Micro-CT scanning was performed with a Phoenix Nanotom M nano-CT 3D scanner (Waygate Technologies) running on the xs control and Phoenix datos|x acquisition software (Waygate Technologies). The coated urea granules were mounted for micro-CT scanning by attaching them to the end of a capillary tube to help maximize resolution by bringing the samples in close proximity to the X-ray source. The urea granules@MPN samples obtained after the 1st and 10th MPN deposition cycles were scanned at a resolution of 2.7 μm using an energy of 55 kV. A current of 200 μA and a tungsten target were used to run the instrument in fast-scan mode. A total of 1199 X-ray projections were collected through a 360° rotation of the samples over the course of a 10 min scan (no averaging or skipped images and an integration time of 500 ms). The urea granules@MPN samples that were synthesized at 60 °C were scanned at a higher resolution of 1.538 μm to collect the full dimensions of the specimen in 2 scans using an energy of 55 kV and a current of 200 μA and a 50-min scan time per section (2200 projections averaging 2 images with no skip). Volume reconstruction of the micro-CT data was performed using Phoenix datos|x reconstruction software (Waygate Technologies) applying a median filter and a region of interest filter during reconstruction. The data were exported as 16-bit volume files for analysis using the Avizo (Thermo Fisher Scientific) software suite. Samples were segmented using the interactive threshold tool of Avizo to create a binary image of the MPN coating (bright white phase), urea granule (intermediate gray phase), and pore space within the granules (dark gray to black phase). The volume fraction of each phase was then determined by comparing the binary images of each phase to a sample mask using the Volume Fraction tool in Avizo.

X-ray Photoelectron Spectroscopy (XPS)

XPS data were obtained on a VG ESCALAB 220i-XL spectrometer equipped with a hemispherical analyzer. Monochromatic Al K α X-ray (1486.6 eV) at 220 W (22 mA and 10 kV) was used as incident radiation. The pass energies were set at 100 and 50 eV for the survey (wide) and high-resolution scans, respectively. Survey scans were accomplished at 1 eV step

size and 10 ms dwell time, whereas high-resolution scans were obtained over a 20 eV binding energy range with a 0.05 eV step size and 100 ms dwell time. The base pressure in the analysis chamber was set to $<8.0 \times 10^{-9}$ mbar and a low energy flood gun was used to compensate for surface charging effects. CasaXPS software was used to process the data, and calibration was performed based on the C 1s peak reference at 285.0 eV for energy calibration. For XPS analysis, the MPN capsules were prepared by dissolving the urea granule (core part) in water and washing with approximately 1 L distilled water to remove all urea residuals from the MPN film and allowed to air-dry.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

The iron content of the MPN films was measured on an Agilent ICP-720 instrument. For sample preparation, the concentrated capsules (MPN films) were obtained by dissolving the urea granules from the urea granules@MPN samples followed by washing with distilled water (~1 L) and drying at 50 °C for 4 h. Aqueous suspensions of known MPN film concentrations were treated with HNO₃ (70%) and diluted with water to reach a final concentration of 0.02 M HNO₃ and subsequently compared to Fe standards of known concentrations of 1, 2, 5, 10, and 20 ppm. Three replicates were performed for each sample.

Raman Spectroscopy

Raman spectroscopy analysis was performed on a Renishaw system (inVia Qonto) equipped with a Peltier-cooled CCD detector and coupled to an Olympus BH-2 confocal microscope. A near-infrared diode laser with a 532 nm wavelength was used as the excitation source. Laser power at the sample was set to 0.01 mW with 1 s step time and 10 min dwell time. The spectra were recorded over a range of 400–1800 cm⁻¹ with a spectral resolution of 1 cm⁻¹ using a 50× microscope objective. For sample preparation, the coated granules were placed on a quartz microscope slide. The collected raw spectra were smoothed using a Savitzky–Golay smoothing filter.

Thermogravimetric Analysis (TGA)

TGA was performed on a NETZSCH TG 209 F1 Libra analyzer and coupled to a Fourier transform infrared module (ALPHA, Bruker). The samples were heated in the range of 30–700 °C at a heating rate of 5 °C min⁻¹ under an O₂/N₂ (80/20 %) stream at a gas flow rate of 20 mL min⁻¹. For sample preparation, the concentrated capsules were extracted by dissolving the urea granules from the urea granules@MPN samples followed by washing with distilled water (~1 L) and drying at 50 °C for 4 h.

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy

ATR-FTIR spectra were collected using a Bruker TENSOR II system in the range of 400–4000 cm⁻¹; a total of 32 scans were measured per run. The samples were prepared by removing the urea granules from the urea granules@MPN samples followed by washing with excessive distilled water and air-drying overnight.

Elemental Analysis

The nitrogen content of the samples was determined using the Dumas Combustion method on a LECO TruMac CNS analyzer in compliance with the standard ISO 1489. Sample calibration was performed with powder urea (99–100.5%) as a standard with the AOAC 993.13 method. The crunched coated granules (~0.1 g) were weighed in a ceramic boat and dried in an oven overnight (102 °C). The boats were loaded into the LECO analyzer and combusted at 1100 °C within the furnace. The average of three replicates for each sample was reported.

Matrix-Assisted Laser Desorption/Ionization–Time-of-Flight (MALDI–ToF) Mass Spectrometry

The degree of substitution of the GA ligand was confirmed by MALDI-ToF mass spectrometry using a Bruker Daltonics Autoflex III mass spectrometer. DHB and NaTFA were dissolved in methanol (10 and 1 mg mL⁻¹, respectively) and then mixed with MPN film (2 mg; washed with 10×50 mL water to remove unreacted urea). The sample was spotted onto a steel target plate and the solvent was allowed to evaporate before the tests. FlexAnalysis V2.2 software was used to analyze the spectra.

UV-vis Spectroscopy

The metal–phenolic coordination and urea concentration were analyzed on an Agilent Cary 300 UV–vis spectrophotometer equipped with a diode array detector.

Atomic Force Microscopy (AFM)

Surface roughness of the coated granules was measured on a Cypher AFM instrument (Asylum Research) on AC mode. For sample analysis, MPN capsules were placed onto mica discs and air-dried overnight. The cantilever Tap-300G (Budget Sensors) with a resonance frequency of 300 kHz and a spring constant of 40 N m^{-1} was used.

Real-Time Particle Size Analysis Using FBRM Technique

Real-time tracking of Fe^{III} –TA particle nucleation and growth in organic solution was measured with an FBRM probe G400 (Mettler Toledo) and OptiMax through iC control (version 5.4) and iC FBRM (version 4.3.2) software using the primary mode. The chord length of the particles was measured in solution. The total counts of chord length indicate the total number of Fe^{III} –TA particles in solution. The scan speed of FBRM was set to 2 m s^{-1} . The FBRM probe was positioned at a 45° inclination in the reactor (OptiMax TM workstation 1001, Mettler Toledo) to increase the sensitivity of detection.

Optical Tensiometry

Water contact angles (WCAs) of the MPN film surfaces were measured using a Theta optical tensiometer (ATA Scientific, Australia), with a droplet of distilled water at room temperature.

Optical Microscopy

Images of urea granules@MPN samples following immersion in water were taken using a Hirox RH-2000 2D/3D microscope in reflection mode.

General Instrumentation

The solution pH was measured using a SevenCompact pH meter S220 (Mettler Toledo) equipped with an InLab Science Pro-ISM electrode. The pH meter was calibrated weekly with

standard solutions (pH 4, 7, and 9.2). Mass measurements were performed using a highly accurate ($\pm 10 \mu\text{g}$) analytical balance (Mettler Toledo XS205).

3.7.1.4 Figures

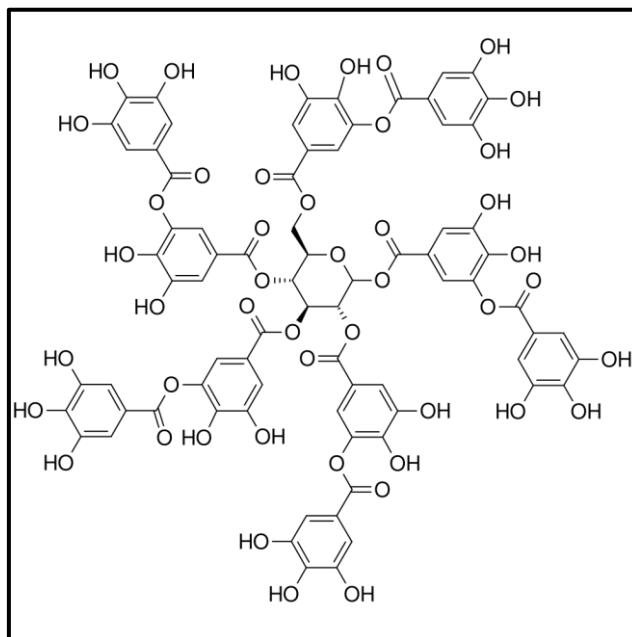


Figure 3S 1. Molecular structure of TA. Although the chemical structure of TA is usually given as a decagalloyl glucose ($C_{76}H_{52}O_{46}$), it is actually a mixture of polygalloyl glucose molecules with different degrees of esterification.

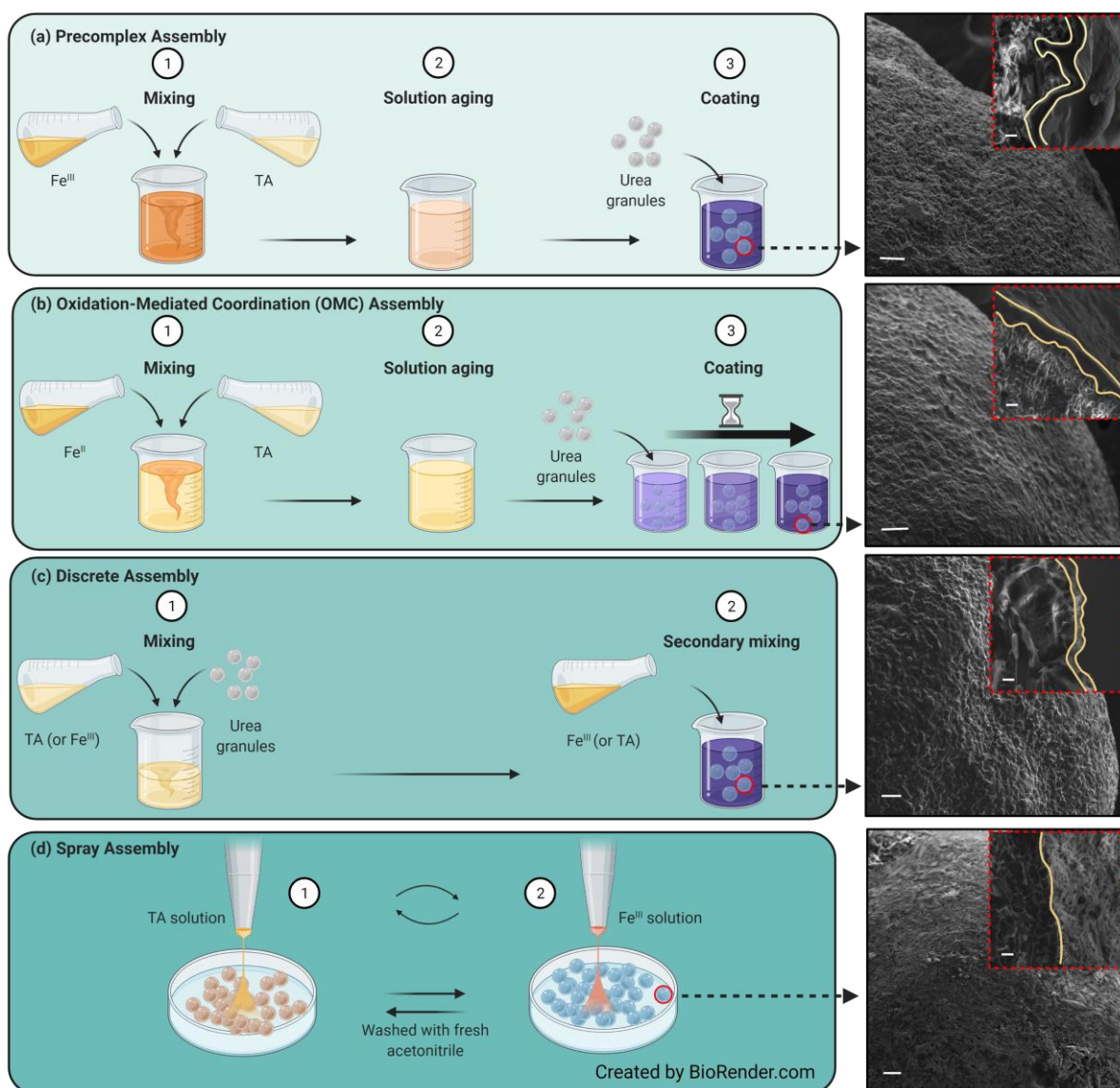


Figure 3S 2. Schematic illustration of different MPN coating processes employed on urea granules and corresponding SEM images of the resulting urea granules@MPN from the surface and cross-section (insets) views (scale bars are 100 and 10 μm , respectively). (a) Preparation of urea granules@MPN via precomplex assembly [108]. After mixing TA and Fe^{III} solutions in ACN, the solution changed to amber and Fe^{III} -TA complexes are formed during solution aging. The aged solution immediately turned blue after the addition of urea granules (Movie S1), indicating the formation of Fe^{III} -TA particles in the solution. The urea granules gradually darkened as coating proceeded via adsorption and fusion of Fe^{III} -TA particles, which formed in the solution, to the surface of the urea granules. (b) Preparation of urea granules@MPN via

OMC assembly [121]. An Fe^{II} source was used to delay coordination formation and this effect on the MPN surface properties was examined. No color change was observed throughout the solution aging. However, after introducing urea granules in the Fe^{II} –TA solution, the color of Fe^{II} –TA solution gradually darkened (from light blue to dark blue) over time as the iron source gradually oxidized to Fe^{III} and then interacted with the catechol and galloyl groups of TA to form Fe^{III} –TA complexes. The surface roughness of the MPN film formed on the urea granules using the OMC assembly method was smoother compared with that of the film formed using the precomplex assembly method as observed from the SEM images (**Figure 3S 2**). However, the thickness of the coatings obtained was the same as that obtained using the precomplex assembly method (Table S1). As discussed in our previous publication [121], Fe^{II} plays an important role in oxidation-mediated coordination assembly in controlling MPN growth temporally and spatially by promoting self-correction of the coordination building blocks. Here, Fe^{II} precursors are used for MPN formation, with the metal ion being oxidized to Fe^{III} during the growth process to stabilize the MPN films. Fe^{II} –catecholate complexes are less stable than those formed with Fe^{III} , and the lower reactivity and stability of Fe^{II} retard instant MPN formation. Thus, the gradual conversion of Fe^{II} –TA to Fe^{III} –TA provides conformational rearrangement and self-correction of the Fe^{III} –TA building blocks, resulting in a more compact network than that obtained via discrete MPN assembly. (c) Preparation of urea granules@MPN by discrete assembly. In this process, the effect of the order of TA and Fe^{III} addition was examined. The literature has shown that the sequential addition of polyphenolic ligand and inorganic cross-linking on a substrate plays a vital role in both the physicochemical properties of the resulting MPN film and mechanistic growth of MPN formation [172]. The addition of urea granules in TA solution, followed by the addition of Fe^{III} source after 15 min generated Fe^{III} –TA particles. These particles adsorb onto the urea granules to make the MPN films. Coatings with a thinner film and same roughness as that obtained by the precomplex assembly

method were formed. Additionally, we noted that unlike in the precomplex assembly, where all Fe^{III} -TA particles adsorbed onto the urea granules, in the discrete assembly, some Fe^{III} -TA particles could not adsorb on the urea granules even after a 24 h coating process, leading to a thinner coating compared with that obtained via the precomplex method. An MPN coating on the urea granules was also obtained by changing the sequence in which the precursor solution was added (that is adding urea granules to the iron solution followed by the addition of the TA solution). However, the coated MPN film detached from the urea granules once the sample was withdrawn from the solution and the liquid-like film became agglomerated (like water droplets) onto the surface of the urea granules. Most likely, the interfacial solid-liquid interaction between TA and urea granules may be stronger than that between metal and urea granules. (d) Spray assembly of MPN onto urea granules [138]. In this method, the ligand and metal solutions in ACN were sequentially deposited onto the urea granules using two spray nozzles. After repeating 20 cycles of coating with TA and iron solutions, a light blue thin layer of MPN (not detectable by SEM) formed on the surface of the granules. A different formation mechanism of MPN on the substrate via spray assembly resulted in the formation of such a thin layer of deposition. Overall, all assembly methods resulted in the formation of MPN film on urea granules. However, given the industrial application interest of the present work, the precomplex assembly was chosen for further studies as thicker MPN coatings and a faster coating process could be both achieved when compared with the other assembly methods. Some comparative results of the urea granules@MPN samples obtained via the different assembly methods are presented in Table S1.

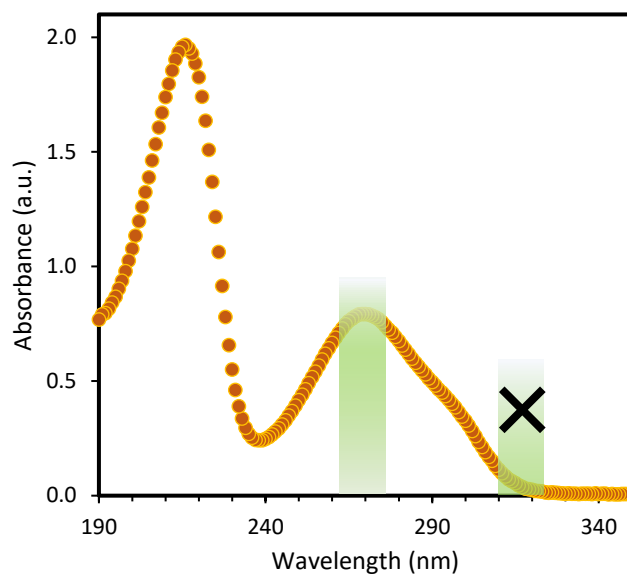


Figure 3S 3. UV–vis absorption spectrum of TA solution in ACN (0.02 mg mL^{-1}). The highlighted areas correspond to the absorbance at around 274 and 325 nm for the neutral and phenolate forms of TA, respectively. The absence of a peak at 325 nm (as denoted by X) indicates that the phenolate species did not form in ACN.

Transition metal ion-induced oxidative oligomerization of TA may occur via the formation of quinone, as an intermediate, at certain pK_a values, M:L ratios, and concentrations. As the pK_a 's of ACN and TA are ~ 25 and $\sim 2.5\text{--}8.8$, respectively, the ionization of TA to the phenolic hydroxyl groups is possible and complicates the complexes formation. However, the absence of the phenolate species in the UV–vis spectrum confirmed that TA was not oxidized and that further polymerization of TA was unlikely.

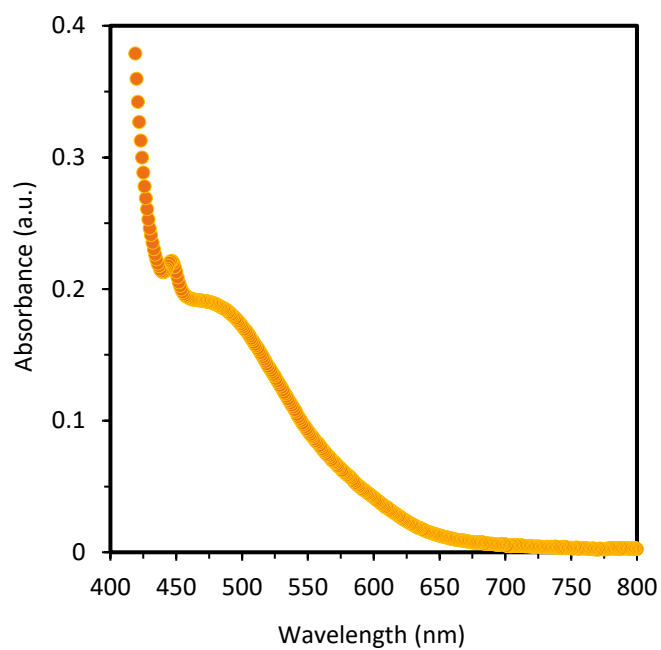


Figure 3S 4. UV-vis absorption spectrum of Fe^{III} -TA in ACN before the addition of urea granules (final TA concentration = 2.3 mM, M:L = 1.5:1, solution aging time = 15 min, temperature = 25 °C)

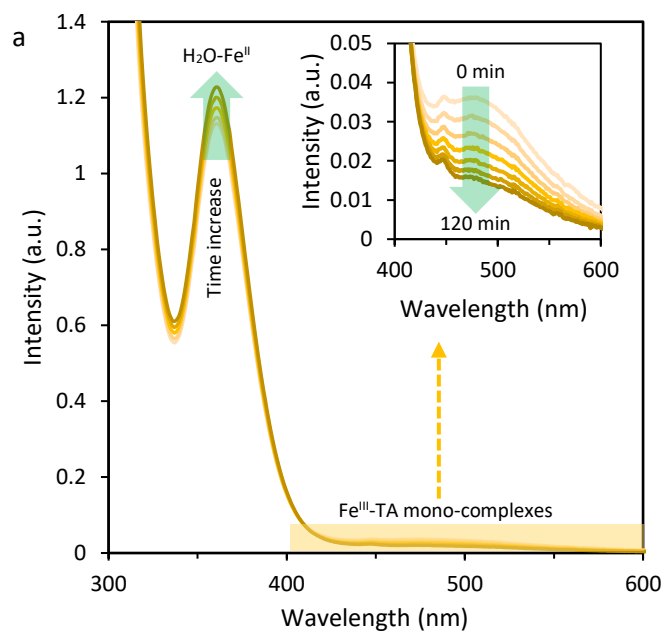


Figure 3S 5. UV–vis spectra of Fe^{III}–TA solutions aged for different times (0–120 min) before the addition of urea granules. The final concentrations of Fe^{III} and TA in ACN were 0.04 mg mL^{−1} and 0.16 mg mL^{−1}, respectively.

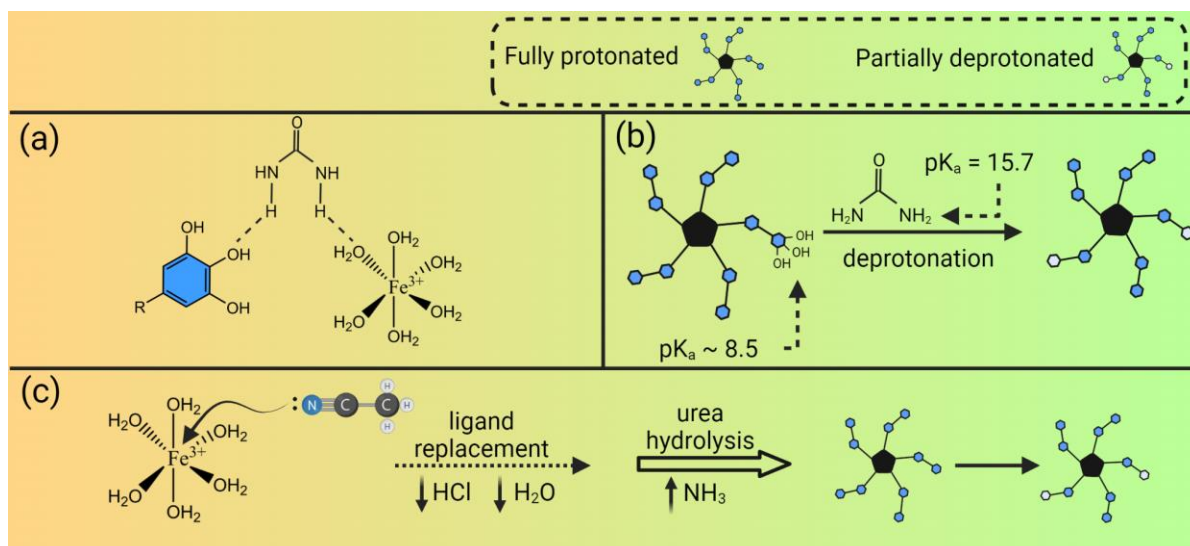


Figure 3S 6. Schematics of proposed factors that contribute to the formation of Fe^{III}-TA MPNs following the addition of urea granules to acetonitrile solution: (a) the role of urea in mediating interactions between the hydroxyl groups of TA and water molecules of FeCl₃·6H₂O via hydrogen bonding; (b) deprotonation of catechol groups of TA in the presence of urea; and (c) generation of ammonia through hydrolysis of urea and further deprotonation of TA molecules.

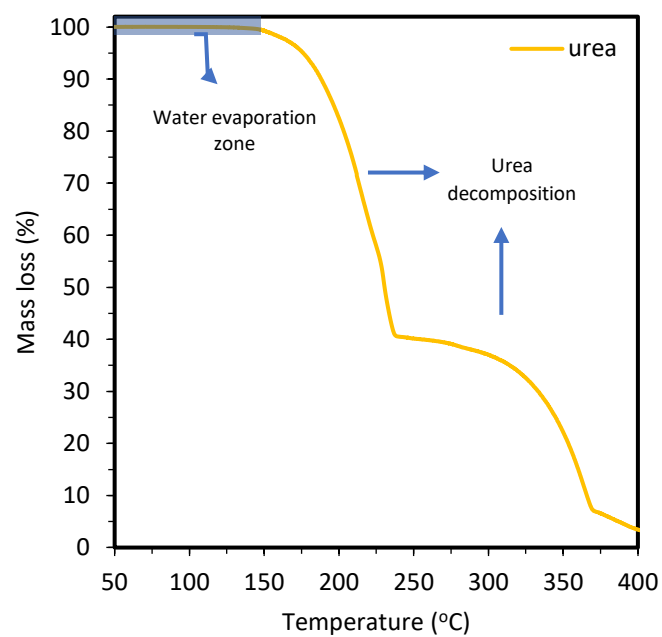


Figure 3S 7. TGA curve of an uncoated commercial urea granule.

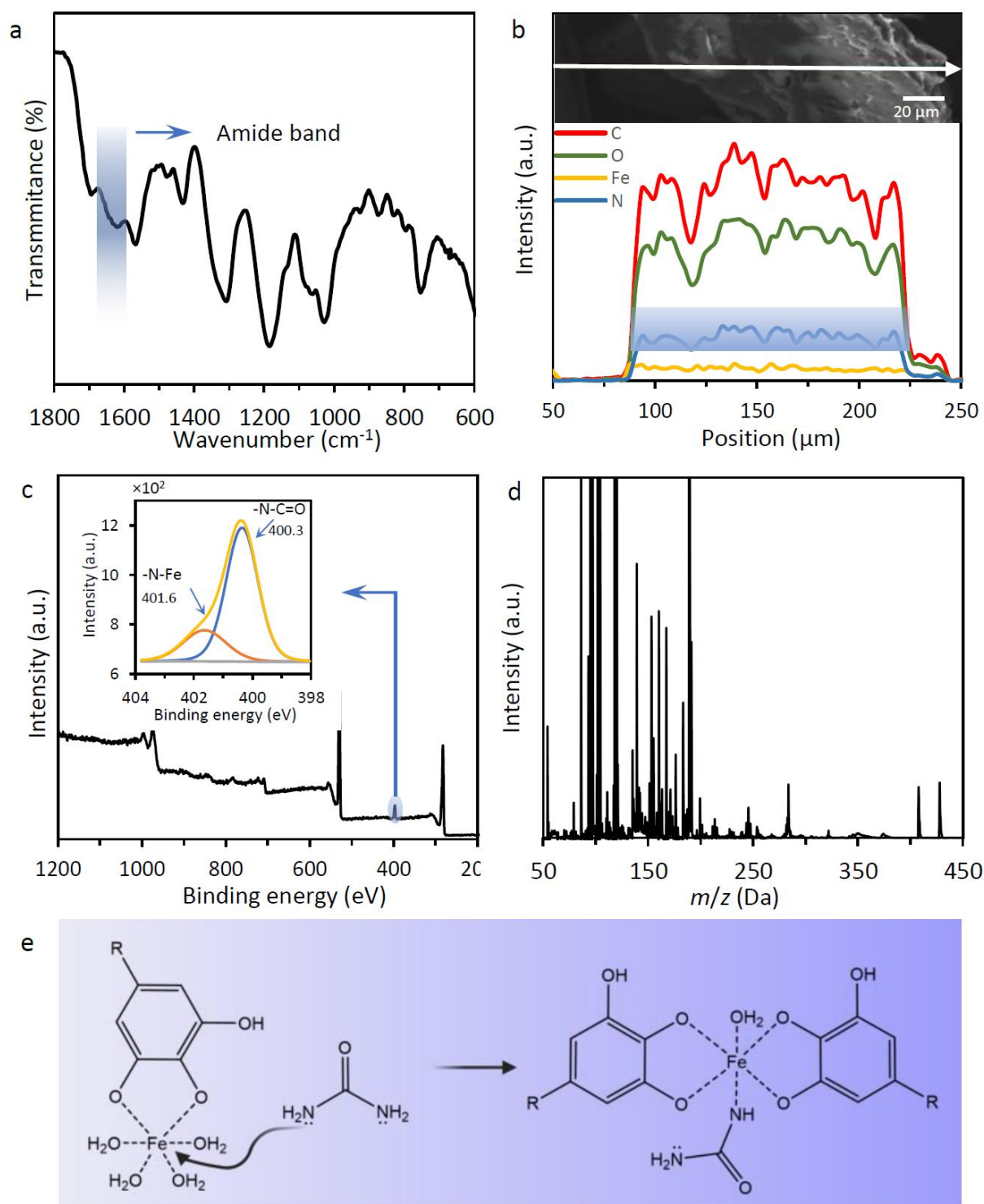


Figure 3S 8. Presence of nitrogen in MPN films. (a) FTIR spectra (the highlighted band between 1610 and 1680 cm^{-1} indicates the presence of amide functional groups) of urea. (b) SEM-EDX line scanning of the MPN film. (c) XPS and (d) MALDI-ToF mass spectrum of the GA-based MPN. (e) Schematic of proposed interactions between urea molecules and mono-

complexes of Fe^{III} -TA. Solid lines represent covalent bonds while dashed lines represent dipolar bonds. All data are for systems prepared with a final TA or GA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min at 25 °C. All characterization was conducted using Fe^{III} -TA MPNs retrieved from the solution and subsequently washed with copious amounts of water.

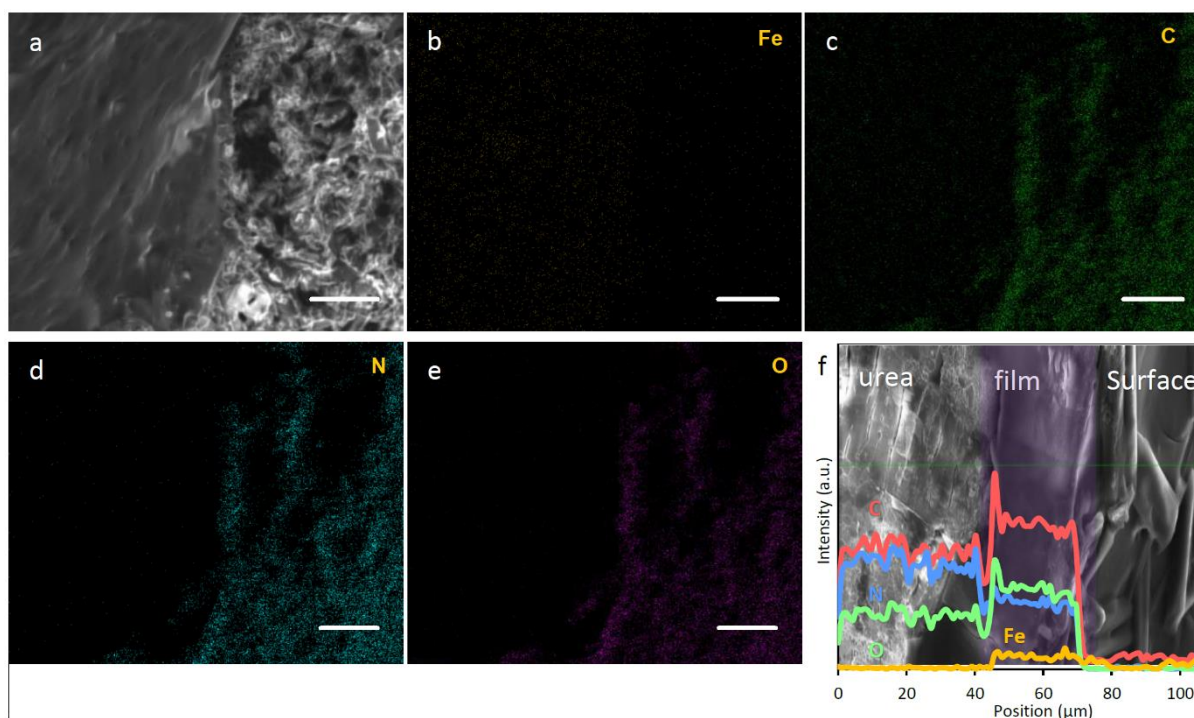


Figure 3S 9. SEM images from MPN films. (a–e) SEM-EDX mapping of elemental species (Fe, C, N, and O) within a cross-section of urea granules@MPN (scale bars are 100 μm) and (f) the corresponding elemental EDX line scanning (Fe, C, N, O) profiles. The urea granules@MPN samples were prepared using a final TA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, a solution aging time of 15 min, and a processing temperature of 25 °C.

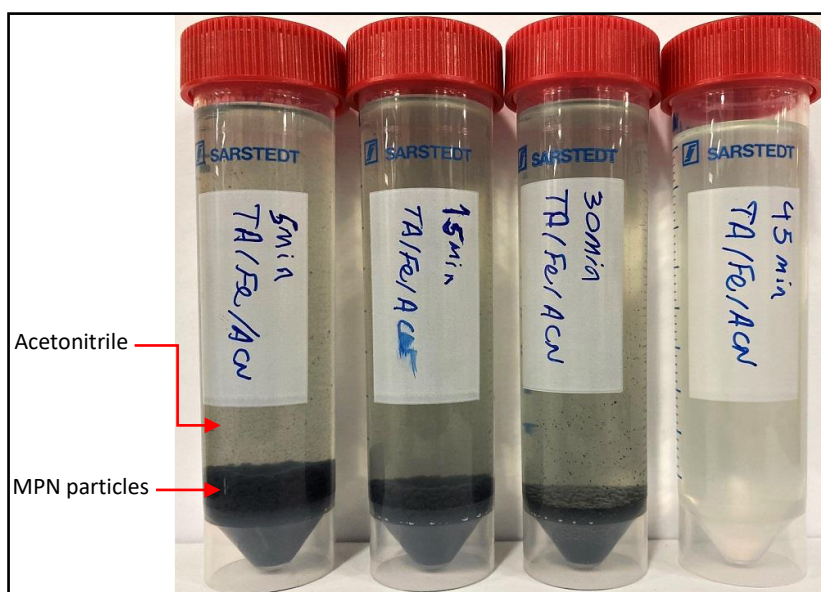


Figure 3S 10. Changes in the depletion of Fe^{III} -TA particles generated after 5, 15, 30, and 45 min of urea granule immersion in Fe^{III} -TA solution. Note: the urea granules were removed from the solution prior to taking the image. A final TA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, a solution aging time of 15 min, and a processing temperature of 25 °C were used.

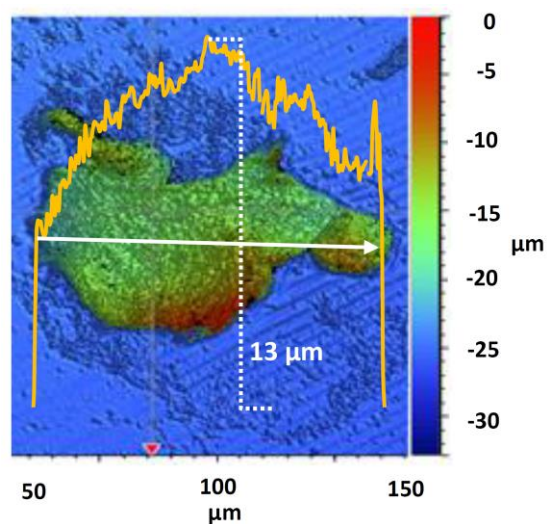


Figure 3S 11. Optical profiler image and corresponding height profile of a zone of MPN film (after dissolution of the urea granule). The urea granules@MPN sample was prepared using a final TA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, a solution aging time of 15 min, and a processing temperature of 25 °C.

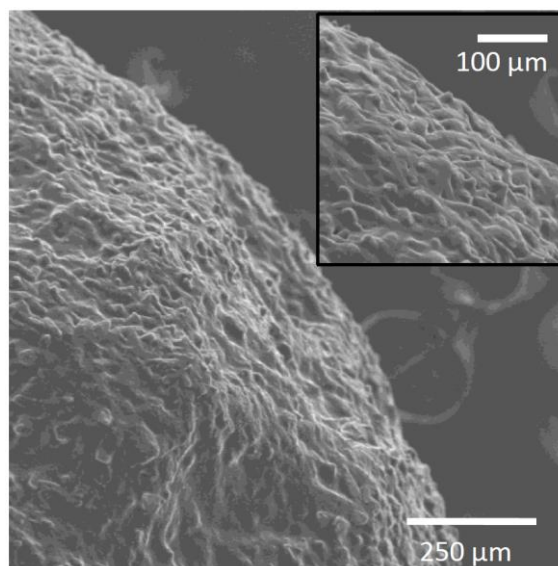


Figure 3S 12. SEM images of urea granules@MPN prepared with anhydrous FeCl_3 precursor. The urea granules@MPN sample was prepared with a final TA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min.

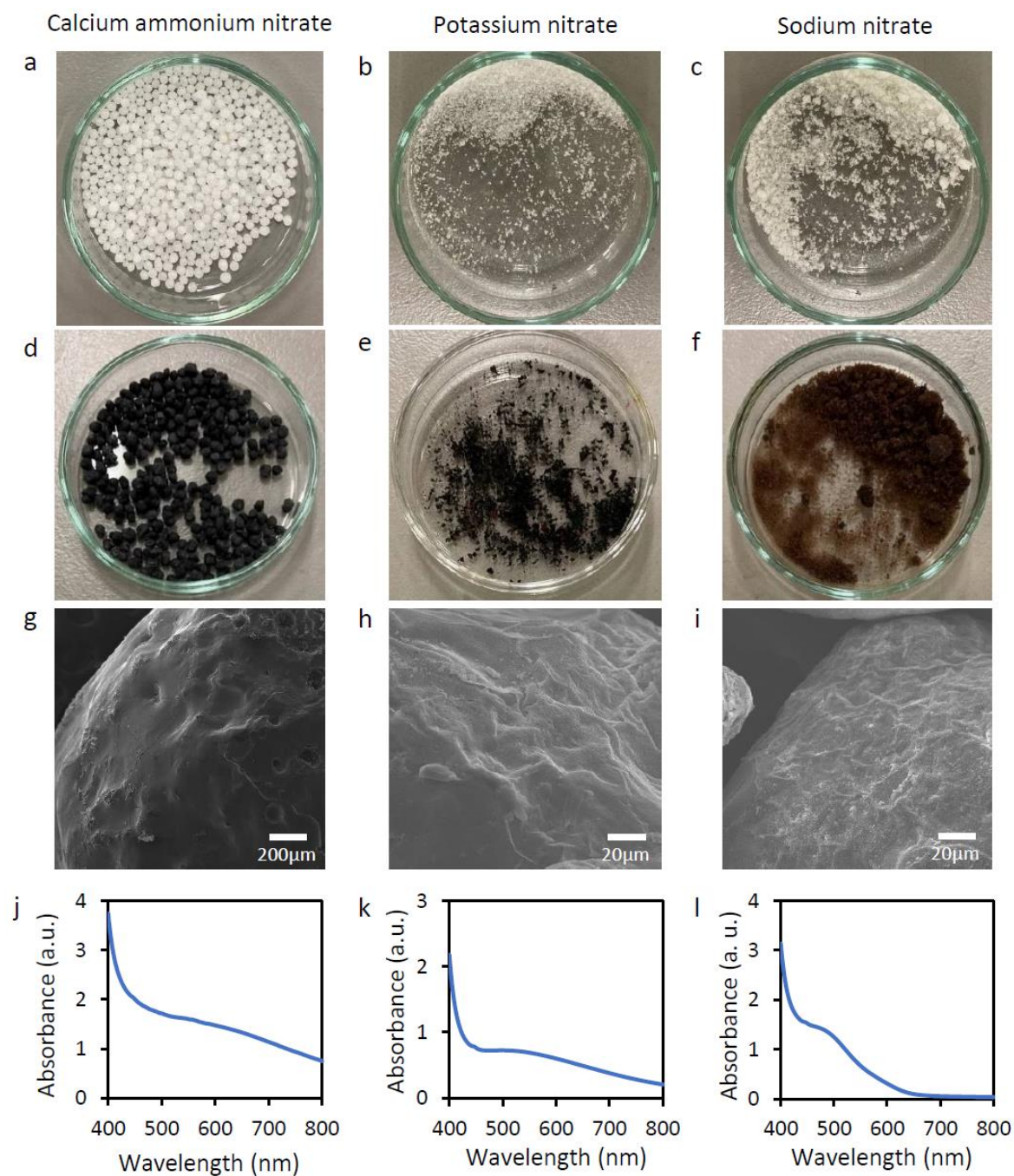


Figure 3S 13. MPN film formation on different water-soluble substrates (calcium ammonium nitrate, potassium nitrate, and sodium nitrate) in acetonitrile. Digital photographs of the (a–c) uncoated substrates and (d–f) MPN-coated substrates. (g–i) SEM images of the surface of the MPN-coated substrates. (j–l) UV–Vis spectra of Fe^{III} -TA acetonitrile solution following substrate immersion. All data are for systems prepared with a final concentration of 2.3 mM TA, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min at 25 °C.

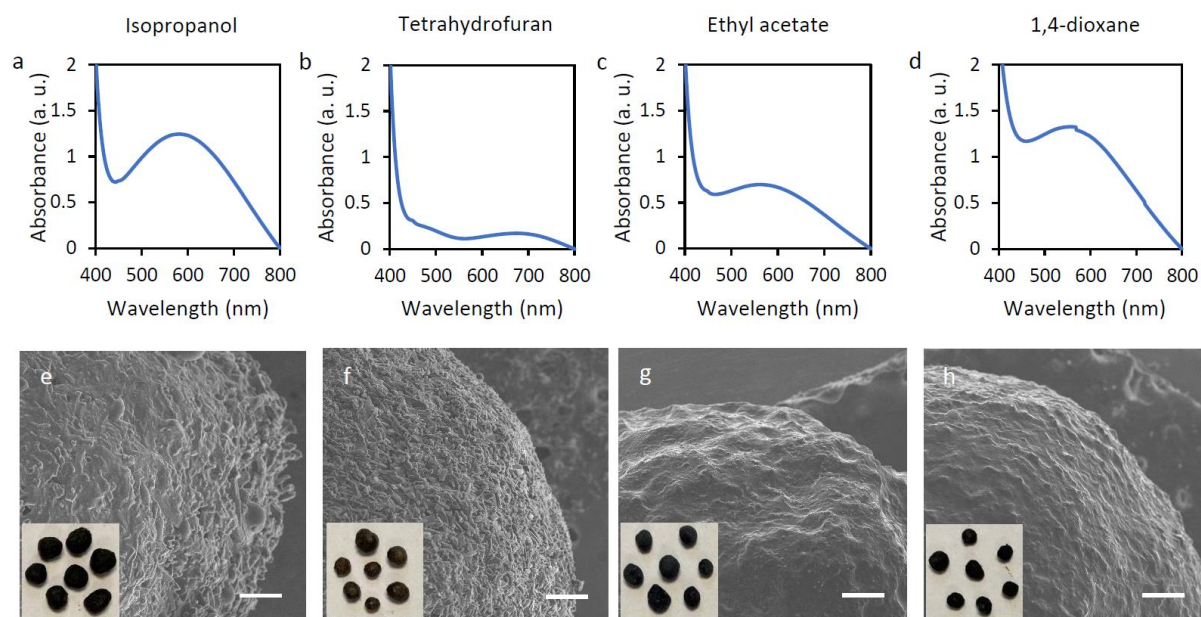


Figure 3S 14. MPN film formation on urea granules in different organic solvents (i.e., isopropanol, tetrahydrofuran, ethyl acetate, and 1,4-dioxane). (a–d) UV–Vis spectra of Fe^{III} –TA solution after immersion of urea granules in different organic solvents. (e–h) SEM images of the surface of urea granules@MPN prepared in different organic solvents. Scale bars are 100 μm (insets show the corresponding digital photographs of urea granules@MPN prepared in different solvents). All data are for systems prepared with a final concentration of 2.3 mM TA, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min at 25 $^{\circ}\text{C}$.

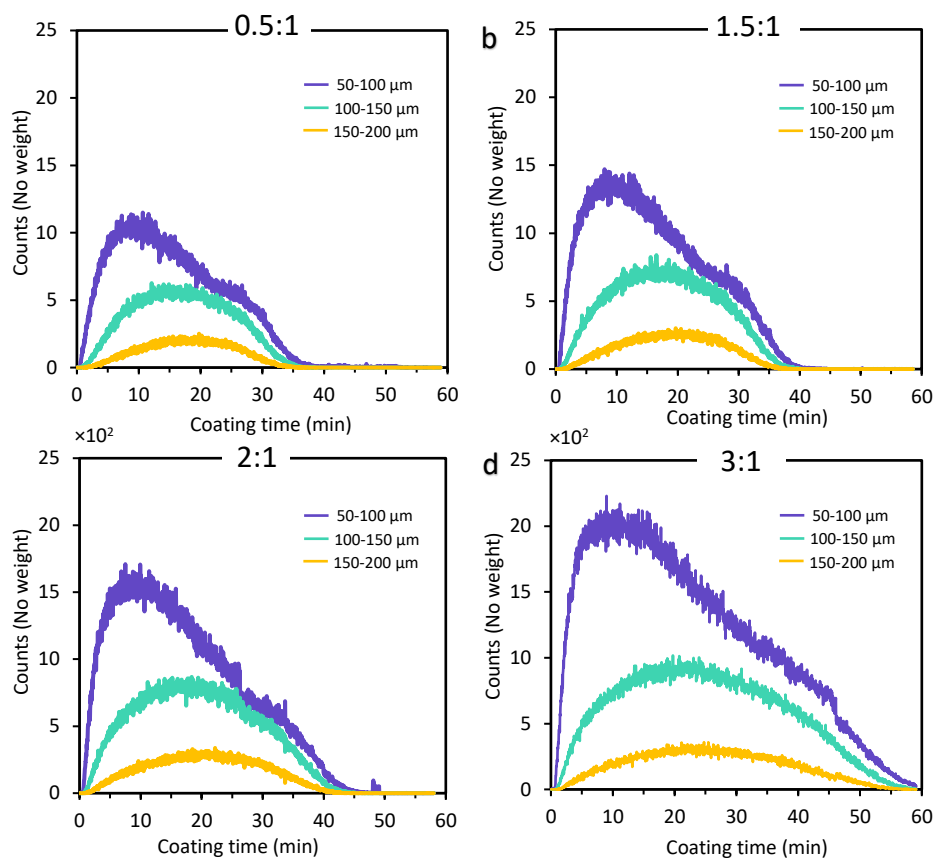


Figure 3S 15. Effect of precursor ratio on MPN film formation after addition of urea granules to Fe^{III} –TA solution. (a–d) FBRM analysis of Fe^{III} –TA particle growth and population distribution at different M:L molar ratios: (a) 0.5:1, (b) 1.5:1, (c) 2:1, and (d) 3:1. All data are for systems prepared with a final TA concentration of 2.3 mM, and a solution aging time of 15 min at 25 °C.

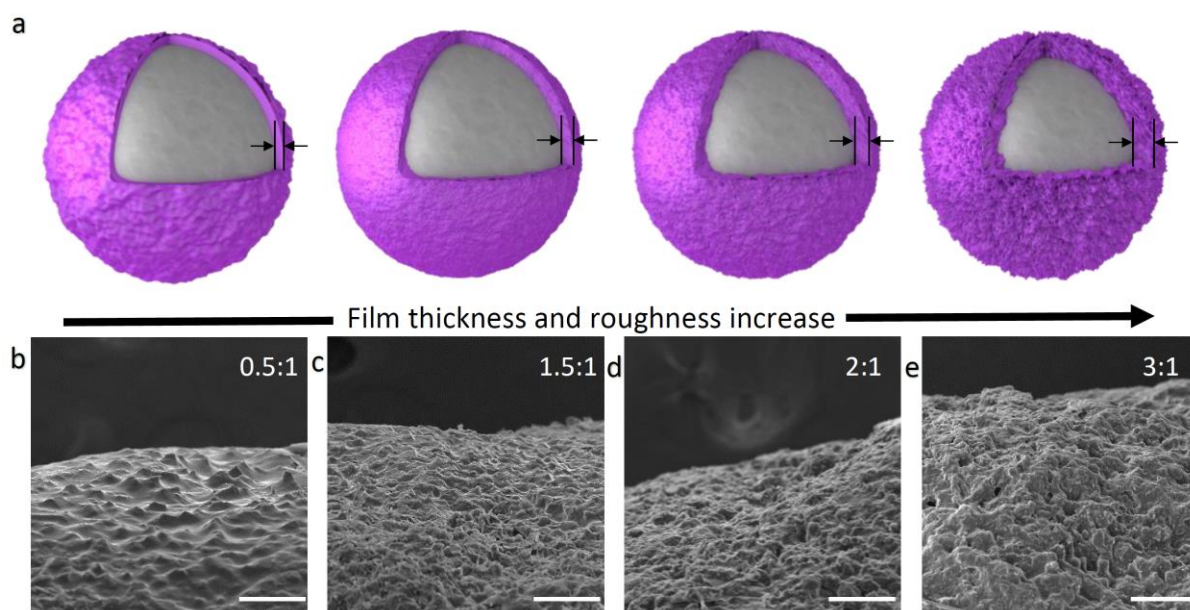


Figure 3S 16. Schematic representation of MPN film formation at varying M:L ratio. (b–e) SEM images of the external surface of MPN films on the urea granules prepared at different M:L ratios: 0.5:1, 1.5:1, 2:1, and 3:1 (scale bars are 100 μm). All data are for systems prepared with a final TA concentration of 2.3 mM, and a solution aging time of 15 min at 25 °C.

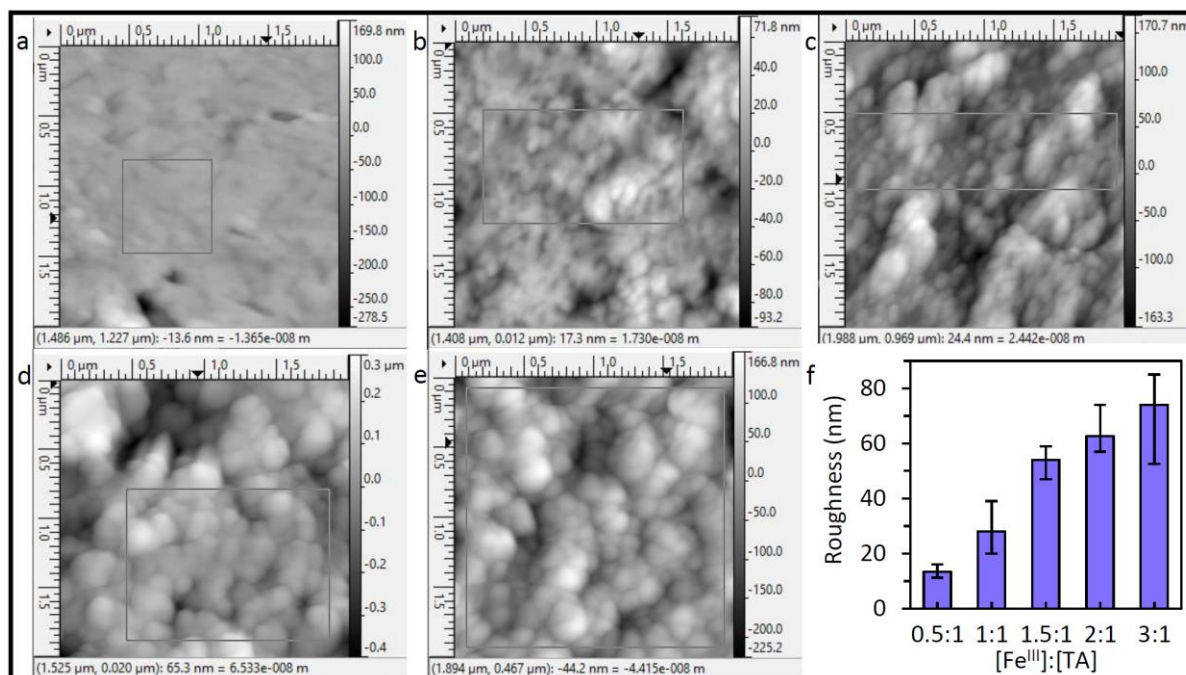


Figure 3S 17. AFM images of MPN films prepared at different M:L molar ratios: 0.5:1 (a), 1:1 (b), 1.5:1 (c), 2:1 (d), and 3:1 (e). (f) Surface roughness of Fe^{III}–TA films prepared at different M:L molar ratios. All data are for systems prepared with a final TA concentration of 2.3 mM, and a solution aging time of 15 min at 25 °C.

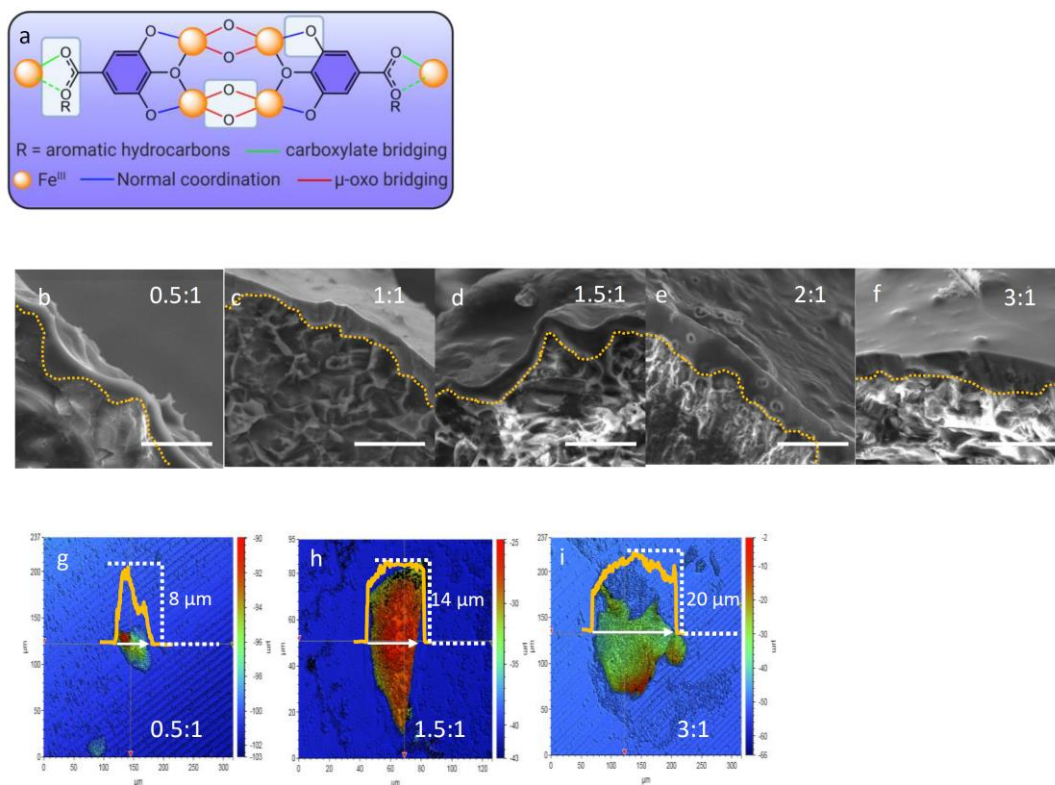


Figure 3S 18. Proposed coordination modes of galloyl groups with Fe^{III} in Fe^{III} -TA system. (b–f) SEM images of the cross-section of urea granules@MPN samples prepared at different M:L molar ratios. Scale bars are 25 μm . (g–i) Optical profiler height images and corresponding height profiles of MPN films prepared at different M:L molar ratios. All data are for systems prepared with a final TA concentration of 2.3 mM, and a solution aging time of 15 min at 25 $^{\circ}\text{C}$.

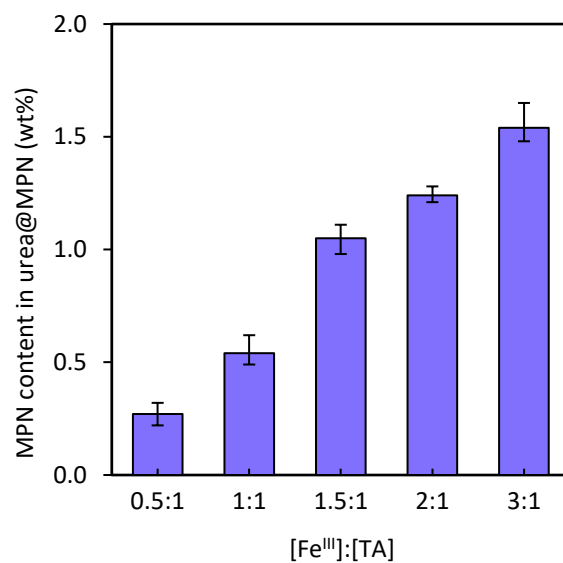


Figure 3S 19. MPN content in urea granules@MPN samples prepared at different M:L molar ratios, as measured by gravimetric method. All data are for systems prepared with a final TA concentration of 2.3 mM, and a solution aging time of 15 min at 25 °C.

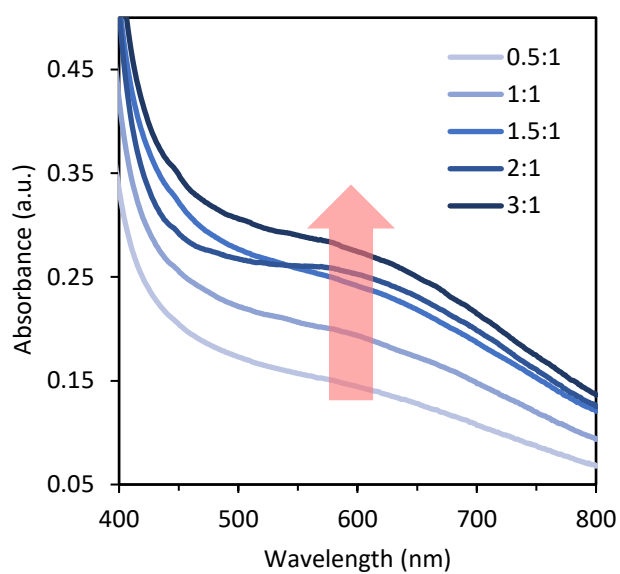


Figure 3S 20. UV-vis absorption spectra of Fe^{III}-TA solutions prepared at different M:L molar ratios. All data are for systems prepared with a final TA concentration of 2.3 mM, and a solution aging time of 15 min at 25 °C.

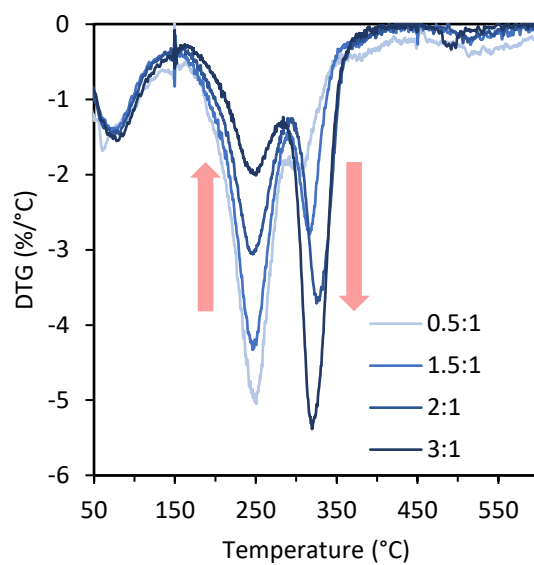


Figure 3S 21. DTG curve of MPN films prepared at different M:L molar ratios (the TA concentration was fixed at 2.3 mM). All data are for systems prepared with a final TA concentration of 2.3 mM, and a solution aging time of 15 min at 25 °C.

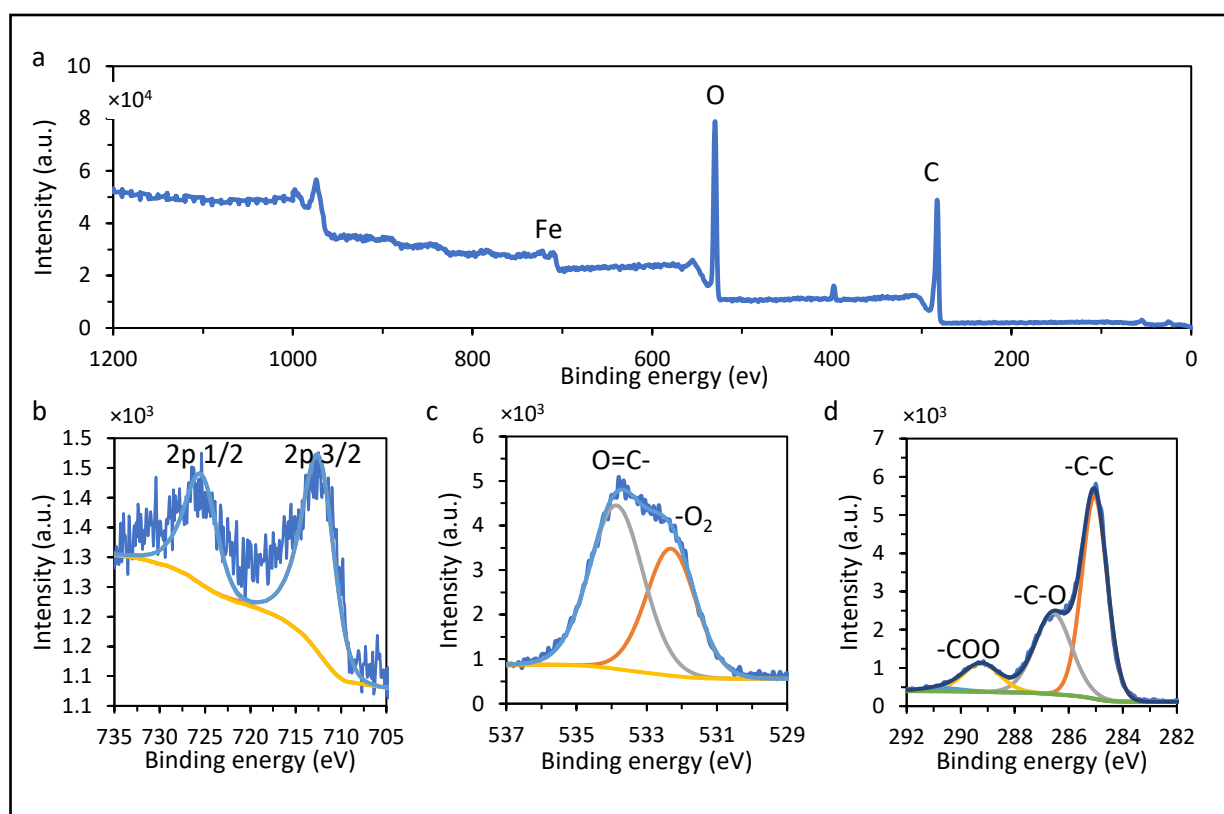


Figure 3S 22. XPS spectra of MPN film (after removal of urea granules) assembled in ACN: XPS spectra of MPN film (after removal of urea granules) assembled in ACN: (a) survey, and (b) Fe 2p, (c) O 1s, and (d) C 1s core-level spectra. The MPN film was prepared using a final TA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min at 25 °C.

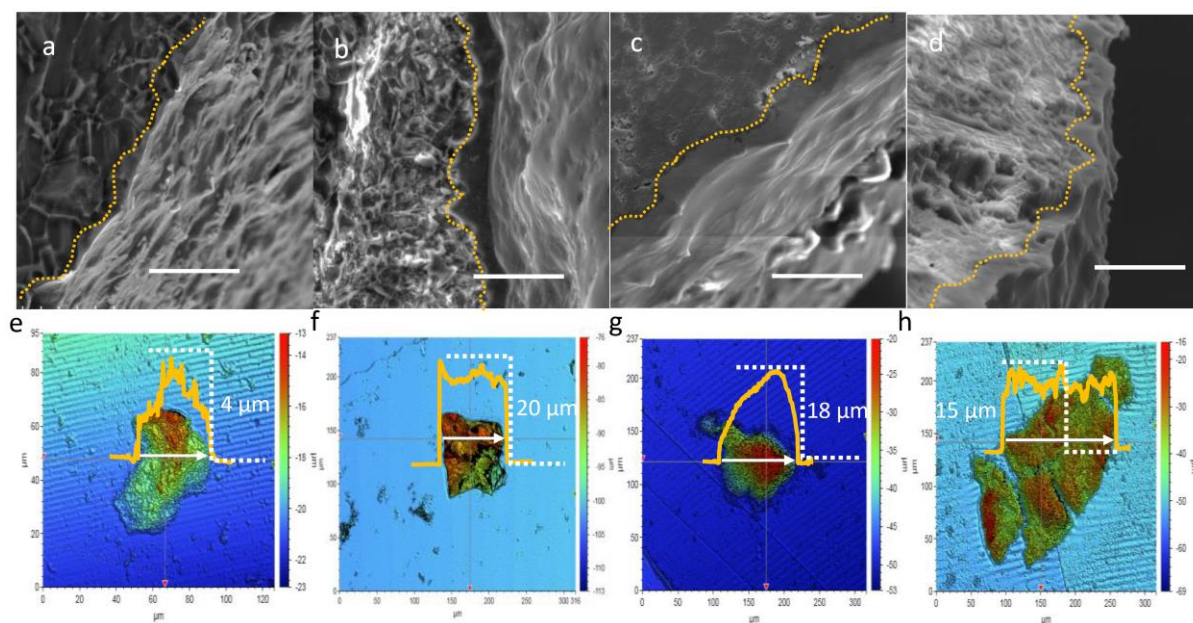


Figure 3S 23. SEM cross-section images of MPN films coated on urea granules (scale bars are 100 μm) prepared at different concentrations of Fe^{III} and TA solutions: 1.7 and 1.1 mM (a), 7.4 and 4.7 mM (b), 18.5 and 11.75 mM (c), and 37 and 23.5 mM (d). (e–h) Optical profiler height images and corresponding height profiles of MPN films prepared at different precursor (Fe^{III} and TA) concentrations: 1.7 and 1.1 mM (e), 7.4 and 4.7 mM (f), 18.5 and 11.75 mM (g), and 37 and 23.5 mM (h). All data are for systems prepared with an M:L molar ratio of 1.5:1, and a solution aging time of 15 min at 25 °C.

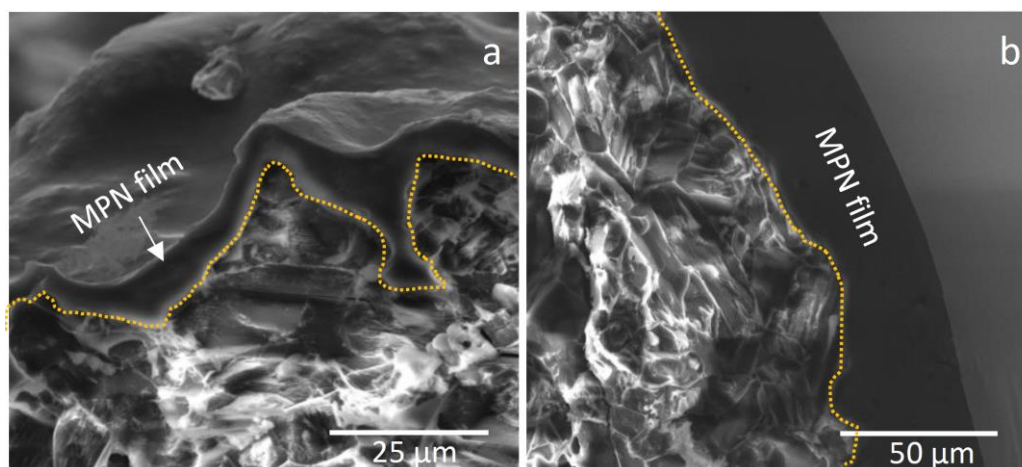


Figure 3S 24. SEM cross-section images of urea granules@MPN samples prepared after (a) 1 and (b) 10 MPN deposition cycles. The urea granules@MPN samples were prepared using a final TA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min at 25 °C.

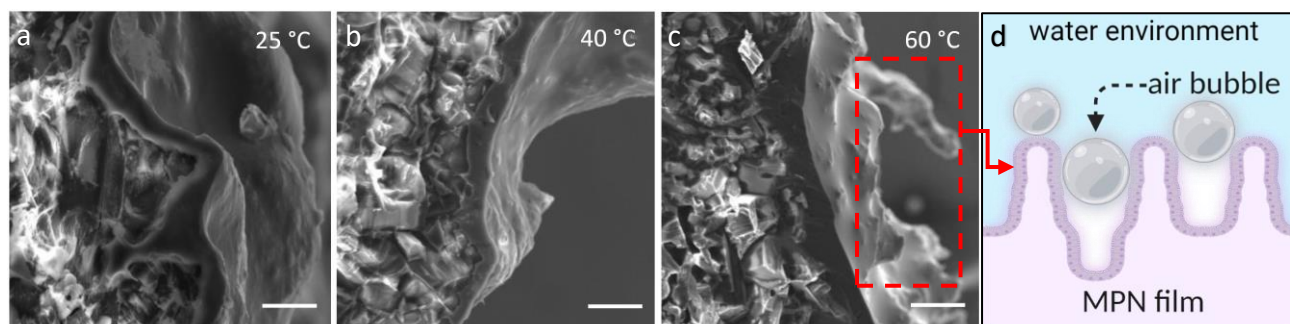


Figure 3S 25. SEM cross-section images of urea granules@MPN prepared at (a) 25, (b) 40, and (c) 60 °C. The scale bars are 25 μm . (d) Schematic of a possible air pocket located between the valley and bulges within urea granules@MPN (prepared at 60 °C) immersed in water. All data are for systems prepared with a final TA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min.

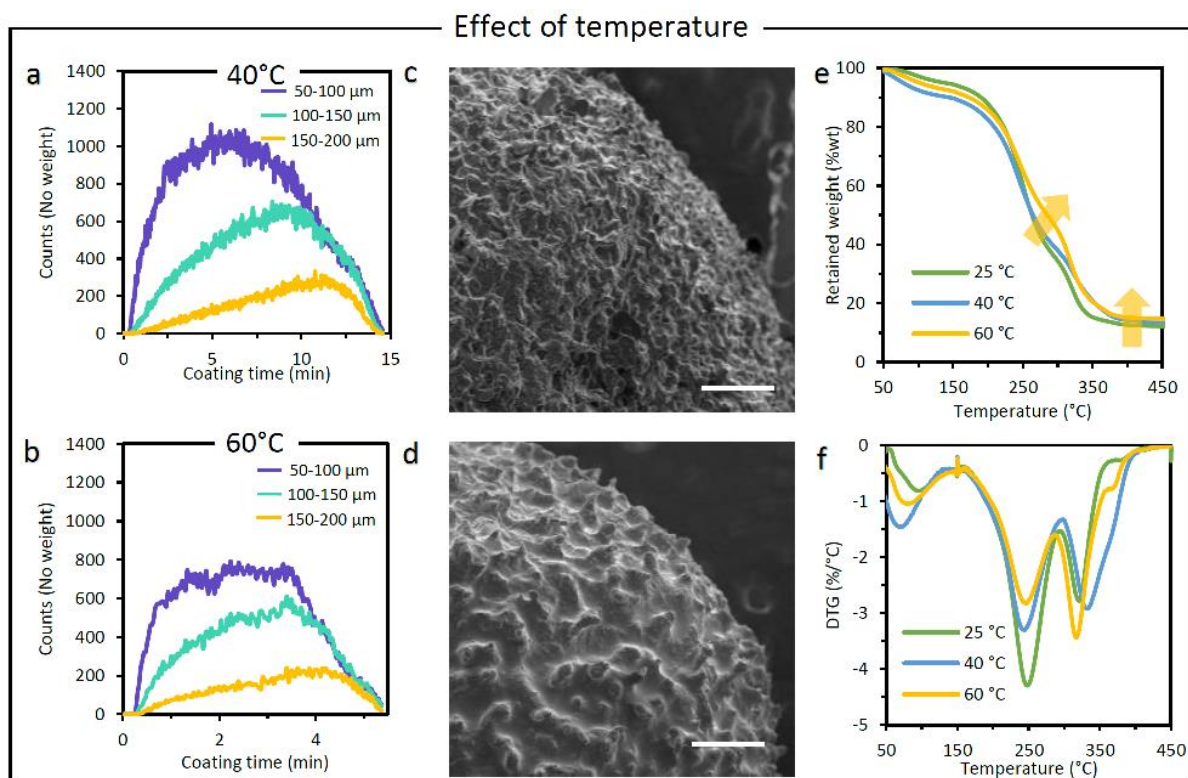


Figure 3S 26. Effect of Fe^{III} -TA solution temperature on MPN film formation. (a,b) FBRM analysis of Fe^{III} -TA particle growth and population distributions generated in solution at 40 and 60 °C, respectively. (c,d) SEM images of the surface morphology of MPN film coated on urea granules at 40 and 60 °C, respectively. The scale bars are 250 μm . (e,f) TGA and DTG curves of MPN films prepared at different temperatures. All data are for systems prepared at a final TA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min.

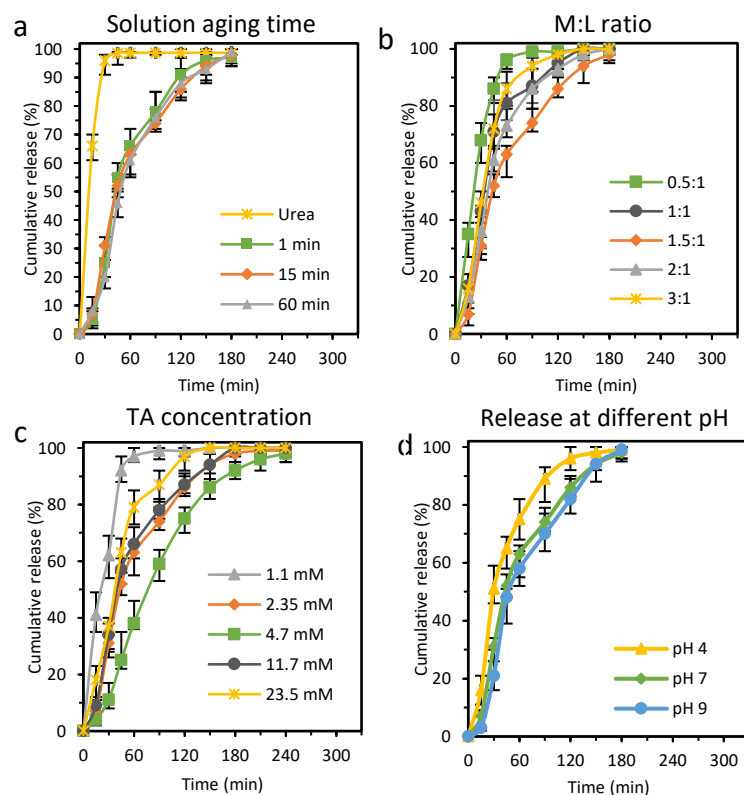


Figure 3S 27. Cumulative release rate of urea in water at 25 °C measured by colorimetric method from different urea granules@MPN samples prepared using different (a) solution aging times, (b) M:L molar ratios, and (c) precursor concentrations. (d) Urea release behavior of urea granules@MPN in water at different pH values (the sample was prepared at a TA concentration of 2.35 mM, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min at 25 °C).

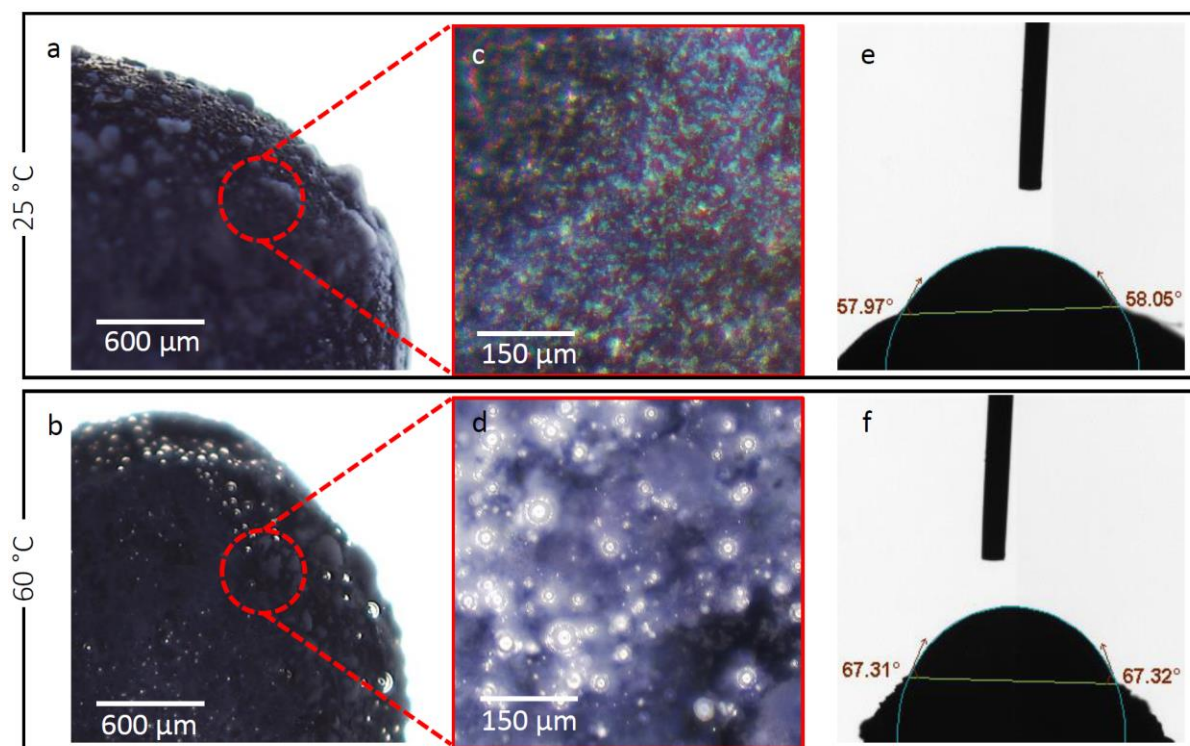


Figure 3S 28. (a–d) Optical microscopy and (e,f) WCA images of urea granules@MPN prepared at 25 and 60 °C, following immersion in water.

The optical microscopy images of urea granules@MPN, which were prepared at 60 °C, following immersion in water show the presence of some air bubbles on the MPN surface. However, these air bubbles were not observed for urea granules@MPN prepared at 25 °C. The air bubbles trapped between spikes can change the hydrophobicity of the MPN coating. Thus, the WCAs of urea granules@MPN prepared at 25 and 60 °C were measured (Figure S28e,f). The WCA of urea granules@MPN prepared at 60 °C was higher (68°) than that (58°) of urea granules@MPN prepared at 25 °C under the same test parameters. This confirms that the film surface of urea granules@MPN prepared at 60 °C is slightly more hydrophobic than the one prepared at 25 °C. The surface of urea granules@MPN prepared at 60 °C became rough due to the “spiked” morphology, which led to a higher WCA value.

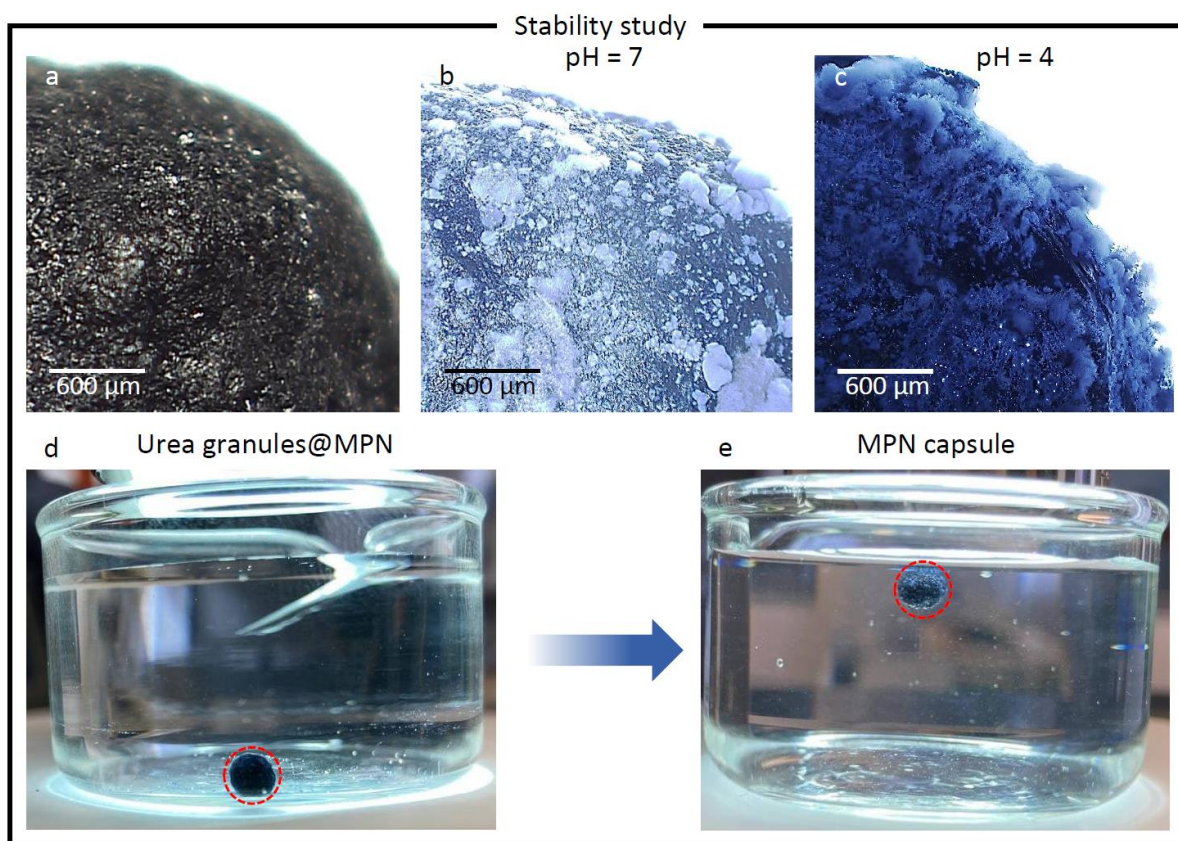


Figure 3S 29. Effect of pH on the morphology of urea granules@MPNs. Optical microscopy images of urea granules@MPN (a) before immersion in water, and after immersion in water at (b) pH 7 and (c) pH 4. Digital photographs of (d) urea granules@MPN and (e) MPN capsule (following the dissolution of urea granule) after immersion in water at pH 4. All urea granules@MPN samples were prepared using a final TA concentration of 2.3 mM, an M:L molar ratio of 1.5:1, a solution aging time of 15 min, and a coating process temperature of 25 °C.

3.7.1.5 Tables

Table 3S 1. Comparative results of urea granules@MPN samples prepared via different assembly methods

MPN assembly method	MPN Coordination type ^[a]	Coating thickness [μm] ^[b]	Coating time [min] ^[c]
Precomplex ^[d]	Bis-complex	12	40
OMC ^[d]	Bis-complex	11.7	180
Discrete ^[d]	Bis-complex	5.3	50
Spray ^[e]	Bis-complex	—	N/A ^[f]

^[a] Determined from UV–vis spectroscopy analysis of solutions after mixing TA, Fe^{II} or Fe^{III}, and urea granules in acetonitrile.

^[b] Measured by SEM.

^[c] Monitored by real-time FBRM analysis.

^[d] Samples were prepared at a TA concentration of 2.35 mM, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min at 25 °C.

^[e] Sample was prepared at a TA concentration of 2.35 mM and an M:L molar ratio of 1.5:1 at 25 °C.

^[f] N/A, not applicable.

Table 3S 2. Urea granules@MPN samples prepared at different solution aging times, M:L ratios, TA concentrations, synthesis temperatures, and deposition cycles, and their corresponding N and Fe contents

Entry	Solution aging time [min]	M:L ratio	TA Concentration [mmol]	Synthesis temperature [°C] ^[a]	Deposition cycle	Film content [wt%] in the sample	N [wt%] ^[b]	Fe [wt%] ^[c]	Fe [g kg ⁻¹] ^[d]
1	1	1.5:1	2.35	r.t	1	0.96	>44	8.47	0.9
2	60	1.5:1	2.35	r.t	1	1.08	>44	8.52	0.9
3	15	0.5:1	2.35	r.t	1	0.27	>45	6.82	0.2
4	15	1:1	2.35	r.t	1	0.54	>45	8.23	0.5
5	15	1.5:1	2.35	r.t	1	1.05	>44	8.59	0.9
6	15	2:1	2.35	r.t	1	1.24	>44	9.03	1.1
7	15	3:1	2.35	r.t	1	1.54	>44	9.29	1.4
8	15	1.5:1	1.175	r.t	1	0.15	>45	5.95	0.1
9	15	1.5:1	4.7	r.t	1	2.3	>43	7.48	1.7
10	15	1.5:1	11.75	r.t	1	1.32	>44	6.76	0.9
11	15	1.5:1	23.5	r.t	1	0.64	>45	6.53	0.4
12	15	1.5:1	2.35	r.t	5	1.52	>44	7.89	1.2
13	15	1.5:1	2.35	r.t	10	2.26	>43	7.64	1.7
14	15	1.5:1	2.35	40	1	1.86	>44	8.19	1.5
15	15	1.5:1	2.35	60	1	2.11	>43	8.64	1.8

^[a] r.t., room temperature

^[b] Total nitrogen content in the urea granules@MPN samples measured by elemental analysis.

^[c] Total Fe metal content in the MPN film measured by ICP-AES.

^[d] Total Fe metal content in the urea granules@MPN samples.

Table 3S 3. Computed analysis of urea granules@MPN samples obtained after 1 or 10 MPN deposition cycles processed by micro-CT and Phoenix datos|x reconstruction software

Sample	Coated MPN volume [mm ³]	Urea granule volume [mm ³]	Porosity volume [mm ³]	Sample volume [mm ³]	Volume coating percentage	Coated MPN thickness [μm]
Urea granules@MPN-1 st	0.67	28.59	1.22	30.48	2.2	14.3
Urea granules@MPN-10 th	1.16	13.07	1.15	15.38	7.5	39.8

CHAPTER 4

Encapsulation of Urea into Metal-Phenolic Networks as Controlled-Release Urea: A Mechanochemical approach

This chapter investigates the formation of metal-phenolic networks under solvent-free conditions in the presence of urea particles and its performance as a controlled-release of urea in soil.

This Page Intentionally Left Blank

4.1 Abstract

N fertilizers are a leading cause of greenhouse gas emissions, responsible for more than 20 percent of total agricultural emissions. Recently, the application of controlled-release fertilizers (CRFs) was recognized as an efficient approach to reduce emissions. Current advances to promote CRFs largely involve the use of solvents, which reduces their appropriateness for large-scale manufacturing. Herein, a one-step mechanochemical approach able to synthesize a versatile solid-state assembly of metal-phenolic networks (MPNs) was proposed in the absence of solvent. Urea is used to mediate the coordination of polyphenols and metals, resulting in an encapsulated urea in MPN (urea@MPN). The fabricated material demonstrates tunable mechanical resistance, crystallinity, stiffness, and wettability properties that adjust with aging and thermal treatments which is shown to rearrange the internal structure of the MPNs and encapsulated urea crystals. An aging treatment of 7 days, for example, induces a considerable increase in the complexation state of MPNs and results in a castable material with increased elasticity and melting point in comparison to unaged urea@MPN. Likewise, thermal treatments (heating at 60 °C for 6 hr) are observed to structurally reorganize the urea crystals from a polycrystalline to a single crystalline state, leading to an overall increase in the Young's modulus (55-fold), which identifies how easily a material can deform, representative of a more robust material. It is demonstrated that the encapsulated urea within urea@MPN can prolong the release period of urea in soil from 1 day, considering unencapsulated urea, to up to 9 days depending on the type of post-treatment applied. Furthermore, the material is seen to maintain the mechanical properties required to withstand the handling requirements present within agricultural applications. As the engineered mechanochemical synthesis of MPNs both facilitates tunable physiochemical properties and has greater practicability for inclusion within large-scale processing, it is deemed appropriate for implementation within a broad range of industries.

4.2 Introduction

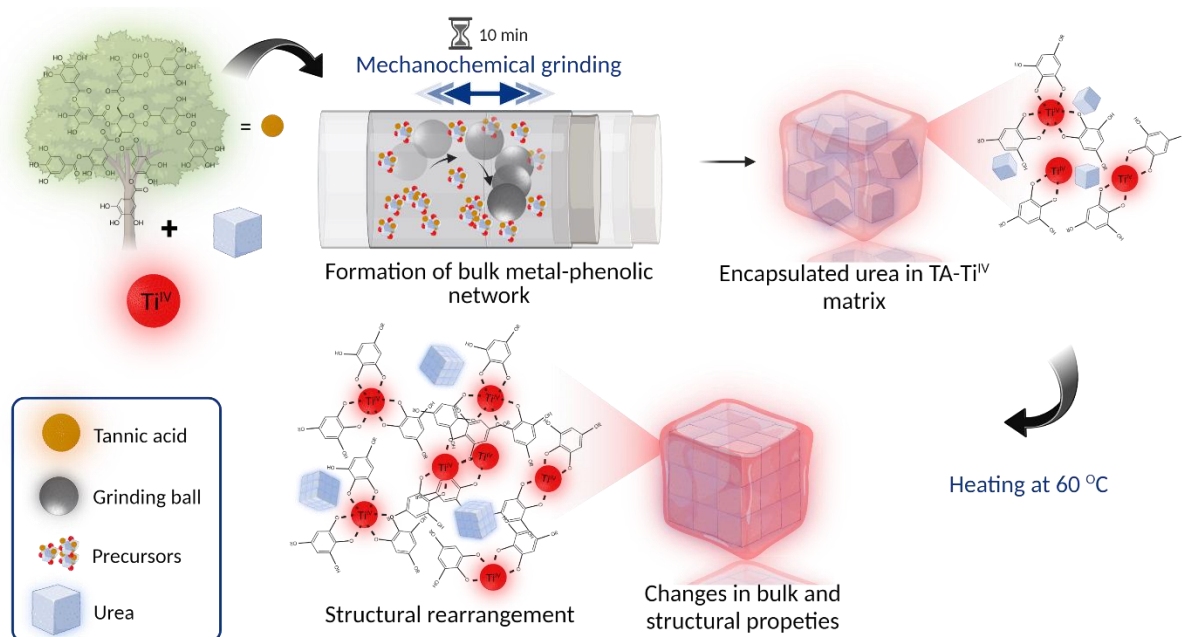
The exponential growth in global population is expected to result in more than 10 billion people by 2050 [1, 173]. The resultant increase in demand for food raises a significant challenge for agriculture and the environment, where fertilizers, especially urea as the dominant nitrogen fertilizer, play a pivotal role in increasing crop production [173, 174]. In this context, the total utilization of urea by plants has been found to be as low as 30–45% due to a huge loss to the environment through leaching and runoff - leading to eutrophication of water bodies- and through gaseous ammonia and nitrous oxide emissions [175]. The poor efficiency of nitrogen use by plants is often due to the lack of synchronicity between the nutrient supply and the plant needs. Therefore, substantial efforts have been directed toward developing Controlled-Release Urea (CRU) to improve utilization and ease the environmental impact of urea while boosting crop yield [2, 8, 11]. Two main strategies, including spray coating of urea granules with a wide range of non-biodegradable polymers (e.g., polysulfone, polyurethane, and polyolefins) and encapsulation of urea nanoparticles in a composite matrix through mixing biodegradable polymers (e.g., aliphatic polyesters and polysaccharides) with urea, are under active development for CRUs [23, 167, 168, 170]. These are associated with some inherent limitations; for example, hydrophobic and impermeable polymers may cause soil contamination if not fully degraded and encapsulation typically involves a multistep procedure, leading to high production costs [59, 176]. Encapsulation of urea via liquid mixing protocols requires the use of organic solvents at 40–130 °C, and crosslinking agents, which complicates the process resulting in inefficiencies and challenges for large-scale production [177-179]. Therefore, the development of straightforward and workable processes for producing a variety of CRUs is still required [1].

Mechanochemistry, mechanical energy-induced chemical reactions, has attracted widespread interest for sustainable production owing to being a solvent-free, energy-saving, one-step

procedure characterized by high-yielding production and low processing temperatures [180]. A wide range of organic molecules [181], metal–organic frameworks [182, 183], supramolecular complexes [184], alloys [185], zeolites [186], main-group elements [187], polymers [188], covalent organic frameworks [189], nanoparticles [190], and carbon materials [191, 192] have been synthesized with this method at both bench and industrial-scales for use in a variety of fields. In particular, the mechanosynthesis of urea ionic cocrystals and mechanochemical activation of layered minerals have been extensively studied for slow-release applications [193-197]; however, synthesizing a biomass-based CRU via the mechanochemical approach is rarely investigated.

Biomass polyphenols, such as tannic acid (TA), are a group of compounds found in plants that can favorably control the dissolution rate of urea in different types of media (i.e., soil and water environments) due to the superior adhesion between polyphenols and urea arising from the hydrogen bonding, electrostatic interactions, and π – π stacking that occur at their interface [198, 199]. These abilities facilitate the formation of Metal-Phenolic Networks (MPNs); through chelation of the catechol or galloyl groups of the phenolic ligands with varying metal ions [107], facile, biocompatible, and scalable MPN coatings are created. The wide choice of applicable metal ions and phenolic ligands holds promise for an array of applications in the environmental, gas storage, biomedicine, and catalysis fields. For instance, the use of MPNs as a controlled-release coating for urea granules was recently investigated; the results demonstrated how minor adjustments to the environment during MPN assembly influence MPN formation and growth on the urea granules, giving rise to a tunable release profile [200]. Due the known and valuable characteristics of MPNs, the development of a mechanochemical synthesized MPN is highly desirable such that it can more easily be incorporated into large-scale manufacturing streams.

Herein, a one-step mechanochemical synthesis for the assembly of MPNs using a ball-mill machine was proposed. Using solid urea as a mediator, the catechol groups of TA are coordinated with metal Ti^{IV} ions via the imposed mechanical energy, and a solid-state MPN with urea encapsulated within, urea@MPN, is assembled (**Scheme 4.1**). Meanwhile, the generated MPNs cause a further decrease in the urea particle size, leading to the formation of a homogenous bulk shape urea@MPN material. Besides, the adhesion property of MPNs (via non-covalent interactions including van der Waals forces, hydrogen bonding, and hydrophobic interactions) to urea provides a suitable host-guest complex. The bulk properties of the resulting urea@MPN material are shown to be drastically different to those of the pristine urea and TA used, due to the formation of a hypoeutectic system. Such changes are enhanced through aging and thermal treatments that are shown to impact the binding strength, stability, and wettability of the MPNs. The crystal lattice of the urea is also observed to change with application of these treatments, resulting in a change in the mechanical resistance, morphology, and porosity of bulk urea@MPN material. Furthermore, the high oxidation state and formal charge of Ti^{IV} help water trapping after applying the materials in the soil via forming a gel. The encapsulation of urea with MPNs coupled with the gelation formation in humid conditions makes urea@MPN suitable as a CRU. Due to the tunable and effective mechanochemical formation of such solid-state MPNs, it is anticipated that they would be appropriate for use within a broad range of industries.



Scheme 4.1. Schematic illustration of the mechanochemical coordination-driven assembly of MPN followed by encapsulation of urea crystals. The high friction conditions produced by mechanochemical grinding provide the required energy for creation of TA- Ti^{IV} coordination in solid-state. The heating treatment changes the structural rearrangement of urea crystals and MPNs.

4.3 Results and Discussion

4.3.1 Mechanochemical formation of MPN

A mechanochemistry approach was adopted for the formation of MPNs under high friction conditions, where Ti^{IV} metal ion was chosen as the central ion and TA was selected as an inexpensive and environmentally friendly polyphenol (**Scheme 4.1**). However, results have shown that stable TA- Ti^{IV} complexes do not form following immersion in water, indicating that a basic compound is required to form stable TA- Ti^{IV} complexes in the solid-state protocol. To evaluate this, urea, a mild alkaline compound, was used to mediate the complexation of TA- Ti^{IV} via the deprotonation of the catechol groups of TA, schematically presented in **Figure 4.1a**. To understand its effect, the chemical interactions that occurred during the MPN assembly process were assessed via a range of analytical techniques.

UV–vis diffuse reflectance spectroscopy (UV-vis DRS) analyses of pure TA, urea, TA-Ti^{IV}, and urea@MPN_{Ti} revealed considerable differences in absorbance patterns (**Figure 4.1b**). For example, TA-Ti^{IV} complexes produced from mechanical grinding featured a weak ligand-to-metal charge-transfer (LMCT) absorption band within the range of $\approx 450\text{--}700$ nm, with a λ_{max} of 570 nm, confirming the formation of TA-Ti^{IV} mono/bis-complexes [201]. However, the resulting TA-Ti^{IV} complexes dissolved after immersion in water, confirming the need for an alkaline component to provide a stable MPN. The formation of MPNs in the presence of urea, urea@MPN_{Ti}, was validated by observing both an increase in the absorption intensity of the peak and a shift to lower values within the range of $\approx 380\text{--}600$ nm, indicative of stable bis-tris TA-Ti^{IV} complexes even after immersing the sample in water [130].

The formation of MPNs was further assessed by performing high-resolution X-ray photoelectron spectroscopy (XPS) on the control samples (i.e. TA and TA-Ti^{IV}) and urea@MPN_{Ti} (**Figure 4.1c,d**). Whilst the Ti 2p_{3/2} signal of TA-Ti^{IV} presented with binding energy (BE) peaks at 458.4 and 463.8 eV, the Ti 2p_{3/2} signal of urea@MPN_{Ti}, shifted to higher energies of 458.6 and 464.1 eV [202]. The BE difference between Ti 2p_{3/2} and Ti 2p_{1/2} is equal to 5.4 in both samples and could be assigned to the Ti^{IV}-O bonds in the TA-Ti^{IV} complexes [130]. In addition, from the core-level O 1s XPS spectra of urea@MPN_{Ti}, the peak appeared at BE of 531.7 and 533.2 eV, which are characteristics of C=O and C-O/O-C-O bonds, respectively. These were shifted to lower energies compared to that of TA-Ti^{IV} and TA, indicative of coordination interactions between TA and Ti^{IV} [203].

To further shed light on the coordination structure of urea@MPN_{Ti}, Raman analysis was conducted and compared to the control samples (urea-TA and TA-Ti^{IV}) (**Figure 4.1e**). The Raman spectrum of urea-TA displays strong bands at 1612 and 1716 cm⁻¹, attributed to the stretching vibration of the benzene ring and C=O stretching modes, observed to undergo a considerable decrease upon interacting with Ti^{IV} in TA-Ti^{IV} and urea@MPN_{Ti} [204]. While the

band at 1716 cm^{-1} almost disappeared in the TA-Ti^{IV} and Urea@MPN_{Ti} spectra, the band peak at 1711 cm^{-1} broadened and shifted to a lower wavelength as a result of complexation with Ti^{IV}. TA-Ti^{IV} and Urea@MPN_{Ti} spectra show three new bands compared to urea-TA with peaks nearing 630 , 1360 (ν_1), and 1495 (ν_2) cm^{-1} , attributed to the restructuring of TA upon coordination of the galloyl and carboxylate groups with Ti^{IV}, respectively. Interestingly, the difference between these two bands ($\Delta\nu_2-\nu_1$) decreases from 136 to 132 cm^{-1} after the addition of urea, suggesting that the structure of some of the carboxylate ($-\text{COO}$)/Ti^{IV} interactions changed from bridging to bidentate mode (**Figure 4.1a**, right most column) [205]. Moreover, the intensity ratio between ν_2/ν_1 increased from 1, for urea@MPN_{Ti}, to 1.19 for TA-Ti^{IV}; these observations support the assertion that metal-phenolic coordination is heavily impacted by the pKa of precursors through the solid-state grinding process, whereby the ionization of phenol to phenolate groups induces a negative mesomeric effect and leads to an enhancement of the ν_2 band intensity [204]. Our findings reveal that the binding strength and stability of the TA-Ti^{IV} complexes facilitate the lateral and longitudinal cross-linking of TA by Ti^{IV} species, leading to the stability improvement of urea@MPN_{Ti}. Scanning electron microscopy (SEM) of TA, ground urea, and urea@MPN_{Ti} indicated that both TA and urea crystals undergo shape restructuring after coordinating with Ti^{IV} metal ions during MPN assembly (**Figure 4.1f-h**). Interestingly, a few small urea crystals were found in urea@MPN_{Ti}, but they were smaller than the urea crystals that resulted after grinding (**Figure 4.1g,h**). It is believed that the presence of TA-Ti^{IV} further facilitates the breakdown and dispersion of urea crystals within MPNs via non-covalent interactions (i.e. van der Waals forces, hydrogen bonding, ionic bonding, and $\pi-\pi$ stacking) and strong surface coordination and assembly (**Figure 4.1a**). Additionally, energy dispersive X-ray spectroscopy (EDX) mapping of a high-angle annular dark-field (HAADF) image from a small urea@MPN_{Ti} patch confirmed the homogeneity of MPN, having uniform Ti, N, and C distribution throughout the structure (**Figure 4.1i**). Therefore, this demonstrates

that TA-Ti^{IV} imparts a set of functional properties to the urea@MPN_{Ti} matrix (see section 2.5), including extensively intercalated small urea crystals, that promote the control of the urea release profile.

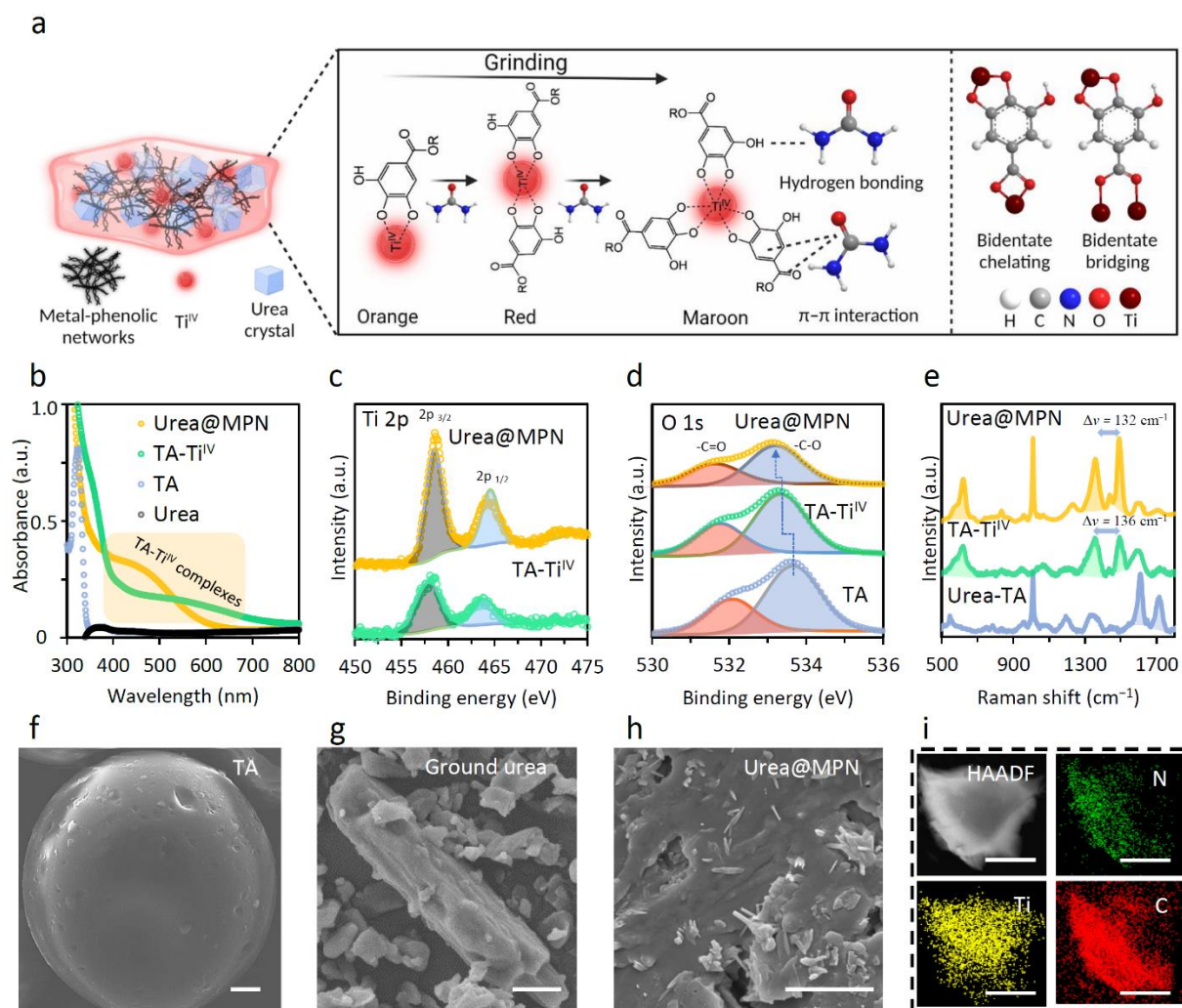


Figure 4.1. Urea-mediated coordination-driven assembly of MPN via grinding. (a) Schematic illustration of the preparation of urea@MPN via grinding of urea, TA, and Ti^{IV} precursors and possible complexation states of TA-Ti^{IV}. (b) UV-Vis DRS spectra of urea, TA, TA-Ti^{IV}, and urea@MPN after grinding; the highlighted area (400–700 nm) corresponds to the LMCT band of the TA-Ti^{IV} complexes. (c) XPS patterns of the TA-Ti^{IV} complexes and urea@MPN (Ti 2p area). (d) XPS patterns of the TA, TA-Ti^{IV} complexes, and urea@MPN (O 1s area). (e) Raman spectra of urea-TA, TA-Ti^{IV} complexes, and urea@MPN. (f-h) SEM images of the surfaces of TA, ground urea, and urea@MPN. Scale bars are 10 μm. (i) HAADF and EDX mapping images of urea@MPN. Scale bars are 5 μm.

4.3.2 Aging and thermal treatment of urea@MPN_{Ti}.

A fundamental understanding of the age- and heat-induced structural reorganization of MPNs could offer opportunities to rationally fine-tune the material properties and its overall performance in specific applications (see section 2.5). Therefore, the effects that aging and thermal treatments had on the fabricated urea@MPN_{Ti} were investigated. Samples were either aged for one week at room temperature or thermally treated at 60 °C for 6 hr, namely, aged, and heated samples, respectively; both treatments were compared with urea@MPN_{Ti} samples immediately following preparation, denoted as ‘fresh’.

The UV-vis DRS elucidated that both aging and heating govern structural changes in the metal-phenolic networks (**Figure 4.2a**). Specifically, aging was shown to primarily increase the extent of metal-phenolic coordination without observing a shift in the LMCT band, indicating the identical complexation state of TA-Ti^{IV} with the fresh sample. Heating, on the other hand, could increase both the rate of coordination and transition the dominant TA-Ti^{IV} complexation state from bis to tris-complexes. In addition, comparing the XPS results of the fresh sample with that of the aged and heated samples (**Figure 4.2b**), the N 1s core-level peak at a BE of 400.1 eV, representative of the -NH₂ group of urea, shifted to a lower energy (399.9 and 399.7, respectively). This likely represents the urea interacting with MPNs via hydrogen bonding [200]. Moreover, C 1s core-level peaks of XPS patterns show that C=O and C-O peaks undergo structural reorganization during sample aging and heating, where the BE of 289.8 and 286.4 eV shifted to lower energy (≈ 0.9 eV) after heating treatment (**Figure 4.2c**). This observation is in line with the Raman analyses of TA-Ti^{IV}, fresh, aged, and heated samples, where an increase in ν_2/ν_1 ratio from 1 to 1.31 and a decrease in the difference $\Delta\nu_2-\nu_1$ bands from 136 to 125 cm⁻¹ (**Figure 4.2d**). It potentially represents higher deprotonation of catechol/galloyl groups and more bidentate Ti^{IV}-COO bridging mode involved through the structural rearrangement after aging or thermal treatment [204]. The broad peak at ≈ 3300 cm⁻¹ observed in the FTIR spectra

of urea-TA, fresh, aged, and heated samples is assigned to the -OH and -COOH groups of TA, in which the intensity of the peak decreases over the aforementioned order (**Figure 4.2e**); the incorporation of -OH and -COOH functional groups of TA with Ti^{IV} into the TA-Ti^{IV} coordination complex can lead to a decrease in the peak intensity [206].

The degree of crystallinity within the $\text{urea@MPN}_{\text{Ti}}$ samples was also observed to increase through the aging and heating treatments (**Figure 4.2f**). Although this is likely due to the partial oxidation of TA that leads to a change in the growing condition of MPNs, the mechanism is still unclear as the crystallinity of urea also needs be incorporated. Overall, these results indicate that physicochemical properties of the $\text{urea@MPN}_{\text{Ti}}$ matrix are age and temperature dependent, displaying age- and heat-induced structural rearrangement.

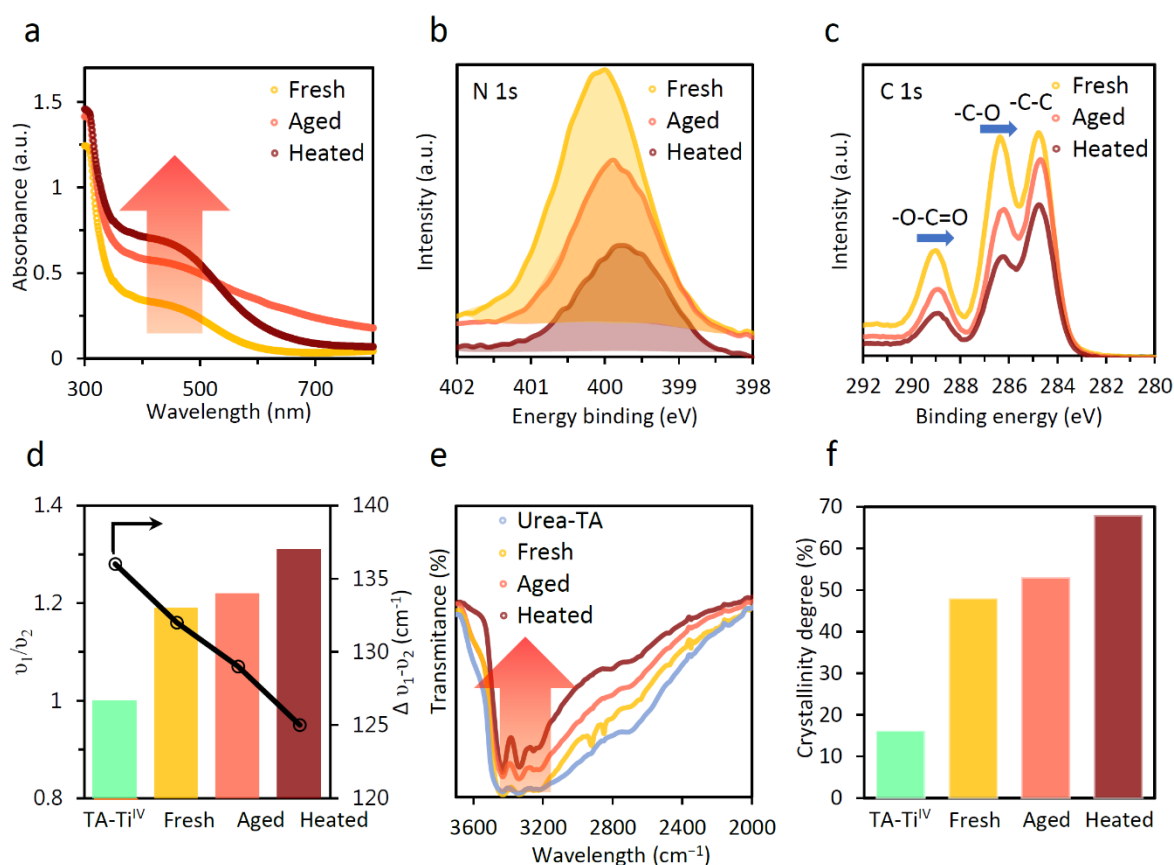


Figure 4.2. Influence of aging and thermal treatments on physicochemical properties of urea@MPN . (a) UV-Vis DRS spectra and (b-c) High resolution XPS spectra of N 1s and C 1s areas of fresh, aged, and heated urea@MPN samples. (d) ν_1/ν_2 ratio profiles (bar graph) and $\Delta\nu_1-\nu_2$ difference (black line) of TA-Ti^{IV} , fresh, aged, and heated urea@MPN samples measured by Raman spectroscopy. (e) FTIR spectra of urea-TA, fresh, aged, and heated

urea@MPN samples. (f) Crystallinity degree of TA-Ti^{IV}, fresh, aged, and heated urea@MPN samples measured by XRD from $2\Theta = 5-80$.

4.3.3 Bulk properties of urea@MPN_{Ti} following aging and thermal treatments

To gain further insight into the underlying mechanism of the age- and heat-induced structural reorganization of the encapsulated urea in MPNs, the mechanical and thermodynamic behavior of urea@MPN_{Ti} samples were examined. The mechanical behavior of the material also provides insight into the feasibility of applying urea@MPN_{Ti} as a controlled-release fertilizer.

A comparative analysis of the mechanical resistance of urea, fresh, aged, and heated urea@MPN_{Ti} samples was conducted by diametral compression test (**Figure 4.3a**). While untreated urea presented with a low compression strength of 127 Pa, all urea@MPN_{Ti} samples had significantly greater mechanical resistance. Notably, both fresh and aged samples showed high malleability, avoiding rupturing even after $\approx 75\%$ deformation was reached. The observed pliability of this material is attributed to the branched structure of TA and the crystallinity type and overall lattice structure of urea within the fabricated MPNs (See section 2.4). Interestingly, the compression strength of the urea@MPN_{Ti} samples further increased following aging and heating treatments. This observation highlights a major role of hydrogen bonding, ionic bonding, and π - π stacking within the samples, whereby increased molecular interactions between the encapsulated urea and MPNs can provide additional mechanical strength [76]. Meanwhile, the strain required for deformation of the aged sample in the elastic region, which corresponds to single crystal deformation, was markedly increased in comparison to the fresh sample. A significant compression strength (≈ 400 Pa) was observed after heating the urea@MPN_{Ti}, in contrast to the plasticity of the fresh and aged samples. Hence, we envisage that a higher level of intermolecular rearrangement between the galloyl groups of TA and TA-Ti^{IV} building blocks leads to the breakage of H-bonding interactions between the encapsulated urea and MPN matrix, which may cause defects in the urea@MPN_{Ti} matrix [207]. On a

molecular level, this suggests that the MPNs become more compact with cooling, leaving the urea crystals less prone to being in a polycrystalline state (See section 2.4). Overall, while the crystallinity of fresh, aged, and heated samples increases in ascending order, urea is prone to be in a single crystal structure rather than in a polycrystalline form. Furthermore, a representative value of the required energy for the deformation of 1 g sample was evaluated and enables comparison of mechanical resistance for different samples. The normalized energy was achieved by integrating the load-deformation plots up to a deformation point of 25% and dividing by the sample mass to ensure direct comparability (**Figure 4.3b**) [51]. Both aged and heated samples take more energy to be compressed. It is believed that the content of a single crystal lattice in urea increases in the order of fresh, aged, and heated samples as the energy required for the deformation of single crystal lattice is higher compared to the same amount of a polycrystalline material. The Young's modulus, a measure of stiffness, of the urea@MPN_{Ti} samples before and after aging/heating treatments was determined from the slope of the compression curves in their elastic regions (**Figure 4.3c**). Fresh samples showed a lower stiffness, having a Young's modulus (E_Y) of 0.1 MPa, whilst the stiffness drastically increased by ≈ 6.9 and 51.1-fold following aging and heating treatments, respectively. The increase in stiffness following aging and heating treatments is ascribed to changes in the crystallinity of urea and the increased complexation state of the TA-Ti^{IV} complexes.

To better interpret the relationship between sample stiffness and crystallinity, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used. All DSC curves for urea@MPN_{Ti} samples showed a lower endothermic peak, 92-114 °C, in comparison to the endothermic peak of pure urea, 135 °C (attributed to its melting point) [208], (**Figure 4.3d**). The homogenous matrix of urea@MPN_{Ti} causes the creation of a hypoeutectic system, presenting an overall lower melting point in comparison to each individual constituent. However, the melting point of the urea@MPN_{Ti} samples was seen to increase after aging and

heating treatments, increasing from 92 °C for the fresh sample, up to 100 and 114 °C for the aged and heated samples, respectively. An increase in the melting point after heating, aside from a change in the stiffness of the heated sample, could potentially indicate the formation of an extended urea single crystal in the coalescent matrix [178]. TGA analyses supported the speculation that the crystallinity increases after aging and heating, as an improvement in the thermal stability of the samples was observed; this is due to more energy being required to dissociate urea single crystal and TA-Ti^{IV} complexes in fresh, aged, and heated samples, respectively (**Figure 4.3e**).

The increasing hydrophobicity of the aged and heated samples was assessed through surface wettability measurements, where the fresh sample presented with a water contact angle of 45°, whilst the aged and heated samples presented with angles of 60 and 68°, respectively; this is likely due to the structural rearrangement of the TA-Ti^{IV} complexes driven by an increase in π - π stacking among the aromatic rings in TA (**Figure 4.3f**) [207].

It was observed that following heating treatment, the urea@MPN_{Ti} samples were inflated in comparison to the aged samples. Thus, X-ray micro-computed tomography (micro-CT) was employed to increase the understanding of the bulk arrangement within the material matrix; both cross-section and computed void volume images were analyzed (**Figure 4.3g-i**). Interestingly, the cross-sectional image of the heated sample showed a large free-space volume in comparison to the aged sample, confirming the inflation observation. This may indicate an important relationship between urea crystal rearrangement and phase change behavior within MPN structures, thus further fundamental studies are needed in solid-state.

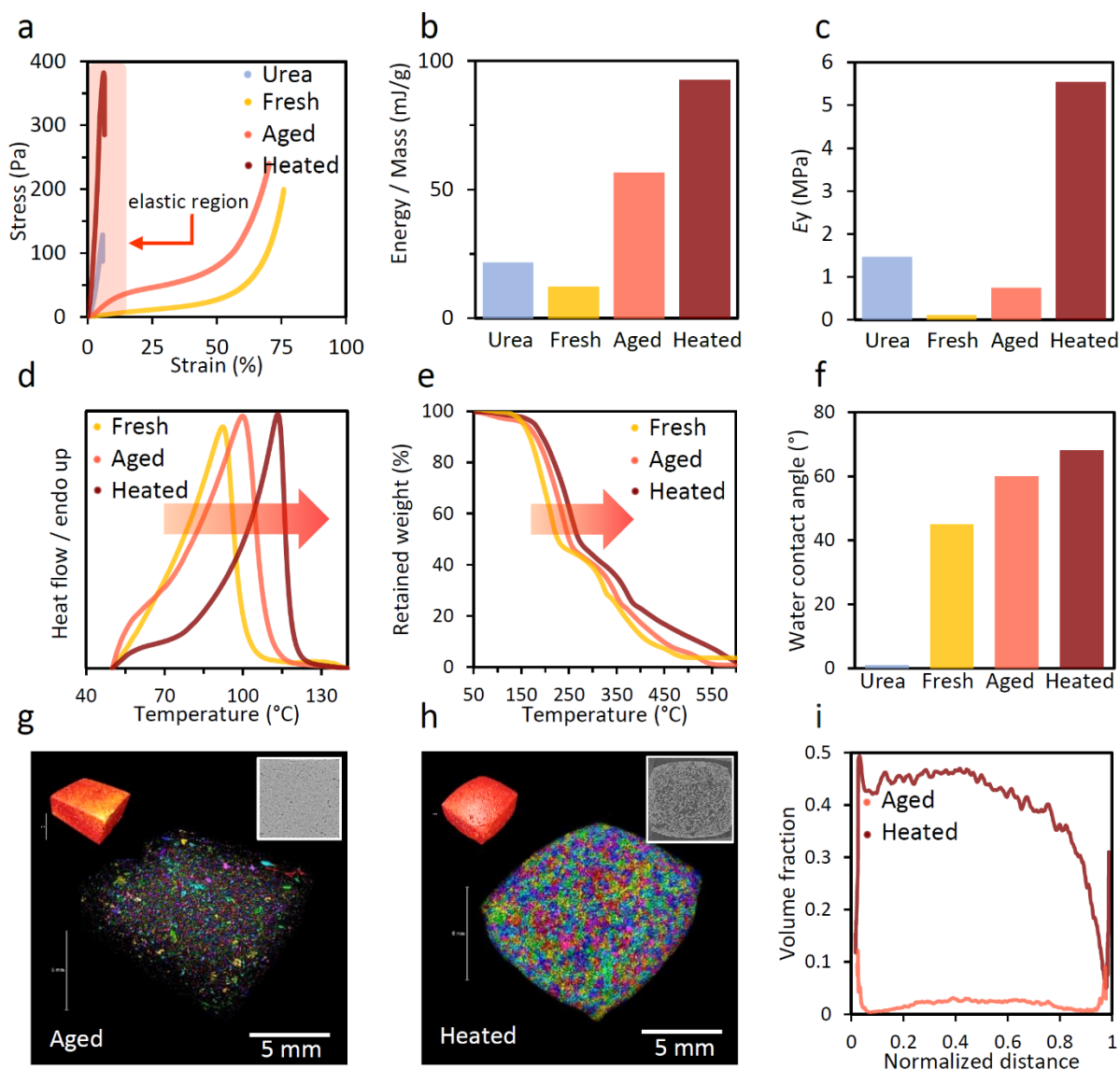


Figure 4.3. Influence of aging and thermal treatments on the mechanical and bulk properties of urea@MPN samples. (a) Compressive stress–strain curves, (b) calculated required energy for 25% deformation, and (c) corresponding Young's modulus values from elastic regions of compression tests of urea, fresh, aged and heated samples. (d) and (e) DSC and TGA, respectively, from fresh, aged, and heated urea@MPN samples. (f) Water contact angle measured from urea, fresh, aged, and heated samples. (g-h) Micro-CT images from urea@MPN samples after aging and thermal treatments, respectively (inset show the cross-section images). (i) volume reconstruction of the micro-CT data from ≈ 1200 scan projections from aged and heated samples.

4.3.4 Structural and lattice properties of urea@MPN_{Ti} after aging and thermal treatments

To have a clearer vision as to why the physical properties of urea@MPN changed after aging and heating treatments, the nano-scale structure of the samples was scrutinized. SEM was used to examine the surface morphology of samples after aging and heating treatments, revealing

that urea@MPN_{Ti} is drastically smoother when it is heated in comparison to when it is aged (**Figure 4.4a,b**). It is likely that the urea crystals coalesce into the MPNs and make a uniform matrix during heat treatment; during aging, small urea crystals, which are covered by MPNs, are still observed and result in a rough surface morphology (**Figure 4.4c**).

To elucidate the crystallographic properties of samples after aging and heating treatments, transmission electron microscopy (TEM) was used. **Figure 4.4d** and **e** show low-magnification images of aged and heated samples, respectively, highlighting that aging and heating processes decrease the urea particle size. The TEM- selected area electron diffraction technique (TEM-SAED) confirmed the crystallinity type of the studied samples (**Figure 4.4f**), where the aged samples showed at least six sets of diffraction rings, which is in consistent with urea crystal dots (i.e. 211, 002, 311, 222, 203, and 411 indices) and indicative of a polycrystalline structure [209]. In contrast, heating treatments changed the crystallinity state from a polycrystalline to a single crystal structure consisting of distinct spots (i.e. 001, 101, 110, and 200 indices), related to the urea tetragonal lattice with P4₂m space group (**Figure 4.4g**) [210]. High-resolution TEM (HRTEM) imaging further investigated the crystalline properties of samples (**Figure 4.4h,i**). Interestingly, several grain boundaries with varying orientations (assigned in random colors) were observed in the aged sample, confirming the hypothesis that a polycrystalline lattice was presented within the aged samples, in line with the physicochemical characterizations; these small crystalline domains are embedded within amorphous MPNs. In contrast, the heated samples featured more crystalline domains with typical lateral sizes of 0.34 and 0.17 nm. Regardless of the degree of crystallinity of the samples, high-angle annular dark-field and elemental mapping revealed a homogeneous distribution of urea and MPN elements (i.e. C, N, and Ti) in both aged and heated samples, representing the successful encapsulation of urea particles within the MPNs (**Figure 4.4j,k**).

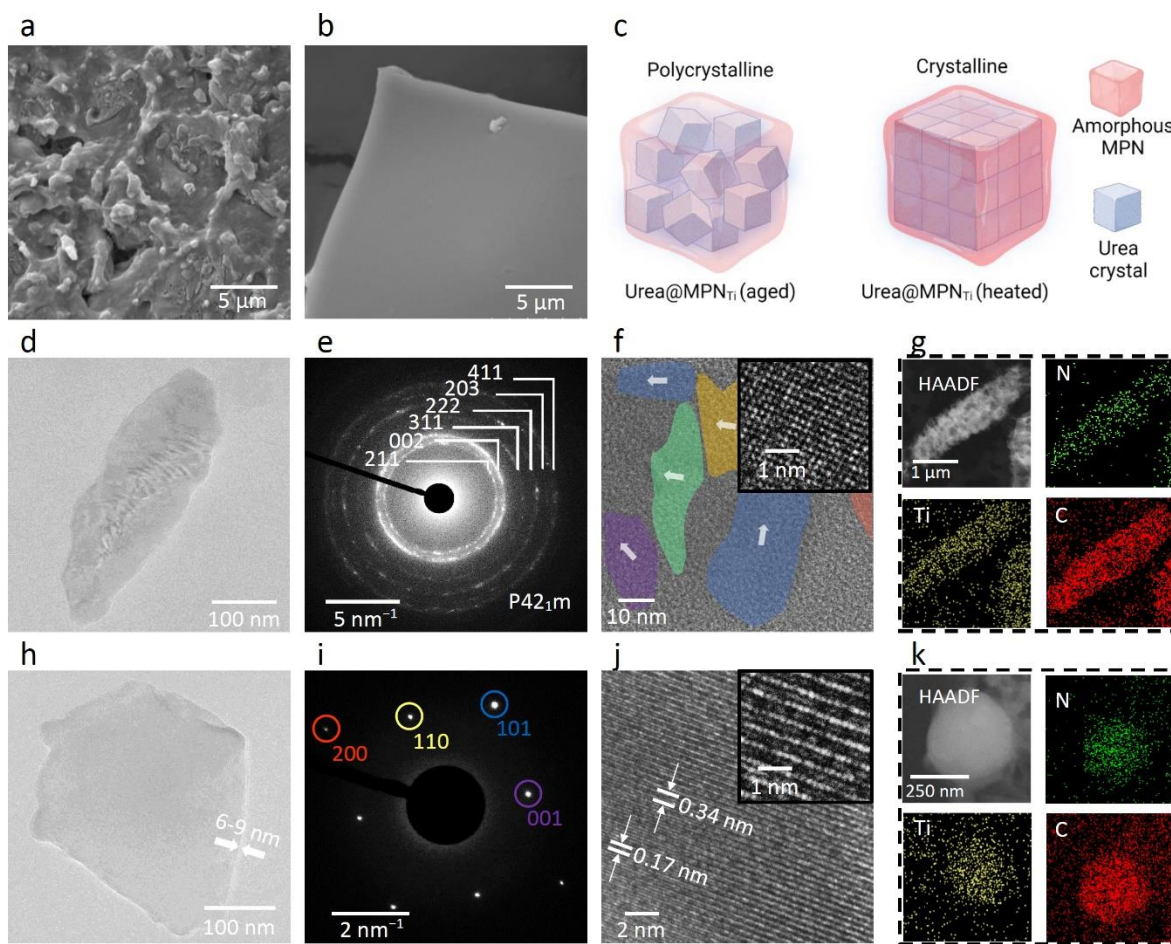


Figure 4.4. Structurally modulated urea crystals in urea@MPN via aging and thermal treatments. (a,b) SEM images of the surface of samples after aging and heating processes. (c) A schematic of urea crystals in the urea@MPN samples after aging and heating treatments. TEM (d,e), SAED (f,g), high-resolution TEM (h,i), and HAADF-mapping images (j,k) of urea@MPN after aging and heating treatments, respectively. Inset in f and j represents the atomic structure of urea crystals.

4.3.5 Agricultural application of urea@MPN as controlled-release urea

This work investigates one plausible application of the urea@MPN material, taking advantage of the encapsulated urea and employing it as a CRU. The cumulative release profile of urea from urea@MPN samples in soil was evaluated and compared against pure urea; A colorimetric method was used to calculate the dissolution of urea from the urea@MPN matrix as a function of time (**Figure 4.5a-f**). The water-filled pore space percentage (WFPS%) and environmental temperature of the soil were kept constant at 60% and 25 °C in all experiments,

respectively, unless otherwise mentioned. The varying urea@MPN samples (fresh, aged, and heated) all showed a prolonged urea release profile in comparison to pure urea, having a complete release time of 3-9 days. As pure urea releases with 1 day, this study confirms the assumption that urea encapsulated in MPNs can be implemented as a CRU (**Figure 4.5b**).

In detail, urea@MPN after aging and heating treatments shows an increasingly better performance for slow-release, reaching >90% of urea release by 5 and 7 days, respectively. The improved performance of the heat-treated sample may be attributed to the increase in the coordination interactions among TA-Ti^{IV} complexes from bis- to tris-complexes. Interestingly, the heated sample exhibited a lag time in the release of urea in the first three days. According to the observed changes in the bulk properties of urea@MPN after heating treatments, the reason for the lag time in urea release may be due to a large amount of free space in the sample, where some of the dissolved urea may be confined inside the macro-pores throughout urea@MPN, leading to impeded release of urea. The increased lag time to 3 days may also be a result of the increased hydrophobicity, as lag periods are generally tied to water infiltration into the material [130, 176, 178]. Due to their improved performance, heated samples were used for the remainder of the urea release studies.

As shown from **Figure 4.5c**, the timeframe to reach complete urea release increased from 3 to 9 days when increasing the MPN content from 10 to 40% in the urea@MPN samples; an increase in the hydroxyl and carboxylic groups present in MPNs leads to an increase in H-bonding with the urea molecules, which further results in reducing the release rate of urea from the sample. As such, all further release studies used 40% MPN content in urea@MPN, unless otherwise mentioned.

The effect that different metal ions (i.e. Fe, Zn, Zr, and Ti) had on the release profile of urea from urea@MPN_M was investigated, where _M indicates the metal ion implemented (**Figure**

4.5d). Urea release was shortened to timeframes nearing 3 days when urea@MPN_{Zn} and urea@MPN_{Fe} were used, whilst the release of urea was lengthened to 9 days when urea@MPN_{Ti} and urea@MPN_{Zr} samples were used. The slower release rate of urea@MPN_{Ti} and _{Zr} is attributed to both the different coordination bonds between TA and varying metal ions, as well as the high oxidation state and formal charge of Ti^{IV} and Zr^{IV} in providing a hydrogel system after absorbing water from the soil, which is of great interest for agriculture [23, 59, 211-216].

The temperature of soil was found to have a significant impact on the urea release profiles from the urea@MPN_{Ti} samples: elevating the temperature from 10 to 40 °C led to an increase in the rate of urea dissolution, with complete release within 11 and 2 days, respectively (**Figure 4.5e**). Higher vapor pressure and the relative humidity value of the system in the container at increased temperatures, facilitates faster water diffusion throughout the sample and causes an increase in the release rate of urea (i.e. at 40 °C). In contrast, varying the moisture content of the soil had minimal effect on the release profile of urea from urea@MPN, with the time taken to achieve complete release being 9 days for all WFPS studied, 30, 40, and 60%. This shows that vapor pressure has a greater impact on urea release rate in comparison to soil moisture (**Figure 4.5f**).

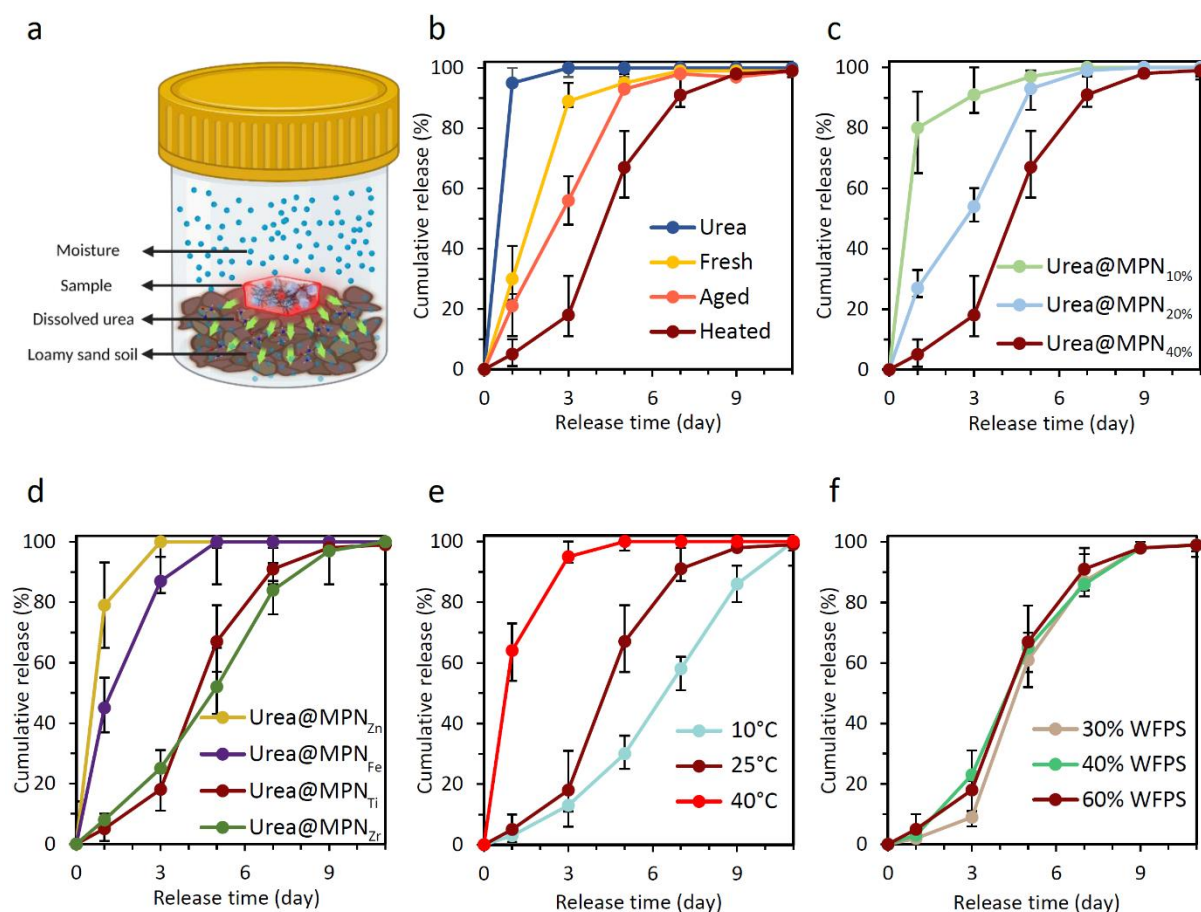


Figure 4.5. Cumulative release rate of urea in soil, measured by colorimetric protocol, from urea@MPN samples as shown in (a) using different treatments (b), MPN contents (c), and metals (d). Cumulative release rate of urea at (e) different environmental temperature, and (f) moisture content of the soil from urea@MPN_{Ti} prepared with 40% MPN content. Three experiments were investigated for each sample, with the data shown as the mean $\pm$ standard deviation.

The nitrogen release profile of CRUs is critical for seedling survival and long-term plant growth. However, the water-holding capacity of the soil in the presence of CRUs is also an important factor to consider. This is a critical parameter due to an ability to reduce the irrigation frequency and the risk of plant death in arid and semi-arid areas by creating a water reservoir (via the swelling of materials) near the plant root zone. Thus, how the water-holding capacity of the materials changes the water-holding capacity of the soil and water-retention of the soil was assessed (**Figure 4.6**). The water-holding capacity of urea@MPN_{Ti} and urea@MPN_{Zr} with different MPN contents (i.e. 10, 20, and 40%) were examined at 25 °C and 70% humidity (**Figure 4.6a**). The water-holding capacity of samples compared to the dried samples improved

from $\approx 20\%$ to $\approx 100\%$ w/w by increasing the MPN content in the urea@MPN samples with a slightly higher absorbency for urea@MPN_{Zr} than urea@MPN_{Ti} demonstrating the capability of urea@MPN samples as hydrogel CRU. After homogenously mixing the urea@MPN samples at different levels from 1 to 3% with the soil, the water-holding capacity of the soil increased from ≈ 10 to 25% compared to the control experiment (no added materials), indicating that the urea@MPN materials can potentially be used as a hydrogel system in the soil (**Figure 4.6b**). In addition, a slower water evaporation rate at 25 °C was observed when 3% of urea@MPN_{Ti} or urea@MPN_{Zr} samples were mixed with soil, indicating that the water-retention of the soil was improved likely due to strong interactions of urea@MPN samples with inorganic and organic matters of the soil (**Figure 4.6c**). Therefore, the application of urea@MPN as a hydrogel CRU could be an alternative practice in agriculture to increase the water-holding capacity of the soil and improve the synchronicity between the nitrogen supply and the plant needs by controlling the release of urea.

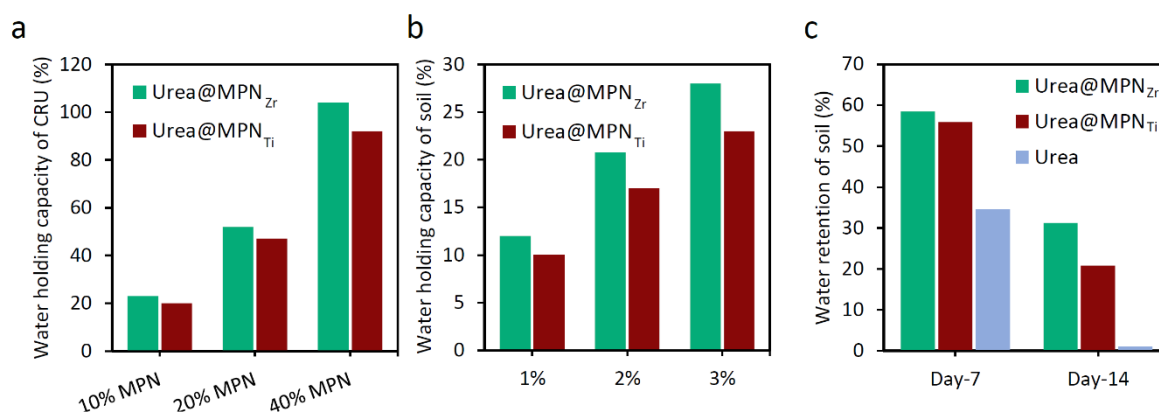


Figure 4.6. Physical property changes of urea@MPN after being in contact with water and soil. Water-holding capacity of urea@MPN_{Zr} and urea@MPN_{Ti} prepared using different content of MPN(a). Water-holding capacity of the soil after applying different percentages of urea@MPN (b), and water-retention of soil after mixing with urea@MPN.

4.4 Conclusion

The assembly of MPNs comprised of TA ligands and Ti^{IV} metal ions via a mechanochemistry method was investigated. Unlike conventional MPN assembly, solid urea was used as an alkaline mediator and an urea encapsulated MPN solid-matrix was formed, $\text{urea@MPN}_{\text{Ti}}$. Through application of aging and heating treatments to the $\text{urea@MPN}_{\text{Ti}}$ material, the complexation state of the TA- Ti^{IV} coordination shifted from bis to tris-complexes, resulting in considerable changes in the material's overall morphology. The crystallinity structure of urea was also observed to change following thermal treatments, transforming from a polycrystalline to a single crystalline lattice; this led to a shift in the materials physiochemical properties including compression resistance, wettability, and stiffness. The in-depth understanding of the mechanochemical synthesis of MPN mediated by urea, and the aged/heated-induced structural rearrangement of MPN and urea crystals within its matrix, provides an opportunity to design tunable materials for numerous industrial applications. Regarding its use as a controlled-release fertilizer, the release of urea could be prolonged to up to 9 days, depending on the type of treatment applied. Thus, this work not only addresses the need for the development of a sustainable and scalable CRU, but it also examines the implementation of MPNs as a CRU within the agricultural landscape.

4.5 Supplementary Information

4.5.1 Experimental Section

4.5.1.1 Materials

Tannic acid (TA, ACS reagent), Titanium(IV) isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, 97%), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%), Zn(II) sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, ACS

reagent, 99.5%), Zr(IV) chloride (ZrCl_4 , ACS reagent, 99.5%), urea powder (ACS reagent, 99–100.5%), 4-(dimethylamino)benzaldehyde (*p*-DMAB, 99%), trichloroacetic acid (TCA, ACS reagent, 99%), hydrochloric acid (HCl, ACS reagent, 37%), ethanol (98%) were purchased from Sigma-Aldrich. High-purity (Milli-Q) H_2O with a resistivity of 18.2 $\text{M}\Omega\text{ cm}$ was obtained from an inline Millipore RiOs/Origin H_2O purification system. All solutions were freshly prepared for immediate use for each experiment.

4.5.1.2 Methods

Preparation of urea@MPN via grinding method. In a typical synthesis, 1.36 g of TA, 0.24 g of Ti^{IV} and 2.4 g of urea powder were mixed using a glass spatula for a few seconds in a screw-capped stainless-steel jar along with one stainless steel ball bearing. Then, this reaction vessel was placed in a ball-mill machine, and components were ground with a frequency vibration setting of 25 Hz for 10 min. After the grinding process was complete, the urea@MPN sample was removed from the jar and exposed to different treatments including aging for 7 days (wrapped with polyethylene plastic and left on the bench at 25 °C) or heated at 60 °C for 6 hr in an oven.

Preparation of urea@MPN via grinding method with different MPN contents

To prepare urea@MPN samples with different MPN contents, 0.23, 0.53, and 1.36 g of TA and 0.04, 0.10, 0.24 g of Ti^{IV} were mixed with 2.4 g of urea in a screw-capped stainless-steel jar along with one stainless steel ball bearing to achieve 10, 20, and 40wt% MPN content in urea@MPN. These were named urea@MPN_{X%}, where X% is the wt% of MPN. Then, this reaction vessel was placed in a ball-mill machine, and components were ground with a frequency vibration setting of 25 Hz for 10 min. After the grinding process was complete, the urea@MPN_{X%} sample was removed from the jar and heated at 60 °C for 6 hr in an oven.

Preparation of urea@MPN via grinding method with different metal ions

To prepare urea@MPN samples with different metals ions, 1.41, 1.38, 1.36, and 1.37 g of TA and 0.19, 0.22, 0.24, and 0.23 g of Zr^{IV} , Fe^{III} , Ti^{IV} , and Zn^{II} , were mixed with 2.4 g of urea in a screw-capped stainless-steel jar along with one stainless steel ball bearing to synthesized urea@MPN_M, where M is the metal. Then, this reaction vessel was placed in a ball-mill machine, and components were ground with a frequency vibration setting of 25 Hz for 10 min. After the grinding process was complete, the urea@MPN_M sample was removed from the jar and heated at 60 °C for 6 hr in an oven.

Urea Release Characteristics of the urea@MPN Samples

The urea release profile of urea@MPN samples was investigated in soil. The soil collected from the Wimmera region (Victoria, Australia) had the following characteristics: loamy sand, soil pH (1:5 H₂O) 8.4, total C 2.1%, NH_4^+ -N 14 mg kg⁻¹, NO_3^- -N 19 mg kg⁻¹. The soils were first sieved (<2mm particle size) to remove stones and air-dried to increase the homogeneity. After determining the water content of the soil via oven drying at 105°C, the required amount of water was calculated to achieve a water-filled pore space (WFPS) of 60%. For each sample, 39 g soil was placed in a 70 mL polypropylene container and preincubated for 3 days by hydrating the soil with the required water amount. After the preincubation period, the soil samples were treated by placing urea@MPN samples on top of the soil with an application N rate of 840 mg kg⁻¹ of soil. The treated soil samples were incubated at either 10, 25, or 40 °C for 11 days. The soil moisture levels were kept constant by adding water based on weight loss every 3 days and samples were aerated at the same time. The urea@MPN samples were taken by a spatula from the soil after 1, 3 5, 7, 9, and 11-day time intervals. Following this, the urea@MPN samples were crushed and immersed in 100 mL water for 3 hr to dissolve the remaining urea, the solution was filtered for urea measurement using a colorimetric method

(the remaining urea in urea@MPN samples was measured on the same date as the sample was taken to minimize the impact of urea hydrolysis). The urea release experiments were conducted with three replicates. To investigate the influence of soil moisture on the release rate of urea from urea@MPN samples, the WFPS of the soil was set at 30, 40, or 60%, and the rest of the experiment followed the procedure mentioned above.

Water holding capacity of urea@MPN samples

Water absorbency of urea@MPN_{Ti} and urea@MPN_{Zr} samples with different MPN contents (10, 20, and 40%) was measured via changes in weight. One gram (1.0 g) of the urea@MPN sample was placed in a petri dish and then it was stored in a pre-adjusted 70% RH incubator at 25 °C. After 6 hr, the sample was taken out of the petri dish and weighed. The percentage absorbency was calculated using Equation S1.

$$\text{Absorbency \%} = \frac{w_2 - w_1}{w_1} \times 100 \quad (\text{Equation S1})$$

where w_1 is the weight of the dried sample and w_2 is the weight of the wet sample.

Water holding capacity of the soil mixed with urea@MPN samples

To investigate the water holding capacity of the soil mixed with urea@MPN, 100 g of dried soil was well mixed with crushed urea@MPN samples at different application ratios (1, 2, and 3%) and was placed in a 4.5 cm diameter PVC tube with a bottom sealed with 200 mesh nylon fabric and weighed (W_1). Then, the soil was slowly drenched with distilled water using a peristaltic pump (2 mL min^{-1}) to saturate the soil and weighed again (W_2). The water-holding capacity (WH%) of the soil was calculated using Equation S2.

$$\text{WH \%} = \frac{W_2 - W_1}{W_1} \times 100 \quad (\text{Equation S2})$$

Water retention of the soil (or mixed with urea@MPN samples)

To evaluate the water retention of the soil, 100 g of the soil was mixed with 3 g sample in a polypropylene container and weighed (W_0). Then, the mixture was drenched with distilled water to reach 60% WFPS moisture content in the soil and the container was weighed (W_1).

The container was incubated at room temperature and weighed every 2 days (W_i) for 14 days.

The water retention of the soil (WR%) was calculated as follows (Equation S3):

$$\text{WR \%} = \frac{W_i - W_0}{W_1 - W_0} \times 100 \quad (\text{Equation S3})$$

Urea Release Evaluated by Colorimetric Analysis

The concentration of urea was determined by UV–vis spectroscopy according to the methodology established by With et al. in 1961 (Scheme S1) [171]. In brief, an Ehrlich reagent was prepared by dissolving *p*-DMAB (5 g) in HCl (37%, 20 mL) and diluting with ethanol in a 100 mL volumetric flask. To analyze the concentration of urea, the sample (0.5 mL; either standard or unknown urea concentration solutions) was mixed with Ehrlich reagent (0.5 mL) in a cuvette. Then, TCA (2 mL, 10% in water) was added to the cuvette. *Caution! Trichloroacetic acid is corrosive and toxic to some organs and should be handled carefully.* A curve of urea concentration (30–1000 ppm) in solution versus absorbance at $\lambda = 420$ nm was obtained with $R^2 = 0.9997$.

4.5.1.3 Characterization

UV–Vis Diffuse Reflectance Spectroscopy (UV–Vis DRS)

Optical absorption spectra were acquired with an Agilent Cary 5000 spectrophotometer equipped with an integrating sphere. A center-mount attachment equipped with a custom-made powder holder was used, enabling the positioning of the samples within the integrating sphere. This qualifies reflectance/scattering losses, therefore obtaining the pure absorptive component of the prepared materials.

X-ray Photoelectron Spectroscopy (XPS)

XPS data were obtained on a VG ESCALAB 220i-XL spectrometer equipped with a hemispherical analyzer. Monochromatic Al $K\alpha$ X-ray (1486.6 eV) at 220 W (22 mA and 10

kV) was used as incident radiation. The pass energies were set at 100 and 50 eV for the survey (wide) and high-resolution scans, respectively. Survey scans were accomplished at 1 eV step size and 10 ms dwell time, whereas high-resolution scans were obtained over a 20 eV binding energy range with a 0.05 eV step size and 100 ms dwell time. The base pressure in the analysis chamber was set to $<8.0 \times 10^{-9}$ mbar and a low-energy flood gun was used to compensate for surface charging effects. CasaXPS software was used to process the data, and calibration was performed based on the C 1s peak reference at 285.0 eV for energy calibration.

Raman Spectroscopy

Raman spectroscopy analysis was performed on a Renishaw system (inVia Qonto) equipped with a Peltier-cooled CCD detector and coupled to an Olympus BH-2 confocal microscope. A near-infrared diode laser with a 532 nm wavelength was used as the excitation source. Laser power at the sample was set to 0.01 mW with 1 s step time and 10 min dwell time. The spectra were recorded over a range of 500–1800 cm^{-1} with a spectral resolution of 1 cm^{-1} using a 50 $\times$ microscope objective. For sample preparation, the samples were placed on a quartz microscope slide. The collected raw spectra were smoothed using a Savitzky–Golay smoothing filter.

Scanning Electron Microscopy (SEM)

The morphology of the urea@MPN samples was studied by SEM (Hitachi FlexSEM 1000) using the secondary electron detector and an accelerating voltage of 20 kV. The surface of the samples was coated with 10-nm gold using an ionization chamber sputter coater (Quorum K575X) before SEM imaging. For each specimen prepared, three samples were randomly chosen for imaging.

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy

ATR-FTIR spectra were collected using a Bruker TENSOR II system in the range of 400–4000 cm^{-1} ; a total of 64 scans were measured per run.

X-ray diffraction (XRD)

XRD spectra were collected on a Bruker D8 Advance X-ray diffractometer equipped with Ni-filtered Cu K α radiation (1.54 Å, 40 mA, and 40 kV); a step size of 0.02 was used.

Compression test

The mechanical properties of the samples were evaluated using compression with a 2 kN load cell in a 5848 Microtester from Instron (Norwood, MA, United States). Compression was executed at 0.0166 mm/s. Recording started after 0.01 N preload was exceeded.

Differential scanning calorimetry (DSC)

DSC analysis was carried out with a PerkinElmer Pyris-1 DSC instrument. P1 was first heated from 20 to 150 °C at a heating rate of 20 °C·min⁻¹, then cooled to 20 °C at a cooling rate of 20 °C·min⁻¹, and P2 was heated from 20 to 150 °C at a heating rate of 20 °C·min⁻¹, then cooled to 20 °C at a cooling rate of 20 °C·min⁻¹.

Thermogravimetric Analysis (TGA)

TGA was performed using a NETZSCH TG 209 F1 Libra analyzer and coupled to a Fourier transform infrared module (ALPHA, Bruker). The samples were heated in the range of 50–600 °C at a heating rate of 10 °C min⁻¹ under an O₂/N₂ (80/20 %) stream at a gas flow rate of 20 mL min⁻¹.

Optical Tensiometry

Water contact angles (WCAs) of the sample surfaces were determined using a Theta optical tensiometer (ATA Scientific, Australia), with a droplet of distilled water at room temperature.

Micro-Computed Tomography (Micro-CT)

Micro-CT scanning was performed with a Phoenix Nanotom M nano-CT 3D scanner (Waygate Technologies) running on the xs control and Phoenix datos|x acquisition software (Waygate Technologies). The samples were placed in 2 mL-plastic vials for micro-CT scanning and bringing the samples in close proximity to the X-ray source. The samples obtained after aging and heating treatments were scanned at a resolution of 7.0 μm using an energy of 60 kV. A

current of 300 μ A and a tungsten target were used to run the instrument in fast-scan mode. A total of 1200 X-ray projections were collected through a 360° rotation of the samples over the course of a 10 min scan (no averaging or skipped images and an integration time of 500 ms). Volume reconstruction of the micro-CT data was carried out using Phoenix datos|x reconstruction software (Waygate Technologies) applying a median filter and a region of interest filter during reconstruction. The data were exported as 16-bit volume files for analysis using the Avizo (Thermo Fisher Scientific) software suite. Samples were segmented using the interactive threshold tool of Avizo to create a binary image of urea@MPN (intermediate gray phase), and pore space within the sample (dark gray to black phase). The volume fraction of each phase was then determined by comparing the binary images of each phase to a sample mask using the Volume Fraction tool in Avizo.

Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX)

TEM and EDX mapping were accomplished on a JEOL 2100f instrument with a 200 kV acceleration voltage, coupled with oxford X-Maxn 5 80T EDS detector Gatan OneView 4k camera. For the preparation, the samples were first dispersed in acetonitrile (0.05wt.% solution), then a single droplet was dropped onto the formvar carbon-coated copper TEM grid and then dried overnight at room temperature in a vacuumed desiccator.

UV–vis Spectroscopy

The urea concentration in the soil studies was analyzed on an Agilent Cary 300 UV–vis spectrophotometer equipped with a diode array detector.

General Instrumentation

Mass measurements were performed using a highly accurate (± 10 μ g) analytical balance (Mettler Toledo XS205). A high-speed vibration machine (TissueLaser II, 300 W motor power) was used for grinding the precursors. The samples were placed in a 4.5 cm (diameter) by 5.5 cm (height) screw-capped stainless-steel jar along with one stainless steel ball bearings (1.5 cm

diameter). An incubator (Thermoline Scientific, TLM-590) was used for the soil studies. The Smart Mist Top™ Connect Humidifier (Breville, Australia) was used for adjusting the relative humidity of the incubator. RH values of the incubator were remotely monitored via humidity gauge (ThermoPro 260FT with $\pm 2\%$ RH accuracy). A peristaltic pump (Gilson, Miniplus evolution) was used for the water absorption capacity of the soil studies.

Software

TEM image analysis was carried out using the Gatan Microscopy Suite 1.8.4. software; then the acquired d-space lattices of urea crystals from Gatan were identified and matched with the database through Vesta software (V. 3.5.7). ChemDraw and Chem3D software (v. 21.0.0) were used to draw the molecular structure of components. The schematic illustrations were created using Biorender online platform and the open access Blender software.

CHAPTER 5

Conclusion and outlooks

This chapter summarizes the research findings of this thesis and discusses their significance for the synthesis of controlled-release urea using metal-phenolic networks. Recommendations for ongoing research are also discussed.

This Page Intentionally Left Blank

5.1 Thesis summary

By reducing the rate at which fertiliser is released into the soil, controlled-release fertilisers (especially urea) show promise for improving fertiliser effectiveness and reducing greenhouse gas emissions like CO₂, NH₃, and NO_x. Although polymer-based controlled-release fertilisers have been widely used to reduce the rate of fertiliser release, their inability to biodegrade and the high cost of the technology provide substantial obstacles to the wide adoption of CRFs for a variety of crops. Thus, this thesis proposed a novel approach through the utilization of environmentally friendly materials to fabricate the controlled-release urea. This section begins by providing an overview of the research methodology, then list the major findings, and last gives a brief summary of each chapter. We then end with a list of recommendations for future work.

This thesis has demonstrated that metal-phenolic networks represent a viable technology for controlling the dissolution of urea, a commonly used nitrogen-rich fertilizer. Through a series of laboratory-based assessments, it was shown that urea (either in granular or grinded forms) can be encapsulated by the metal-phenolic networks in non-aqueous media or solvent-free conditions. Through this, the overarching objective of this thesis - determining whether metal-phenolic networks can prolong the dissolution of urea in either water or soil systems - has been answered in the affirmative. However, an understanding of the mechanism of metal-phenolic networks formation in the presence of urea in either non-aqueous media or solvent-free conditions is key when attempting to coat urea, and is required for effective utilization of metal-phenolic networks coated urea as controlled-release urea. Therefore, *Chapters 3 and 4* assessed the efficacy of various parameters involved in the formation of metal-phenolic networks; the complex coordination of tannic acid as a naturally abundant phenolic ligand with different metal ions was considered.

In *Chapter 3*, a versatile approach was reported to engineer thickness-tunable coatings of metal-phenolic networks (2-25 μm) on urea granules through the self-assembly technique in acetonitrile. It was shown that the coordination assembly of metal-phenolic networks is distinct from that in aqueous media due to the differences in the pKa of the solvent and the role of acetonitrile as a ligand in the coordination of metal-phenolic complexes. These differences change the kinetics of coating formation, which subsequently impacts the physicochemical properties of the coating. Furthermore, the variables involved in the kinetics of metal-phenolic networks assembly, including metal-phenolic network self-assembly method, solution aging time, metal-to-ligand molar ratio, deposition cycle, precursor concentration, and processing temperature changed the thickness and surface roughness of the films, which consequently changed the release profile of urea. Among the parameters able to be varied, the processing temperature and the deposition cycle of metal-phenolic network coatings showed a significant impact on the release rate of urea in water. It was demonstrated that the coated urea can successfully prolong the release period of urea from 30 min, considering the uncoated urea, to up to 300 mins depending on the type of coating treatment applied. In conclusion, the strong interfacial interaction between urea granules and metal-phenolic networks enables the establishment of robust coatings. The porous nature of the metal-phenolic building blocks, however, made it simple for water to permeate the coating, which led to a rapid release of urea from the CRU.

In *Chapter 4*, to aid scalability and ultimate deployment of controlled-release urea fabricated by metal-phenolic network coating, the mechanochemical grinding method was applied. Through this, a versatile solid-state assembly of metal-phenolic networks was developed in the absence of solvent in which urea first mediated the complex formation followed by encapsulation of the grinded urea. The mechanical resistance, crystallinity, stiffness, and wettability properties of encapsulated urea were adjusted with aging and thermal treatments.

Aging and thermal treatments induced a considerable increase in the metal-phenolic complexation and resulted in a significant interaction between urea and metal-phenolic species. It is hypothesized that grinding urea into very small particles (<5 nm) provides a great surface area for the metal-phenolic coating, which successfully slowed the dissolution rate of urea in soil, such that the release of urea could be prolonged for up to 9 days, depending on the type of treatment applied. The water-holding capability of encapsulated urea within metal-phenolic networks suggests that the developed materials can increase the water-holding capacity of soil, which is a critical parameter to reduce the irrigation frequency and decrease the death rate of plants in arid and semi-arid areas. To sum up, a solvent-free production of controlled-release urea using metal-phenolic networks provides promising results for the large-scale fabrication of controlled-release fertilizers, where a minor change in the type of ligand and metal can significantly tune the physicochemical properties of the materials.

Finally, the new development in our understanding and knowledge of metal-phenolic networks fabrication for controlled-release urea can be directly applied to the development and design of a wide range of controlled-release fertilizers with some modifications.

5.2 Recommendations for future work

Although the studies undertaken in this thesis have begun to address the research objectives initially established, a number of interesting research questions have arisen that should drive the direction of future research. They are outlined as follows:

- In accordance with Chapter 3, it was shown that metal-phenolic networks could be formed in acetonitrile via precomplex assembly. Although different parameters involved in the coordination were investigated, using other phenolic compounds were not. Based on findings in the literature, it is expected that changing the polarity, hydrophobicity and the size of polyphenols can change the pore size of metal-phenolic

networks, which can consequently change the release profile of urea. Furthermore, changing the viscosity of the system through using solvents with different viscosities can alter the kinetic of the metal-ligand complex formation. These changes can end up changing the porosity of the coating which is crucial for water diffusion. Thus, it would be ideal to pursue this aspect in future work.

- With further regard to microbiome processes, previous studies have shown that the release rate of urea from coated urea can be accelerated due to the degradation of the coating over time. Although the developed materials have shown promising results when applied, microbiome activity has not yet been considered. With this in mind, it would be beneficial to gain an understanding of how the microbiome activities affect the performance of coatings.
- The rapid hydrolysis of urea, catalyzed by urease enzymes, leads to potential ammonia volatilization and subsequent nitrification-denitrification. Phenols have been shown to be effective as urease inhibitors. Therefore, it is recommended that a full assessment of urea conversion to ammonia, ammonium, nitrite, and nitrate through hydrolysis and nitrification processes be conducted using the developed materials. Similarly, changing metals, such as Zn, incorporated into the metal-phenolic networks can potentially influence urea conversion, and this should also be investigated.
- Chapter 4 demonstrated that when applying the encapsulated urea to soil, the water-holding capacity of soil could be improved. It is recommended that future work assess how material swelling can be controlled and potentially increased.
- Lastly, the release of urea and the urea hydrolysis can be changed when the developed controlled-release urea is applied in different soils with different properties, such as texture, pH, and microbiome activities of soils are varied. Thus, it would be useful to

investigate the efficacy of the developed materials on different soils and crops in field trials.

References

1. Lam, S.K., et al., Next-generation enhanced-efficiency fertilizers for sustained food security, *Nature Food*, 2022, **3**, 575-580.
2. Jariwala, H., et al., Controlled release fertilizers (CRFs) for climate-smart agriculture practices: a comprehensive review on release mechanism, materials, methods of preparation, and effect on environmental parameters, *Environmental Science and Pollution Research*, 2022, **22**, 53967–53995
3. Lawrencica, D., et al., Controlled Release Fertilizers: A Review on Coating Materials and Mechanism of Release, *Plants*, 2021, **10**, 238.
4. Beig, B., et al., Coating materials for slow release of nitrogen from urea fertilizer: a review, *Journal of Plant Nutrition*, 2020, **43**, 1510-1533.
5. Hristov, A.N., et al., Review: Ammonia emissions from dairy farms and beef feedlots, *Canadian Journal of Animal Science*, 2011, **91**, 1-35.
6. Naz, M.Y., et al., Slow release coating remedy for nitrogen loss from conventional urea: a review, *Journal of Controlled Release*, 2016, **225**, 109-120.
7. Lu, H., et al., Improvement of bio-based polyurethane and its optimal application in controlled release fertilizer, *Journal of Controlled Release*, 2022, **350**, 748-760.
8. Pang, L., et al., Cellulose based materials for controlled release formulations of agrochemicals: A review of modifications and applications, *Journal of Controlled Release*, 2019, **316**, 105-115.
9. Zhou, J., et al., Polyphenol-Mediated Assembly for Particle Engineering, *Accounts of Chemical Research*, 2020, **53**, 1269-1278.
10. Shaviv, A., Advances in controlled-release fertilizers, *Advances in Agronomy*, 2001, **71**, 1-49.
11. Azeem, B., et al., Review on materials & methods to produce controlled release coated urea fertilizer, *Journal of Controlled Release*, 2014, **181**, 11-21.
12. Fu, J., et al., Classification research and types of slow controlled release fertilizers (SRFs) used-a review, *Communications in Soil Science and plant Analysis*, 2018, **49**, 2219-2230.
13. Ramli, R.A., Slow release fertilizer hydrogels: a review, *Polymer Chemistry*, 2019, **10**, 6073-6090.
14. Xiang, Y., et al., Granular, slow-release fertilizer from urea-formaldehyde, ammonium polyphosphate, and amorphous silica gel: a new strategy using cold extrusion, *Journal of Agricultural and Food Chemistry*, 2018, **66**, 7606-7615.
15. Lam, S.K., et al., Using urease and nitrification inhibitors to decrease ammonia and nitrous oxide emissions and improve productivity in a subtropical pasture, *Science of the Total Environment*, 2018, **644**, 1531-1535.
16. Kafarski, P., et al., Recent advances in design of new urease inhibitors: A review, *Journal of Advanced Research*, 2018, **13**, 101-112.
17. Maris, S.C., et al., Effect of irrigation, nitrogen application, and a nitrification inhibitor on nitrous oxide, carbon dioxide and methane emissions from an olive (*Olea europaea* L.) orchard, *Science of the Total Environment*, 2015, **538**, 966-978.
18. Blouin, G.M., et al., *Method of making sulfur-coated fertilizer pellet having a controlled dissolution rate*. 1967, US Patent.
19. Blouin, G.M., et al., Sulfur-coated fertilizers for controlled release. Pilot-plant production, *Journal of Agricultural and Food Chemistry*, 1971, **19**, 801-808.
20. Tsai, B.S., *Continuous spouted bed process for sulphur-coating urea*. 1986, University of British Columbia.

21. Detrick, J.H., *Process for producing improved sulfur-coated urea slow release fertilizers*. 1997, US Patent.
22. Detrick, J.H., et al., *Polymer-sulfur-polymer coated fertilizers*. 2002, US Patent.
23. Mann, M., et al., Sulfur polymer composites as controlled-release fertilisers, *Organic & Biomolecular Chemistry*, 2019, **17**, 1929-1936.
24. Rindt, D., et al., Sulfur coating on nitrogen fertilizer to reduce dissolution rate, *Journal of Agricultural and Food Chemistry*, 1968, **16**, 773-778.
25. Liu, L., et al., *A review: controlled release systems for agricultural and food applications*. 2008, ACS Symposium Series.
26. Pereira, E.I., et al., Urea–montmorillonite-extruded nanocomposites: a novel slow-release material, *Journal of Agricultural and Food Chemistry*, 2012, **60**, 5267-5272.
27. Ni, B., et al., Novel multinutrient fertilizer and its effect on slow release, water holding, and soil amending, *Industrial and Engineering Chemistry Research*, 2012, **51**, 12993-13000.
28. Tomaszewska, M., et al., Use of Polysulfone in Controlled-Release NPK Fertilizer Formulations, *Journal of Agricultural and Food Chemistry*, 2002, **50**, 4634-4639.
29. Markusch, P.H., et al., *Polyurethane encapsulated fertilizer having improved slow-release properties*. 2002, US Patent.
30. Rosenthal, E., et al., *Polyurethane encapsulated fertilizer*. 2007, US Patent.
31. Cong, Z., et al., Evaluation of Waterborne Coating for Controlled-Release Fertilizer Using Wurster Fluidized Bed, *Industrial & Engineering Chemistry Research*, 2010, **49**, 9644-9647.
32. Al-Zahrani, S.M., Utilization of Polyethylene and Paraffin Waxes as Controlled Delivery Systems for Different Fertilizers, *Industrial & Engineering Chemistry Research*, 2000, **39**, 367-371.
33. Salman, O.A., Polyethylene-coated urea. 1. Improved storage and handling properties, *Industrial & Engineering Chemistry Research*, 1989, **28**, 630-632.
34. Salman, O.A., et al., Polyethylene-coated urea. 2. Urea release as affected by coating material, soil type and temperature, *Industrial & Engineering Chemistry Research*, 1989, **28**, 633-638.
35. Abraham, J., et al., Membrane-encapsulated controlled-release urea fertilizers based on acrylamide copolymers, *Journal of Applied Polymer Science*, 1996, **60**, 2347-2351.
36. Kosuge, N., et al., *Coated granular fertilizer*. 1992, US Patent.
37. Zvomuya, F., et al., Nitrate Leaching and Nitrogen Recovery Following Application of Polyolefin-Coated Urea to Potato, *Journal of Environmental Quality*, 2003, **32**, 480-489.
38. Chen, D., et al., Evaluation of a polyolefin coated urea (Meister) as a fertilizer for irrigated cotton, *Nutrient Cycling in Agroecosystems*, 2008, **81**, 245-254.
39. Pipko, G., et al., *Method for the manufacture of slow release fertilizers*. 1990, US Patent.
40. Donida, M.W., et al., Coating of urea with an aqueous polymeric suspension in a two-dimensional spouted bed, *Drying Technology*, 2002, **20**, 685-704.
41. Mathews, A.S., et al., Poly[N-isopropyl acrylamide]-co-polyurethane copolymers for controlled release of urea, *Journal of Polymer Science Part A: Polymer Chemistry*, 2010, **48**, 3236-3243.
42. Li, Q., et al., Synthesis and performance of polyurethane coated urea as slow/controlled release fertilizer, *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, 2012, **27**, 126-129.

43. Lubkowski, K., et al., Controlled-Release Fertilizer Prepared Using a Biodegradable Aliphatic Copolyester of Poly(butylene succinate) and Dimerized Fatty Acid, *Journal of Agricultural and Food Chemistry*, 2015, **63**, 2597-2605.
44. Baldanza, V.A.R., et al., Controlled-release fertilizer based on poly(butylene succinate)/urea/clay and its effect on lettuce growth, *Journal of Applied Polymer Science*, 2018, **135**, 46858.
45. Feng, C., et al., "Smart" Fertilizer with Temperature- and pH-Responsive Behavior via Surface-Initiated Polymerization for Controlled Release of Nutrients, *ACS Sustainable Chemistry & Engineering*, 2015, **3**, 3157-3166.
46. Ma, Z., et al., Mussel-Inspired Thermosensitive Polydopamine-graft-Poly(N-isopropylacrylamide) Coating for Controlled-Release Fertilizer, *Journal of Agricultural and Food Chemistry*, 2013, **61**, 12232-12237.
47. Lu, P., et al., Use of polyurea from urea for coating of urea granules, *SpringerPlus*, 2016, **5**, 457.
48. Emami, N., et al., Fabrication of smart magnetic nanocomposite asymmetric membrane capsules for the controlled release of nitrate, *Environmental Nanotechnology, Monitoring & Management*, 2017, **8**, 233-243.
49. Boyandin, A.N., et al., Constructing Slow-Release Formulations of Ammonium Nitrate Fertilizer Based on Degradable Poly(3-hydroxybutyrate), *Journal of Agricultural and Food Chemistry*, 2017, **65**, 6745-6752.
50. Chanprateep, S., Current trends in biodegradable polyhydroxyalkanoates, *Journal of Bioscience and Bioengineering*, 2010, **110**, 621-632.
51. Schmücker, C., et al., Liquid marble formation and solvent vapor treatment of the biodegradable polymers polylactic acid and polycaprolactone, *Journal of Colloid and Interface Science*, 2018, **514**, 349-356.
52. Shen, Y., et al., Application of Nano FeIII–Tannic Acid Complexes in Modifying Aqueous Acrylic Latex for Controlled-Release Coated Urea, *Journal of Agricultural and Food Chemistry*, 2017, **65**, 1030-1036.
53. Shen, Y., et al., Application of waterborne acrylic emulsions in coated controlled release fertilizer using reacted layer technology, *Chinese Journal of Chemical Engineering*, 2015, **23**, 309-314.
54. Shen, Y., et al., Aqueous polyacrylate/poly(silicone-co-acrylate) emulsion coated fertilizers for slow nutrient-release application, *Journal of Applied Polymer Science*, 2014, **131**.
55. Shen, Y., et al., The Facile Modification of Polyacrylate Emulsion via Hexadecane to Enhance Controlled-release Profiles of Coated Urea, *Scientific Reports*, 2018, **8**, 12279.
56. Zhou, Z., et al., Thermal post-treatment alters nutrient release from a controlled-release fertilizer coated with a waterborne polymer, *Scientific Reports*, 2015, **5**, 13820.
57. Dashtizadeh, A., et al., Acrylic coatings exhibiting improved hardness, solvent resistance and glossiness by using silica nano-composites, *Applied Surface Science*, 2011, **257**, 2118-2125.
58. Zhang, B., et al., A novel approach for the preparation of organic-siloxane oligomers and the creation of hydrophobic surface, *Applied Surface Science*, 2007, **254**, 452-458.
59. Xiang, Y., et al., Preparation and Properties of a Novel Semi-IPN Slow-Release Fertilizer with the Function of Water Retention, *Journal of Agricultural and Food Chemistry*, 2017, **65**, 10851-10858.

60. Lligadas, G., et al., Renewable polymeric materials from vegetable oils: a perspective, *Materials Today*, 2013, **16**, 337-343.
61. Yang, Y.C., et al., Improving the Quality of Polymer-Coated Urea with Recycled Plastic, Proper Additives, and Large Tablets, *Journal of Agricultural and Food Chemistry*, 2012, **60**, 11229-11237.
62. Zhang, S., et al., One-step synthesis of superhydrophobic and multifunctional nano copper-modified bio-polyurethane for controlled-release fertilizers with “multilayer air shields”: new insight of improvement mechanism, *Journal of Materials Chemistry A*, 2019, **7**, 9503-9509.
63. Liang, D., et al., Tunable thermo-physical performance of castor oil-based polyurethanes with tailored release of coated fertilizers, *Journal of Cleaner Production*, 2019, **210**, 1207-1215.
64. Liu, X., et al., Environmentally Friendly Slow-Release Urea Fertilizers Based on Waste Frying Oil for Sustained Nutrient Release, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 6036-6045.
65. Feng, G.d., et al., Polyurethane-coated urea using fully vegetable oil-based polyols: Design, nutrient release and degradation, *Progress in Organic Coatings*, 2019, **133**, 267-275.
66. Xie, J., et al., Biomimetic Superhydrophobic Biobased Polyurethane-Coated Fertilizer with Atmosphere “Outerwear”, *ACS Applied Materials & Interfaces*, 2017, **9**, 15868-15879.
67. Zhang, S., et al., Superhydrophobic controlled-release fertilizers coated with bio-based polymers with organosilicon and nano-silica modifications, *Journal of Materials Chemistry A*, 2017, **5**, 19943-19953.
68. Tian, H., et al., Biobased Polyurethane, Epoxy Resin, and Polyolefin Wax Composite Coating for Controlled-Release Fertilizer, *ACS Appl. Mater. Interfaces*, 2019, **11**, 5380-5392.
69. Ma, X., et al., Siloxane and polyether dual modification improves hydrophobicity and interpenetrating polymer network of bio-polymer for coated fertilizers with enhanced slow release characteristics, *Chemical Engineering Journal*, 2018, **350**, 1125-1134.
70. Liang, R., et al., Preparation of poly(acrylic acid-co-acrylamide)/kaolin and release kinetics of urea from it, *Journal of Applied Polymer Science*, 2007, **106**, 3007-3015.
71. Cheng, D., et al., Water- and Fertilizer-Integrated Hydrogel Derived from the Polymerization of Acrylic Acid and Urea as a Slow-Release N Fertilizer and Water Retention in Agriculture, *Journal of Agricultural and Food Chemistry*, 2018, **66**, 5762-5769.
72. Erceg, T., et al., The properties of conventionally and microwave synthesized poly(acrylamide-co-acrylic acid) hydrogels, *Polymer Bulletin*, 2019, **77**, 2089–2110.
73. Helaly, F.M., et al., Slow Release of Urea as a Source of Nitrogen from Some Acrylamide and Acrylic Acid Hydrogels, *Polymer-Plastics Technology and Engineering*, 2005, **44**, 253-263.
74. Tyliszczak, B., et al., Preparation and Properties of Biodegradable Slow-Release PAA Superabsorbent Matrixes for Phosphorus Fertilizers, 2009, **279**, 236-242.
75. Liu, M., et al., Preparation of superabsorbent slow release nitrogen fertilizer by inverse suspension polymerization, *Polymer International*, 2007, **56**, 729-737.
76. Pereira, E.I., et al., Novel Slow-Release Nanocomposite Nitrogen Fertilizers: The Impact of Polymers on Nanocomposite Properties and Function, *Industrial & Engineering Chemistry Research*, 2015, **54**, 3717-3725.

77. Calabria, L., et al., Soy protein isolate/poly(lactic acid) injection-molded biodegradable blends for slow release of fertilizers, *Industrial Crops and Products*, 2012, **36**, 41-46.
78. Wang, Y., et al., κ -Carrageenan–Sodium Alginate Beads and Superabsorbent Coated Nitrogen Fertilizer with Slow-Release, Water-Retention, and Anticompaction Properties, *Industrial & Engineering Chemistry Research*, 2012, **51**, 1413-1422.
79. Wen, P., et al., Microwave-Assisted Synthesis of a Semi-interpenetrating Polymer Network Slow-Release Nitrogen Fertilizer with Water Absorbency from Cotton Stalks, *ACS Sustainable Chemistry & Engineering*, 2016, **4**, 6572-6579.
80. Wen, P., et al., Microwave-Assisted Synthesis of a Novel Biochar-Based Slow-Release Nitrogen Fertilizer with Enhanced Water-Retention Capacity, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 7374-7382.
81. Bortolin, A., et al., Nanocomposite PAAm/Methyl Cellulose/Montmorillonite Hydrogel: Evidence of Synergistic Effects for the Slow Release of Fertilizers, *Journal of Agricultural and Food Chemistry*, 2013, **61**, 7431-7439.
82. Senna, A.M., et al., Synthesis, characterization and application of hydrogel derived from cellulose acetate as a substrate for slow-release NPK fertilizer and water retention in soil, *Journal of Environmental Chemical Engineering*, 2015, **3**, 996-1002.
83. Senna, A.M., et al., Biodegradable hydrogel derived from cellulose acetate and EDTA as a reduction substrate of leaching NPK compound fertilizer and water retention in soil, *Journal of Controlled Release*, 2017, **260**, 194-201.
84. Huang, A., et al., Solid-phase synthesis of cellulose acetate butyrate as microsphere wall materials for sustained release of emamectin benzoate, *Polymer*, 2018, **10**, 1381.
85. Martin, A.I., et al., Synthesis, characterization and controlled release behaviour of adducts from chloroacetylated cellulose and α -naphthylacetic acid, *Reactive and Functional Polymers*, 1999, **39**, 179-187.
86. Shang, Y., et al., Adsorption of phosphate by the cellulose-based biomaterial and its sustained release of laden phosphate in aqueous solution and soil, *International Journal of Biological Macromolecules*, 2018, **109**, 524-534.
87. Romi, R., et al., Bioengineering of a Cellulosic Fabric for Insecticide Delivery via Grafted Cyclodextrin, *Biotechnology Progress*, 2005, **21**, 1724-1730.
88. Pang, L., et al., Preparation of pH-responsive cellulose derivative with surfactant-property for methyl 1-Naphthylacetate controlled release, *Industrial Crops and Products*, 2019, **135**, 57-63.
89. Wen, P., et al., Microwave-assisted one-step synthesis and characterization of a slow release nitrogen fertilizer with inorganic and organic composites, *Rsc advances*, 2016, **6**, 37337-37346.
90. Mahfoudhi, N., et al., Poly (acrylic acid-co-acrylamide)/cellulose nanofibrils nanocomposite hydrogels: effects of CNFs content on the hydrogel properties, *Cellulose*, 2016, **23**, 3691-3701.
91. Olad, A., et al., Superabsorbent nanocomposite based on maize bran with integration of water-retaining and slow-release NPK fertilizer, *Advances in Polymer Technology*, 2018, **37**, 1682-1694.
92. Rop, K., et al., Formulation of slow release NPK fertilizer (cellulose-graft-poly(acrylamide)/nano-hydroxyapatite/soluble fertilizer) composite and evaluating its N mineralization potential, *Annals of Agricultural Sciences*, 2018, **63**, 163-172.
93. Guo, M., et al., Preparation and properties of a slow release NP compound fertilizer with superabsorbent and moisture preservation, *Journal of Applied Polymer Science*, 2005, **96**, 2132-2138.

94. Teodorescu, M., et al., Preparation and Properties of Novel Slow-Release NPK Agrochemical Formulations Based on Poly(acrylic acid) Hydrogels and Liquid Fertilizers, *Industrial & Engineering Chemistry Research*, 2009, **48**, 6527-6534.
95. Rolston, D.E., Introduction to Environmental Soil Physics, *Soil Science*, 2005, **170**, 1051-1052.
96. Liang, R., et al., Synthesis of wheat straw-g-poly(acrylic acid) superabsorbent composites and release of urea from it, *Carbohydrate Polymers*, 2009, **77**, 181-187.
97. Wu, F., et al., Synthesis and characterization of a novel cellulose-g-poly(acrylic acid-co-acrylamide) superabsorbent composite based on flax yarn waste, *Carbohydrate Polymers*, 2012, **87**, 2519-2525.
98. Abd El-Rehim, H.A., et al., Effect of various environmental conditions on the swelling property of PAAm/PAAcK superabsorbent hydrogel prepared by ionizing radiation, *Journal of Applied Polymer Science*, 2006, **101**, 3955-3962.
99. Ward, J.H., et al., Preparation of controlled release systems by free-radical UV polymerizations in the presence of a drug, *Journal of Controlled Release*, 2001, **71**, 183-192.
100. Guo, et al., Preparation and Properties of a Slow-Release Membrane-Encapsulated Urea Fertilizer with Superabsorbent and Moisture Preservation, *Industrial & Engineering Chemistry Research*, 2005, **44**, 4206-4211.
101. Liang, R., et al., Controlled release NPK compound fertilizer with the function of water retention, *Reactive and Functional Polymers*, 2007, **67**, 769-779.
102. Wu, L., et al., Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention, *Carbohydrate Polymers*, 2008, **72**, 240-247.
103. *Controlled Release Fertilizer solution for different segments*. Available from: <https://www.haifa-group.com/articles/controlled-release-fertilizer-solution-different-segments>.
104. Xie, L., et al., Utilization of Wheat Straw for the Preparation of Coated Controlled-Release Fertilizer with the Function of Water Retention, *Journal of Agricultural and Food Chemistry*, 2012, **60**, 6921-6928.
105. Essawy, H.A., et al., Superabsorbent hydrogels via graft polymerization of acrylic acid from chitosan-cellulose hybrid and their potential in controlled release of soil nutrients, *International Journal of Biological Macromolecules*, 2016, **89**, 144-151.
106. Calcagnile, P., et al., Biodegradable poly(lactic acid)/cellulose-based superabsorbent hydrogel composite material as water and fertilizer reservoir in agricultural applications, *Journal of Applied Polymer Science*, 2019, **136**, 47546.
107. Ejima, H., et al., One-Step Assembly of Coordination Complexes for Versatile Film and Particle Engineering, *Science*, 2013, **341**, 154.
108. Yun, G., et al., Self-Assembly of Nano- to Macroscopic Metal–Phenolic Materials, *Chemistry of Materials*, 2018, **30**, 5750-5758.
109. Geng, H., et al., Metal Ion-Directed Functional Metal–Phenolic Materials, *Chemical Reviews*, 2022, **122**, 11432-11473.
110. Guo, J., et al., Modular Assembly of Biomaterials Using Polyphenols as Building Blocks, *ACS Biomaterials Science & Engineering*, 2019, **5**, 5578-5596.
111. Naus, P.J., et al., Tannic acid synergizes the cytotoxicity of chemotherapeutic drugs in human cholangiocarcinoma by modulating drug efflux pathways, *Journal of hepatology*, 2007, **46**, 222-229.
112. Guo, J., et al., Engineering Multifunctional Capsules through the Assembly of Metal–Phenolic Networks, *Angewandte Chemie International Edition*, 2014, **53**, 5546-5551.

113. Rahim, M.A., et al., Coordination-Driven Multistep Assembly of Metal–Polyphenol Films and Capsules, *Chemistry of Materials*, 2014, **26**, 1645-1653.
114. Yun, G., et al., Self-Assembly of Nano- to Macroscopic Metal–Phenolic Materials, *Chemistry of Materials*, 2018, **30**, 5750-5758.
115. Guo, J., et al., Influence of Ionic Strength on the Deposition of Metal–Phenolic Networks, *Langmuir*, 2017, **33**, 10616-10622.
116. Chen, J., et al., Metal–Phenolic Networks as Tunable Buffering Systems, *Chemistry of Materials*, 2021, **33**, 2557-2566.
117. Cherepanov, P.V., et al., Electrochemical Behavior and Redox-Dependent Disassembly of Gallic Acid/FeIII Metal–Phenolic Networks, *ACS Applied Materials & Interfaces*, 2018, **10**, 5828-5834.
118. Maerten, C., et al., Electrotriggered Confined Self-assembly of Metal–Polyphenol Nanocoatings Using a Morphogenic Approach, *Chemistry of Materials*, 2017, **29**, 9668-9679.
119. Rahim, M.A., et al., Rust-Mediated Continuous Assembly of Metal–Phenolic Networks, *Advanced Materials*, 2017, **29**, 1606717.
120. Rahim, M.A., et al., Multiligand Metal–Phenolic Assembly from Green Tea Infusions, *ACS Applied Materials & Interfaces*, 2018, **10**, 7632-7639.
121. Zhong, Q.-Z., et al., Oxidation-Mediated Kinetic Strategies for Engineering Metal–Phenolic Networks, *Angewandte Chemie International Edition*, 2019, **58**, 12563-12568.
122. Lee, H., et al., Iron Gall Ink Revisited: In Situ Oxidation of Fe(II)–Tannin Complex for Fluidic-Interface Engineering, *Advanced Materials*, 2018, **30**, 1805091.
123. Kim, B.J., et al., Biphasic Supramolecular Self-Assembly of Ferric Ions and Tannic Acid across Interfaces for Nanofilm Formation, *Advanced Materials*, 2017, **29**, 1700784.
124. Besford, Q.A., et al., Self-Assembled Metal–Phenolic Networks on Emulsions as Low-Fouling and pH-Responsive Particles, *Small*, 2018, **14**, 1802342.
125. Mkam Tsengam, I.K., et al., Clusters of Nanoscale Liposomes Modulate the Release of Encapsulated Species and Mimic the Compartmentalization Intrinsic in Cell Structures, *ACS Applied Nano Materials*, 2019, **2**, 7134-7143.
126. Yang, B., et al., Super-assembled core-shell mesoporous silica-metal-phenolic network nanoparticles for combinatorial photothermal therapy and chemotherapy, *Nano Research*, 2020, **13**, 1013-1019.
127. Yun, G., et al., The Biomolecular Corona in 2D and Reverse: Patterning Metal–Phenolic Networks on Proteins, Lipids, Nucleic Acids, Polysaccharides, and Fingerprints, *Advanced Functional Materials*, 2020, **30**, 1905805.
128. Yun, G., et al., Synthesis of Metal Nanoparticles in Metal-Phenolic Networks: Catalytic and Antimicrobial Applications of Coated Textiles, *Advanced Healthcare Materials*, 2018, **7**, 1700934.
129. Lin, G., et al., Programmable Phototaxis of Metal-Phenolic Particle Microswimmers, *Advanced Materials*, 2021, **33**, 2006177.
130. Rahim, M.A., et al., Metal–Phenolic Supramolecular Gelation, *Angewandte Chemie International Edition*, 2016, **55**, 13803-13807.
131. Zhou, X., et al., Metal–Phenolic Network-Encapsulated Nanovaccine with pH and Reduction Dual Responsiveness for Enhanced Cancer Immunotherapy, *Molecular Pharmaceutics*, 2020, **17**, 4603-4615.
132. Li, K., et al., Targeted Therapy against Metastatic Melanoma Based on Self-Assembled Metal-Phenolic Nanocomplexes Comprised of Green Tea Catechin, *Advanced Science*, 2019, **6**, 1801688.

133. Oh, J.Y., et al., Metal–Phenolic Carbon Nanocomposites for Robust and Flexible Energy-Storage Devices, *ChemSusChem*, 2017, **10**, 1675-1682.
134. Xiao, Z., et al., General and precise carbon confinement of functional nanostructures derived from assembled metal–phenolic networks for enhanced lithium storage, *Journal of Materials Chemistry A*, 2018, **6**, 18605-18614.
135. Park, J.H., et al., Antimicrobial spray nanocoating of supramolecular Fe(III)-tannic acid metal-organic coordination complex: applications to shoe insoles and fruits, *Scientific Reports*, 2017, **7**, 6980.
136. Dai, Q., et al., Advancing Metal–Phenolic Networks for Visual Information Storage, *ACS Applied Materials & Interfaces*, 2019, **11**, 29305-29311.
137. Wang, R., et al., Superwetting Oil/Water Separation Membrane Constructed from In Situ Assembled Metal–Phenolic Networks and Metal–Organic Frameworks, *ACS Applied Materials & Interfaces*, 2020, **12**, 10000-10008.
138. Zhong, Q.-Z., et al., Spray Assembly of Metal–Phenolic Networks: Formation, Growth, and Applications, *ACS Applied Materials & Interfaces*, 2018, **10**, 33721-33729.
139. Geng, H., et al., Interfacial Assembly of Metal–Phenolic Networks for Hair Dyeing, *ACS Applied Materials & Interfaces*, 2020, **12**, 29826-29834.
140. Yu, J., et al., Mussel protein adhesion depends on interprotein thiol-mediated redox modulation, *Nature Chemical Biology*, 2011, **7**, 588-590.
141. Wei, W., et al., Hydrophobic Enhancement of Dopa-Mediated Adhesion in a Mussel Foot Protein, *Journal of the American Chemical Society*, 2013, **135**, 377-383.
142. Burger, K., *4-Donor-Acceptor Interactions. the Donor and Acceptor Strengths of Solvents*, in *Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents*. 1983, Elsevier. p. 42-92.
143. Rach, S.F., et al., Nitrile Ligated Transition Metal Complexes with Weakly Coordinating Counteranions and Their Catalytic Applications, *Chemical Reviews*, 2009, **109**, 2061-2080.
144. Dong, Y., et al., Preparation and photocatalytic performance of Fe (III)-amidoximated PAN fiber complex for oxidative degradation of azo dye under visible light irradiation, *Science of the Total Environment*, 2010, **408**, 2245-2253.
145. Vančová, V., et al., Oxidation of triphenylphosphine in chloroiron (III) complexes, *Chemical Papers*, 1976, **30**, 86-89.
146. Loures, C.C.A., et al., Advanced Oxidative Degradation Processes: Fundamentals and Applications, *International Review of Chemical Engineering*, 2013, **5**, 102-120.
147. Agustina, E., et al., Simple and Precise Quantification of Iron Catalyst Content in Carbon Nanotubes Using UV/Visible Spectroscopy, *ChemistryOpen*, 2015, **4**, 613-619.
148. Li, Z., et al., Multilayer Deposition of Metal–Phenolic Networks for Coating of Energetic Crystals: Modulated Surface Structures and Highly Enhanced Thermal Stability, *ACS Applied Energy Materials*, 2020, **3**, 11091-11098.
149. Liu, Y., et al., Competitive Binding-Modulated Metal–Phenolic Assemblies for Adaptable Nanofilm Engineering, *Chemistry of Materials*, 2021, **33**, 4733-4744.
150. Yang, Z., et al., Metal-Phenolic Surfaces for Generating Therapeutic Nitric Oxide Gas, *Chemistry of Materials*, 2018, **30**, 5220-5226.
151. Yang, Z., et al., Construction of Polyfunctional Coatings Assisted by Gallic Acid to Facilitate Co-Immobilization of Diverse Biomolecules, *ACS Applied Materials & Interfaces*, 2013, **5**, 10495-10501.

152. Tu, Q., et al., A facile metal–phenolic–amine strategy for dual-functionalization of blood-contacting devices with antibacterial and anticoagulant properties, *Materials Chemistry Frontiers*, 2019, **3**, 265-275.
153. Ibrahim, O.B., Complexes of urea with Mn(II), Fe(III), Co(II), and Cu(II) metal ions, *Advances in Applied Science Research*, 2012, **3**, 3522-3539.
154. Megahed, A.S., et al., Structure and properties of some metal-urea complexes obtained at low temperature: Cr(III), Mn(II), Fe(III), Co(II) and Ni(II) ions, *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 2014, **5**, 960-969.
155. Jamil, Y.M.S., et al., Synthesis, Characterization and Comparative Thermal degradation study of Co(II), Ni(II) and Cu(II) complexes with Asparagine and Urea as mixed ligands, *Eclética Química Journal*, 2018, **43**, 11-24.
156. Kryatov, S.V., et al., A dinuclear iron(iii) complex with a bridging urea anion: implications for the urease mechanism, *Chemical Communications*, 2000, 921-922.
157. Rahim, M.A., et al., Surface-Confined Amorphous Films from Metal-Coordinated Simple Phenolic Ligands, *Chemistry of Materials*, 2015, **27**, 5825-5832.
158. Reyhani, A., et al., Temporal control of RAFT polymerization via magnetic catalysis, *Polymer Chemistry*, 2020, **11**, 2838-2846.
159. Alivand, M.S., et al., Catalytic Solvent Regeneration for Energy-Efficient CO₂ Capture, *ACS Sustainable Chemistry & Engineering*, 2020, **8**, 18755-18788.
160. Wu, Y., et al., Precipitating Characteristics of Potassium Bicarbonate Using Concentrated Potassium Carbonate Solvent for Carbon Dioxide Capture. Part 1. Nucleation, *Industrial & Engineering Chemistry Research*, 2017, **56**, 6764-6774.
161. Wu, Y., et al., Precipitating Characteristics of Potassium Bicarbonate Using Concentrated Potassium Carbonate Solvent for Carbon Dioxide Capture. Part 2: Crystal Growth, *Industrial & Engineering Chemistry Research*, 2017, **56**, 15131-15142.
162. Chen, J., et al., Programmable Permeability of Metal–Phenolic Network Microcapsules, *Chemistry of Materials*, 2020, **32**, 6975-6982.
163. Xu, S., et al., Characterization of slow-release collagen-g-poly(acrylic acid-co-2-acrylamido-2-methyl-1-propane sulfonic acid)–iron(III) superabsorbent polymer containing fertilizer, *Journal of Applied Polymer Science*, 2019, **136**, 47178.
164. Zheng, Z.P., et al., Terahertz and mid-infrared spectroscopy of benzene-1,2-diol, *Journal of Molecular Spectroscopy*, 2012, **281**, 13-17.
165. Xia, Z., et al., Unraveling the mechanism of thermal and thermo-oxidative degradation of tannic acid, *Thermochimica Acta*, 2015, **605**, 77-85.
166. Bortoletto Santos, R., et al., Biodegradable oil-based polymeric coatings on urea fertilizer: N release kinetic transformations of urea in soil, *Scientia Agricola*, 2020, **77**, 1-9.
167. Liu, L., et al., Sustainable and Biodegradable Copolymers from SO₂ and Renewable Eugenol: A Novel Urea Fertilizer Coating Material with Superior Slow Release Performance, *Macromolecules*, 2020, **53**, 936-945.
168. Zhang, S., et al., Self-Assembly of Hydrophobic and Self-Healing Bionanocomposite-Coated Controlled-Release Fertilizers, *ACS Applied Materials & Interfaces*, 2020, **12**, 27598-27606.
169. Jokinen, V., et al., Superhydrophobic Blood-Repellent Surfaces, *Advanced Materials*, 2018, **30**, 1705104.
170. Xie, J., et al., Magnetic-Sensitive Nanoparticle Self-Assembled Superhydrophobic Biopolymer-Coated Slow-Release Fertilizer: Fabrication, Enhanced Performance, and Mechanism, *ACS Nano*, 2019, **13**, 3320-3333.

171. With, T.K., et al., A simple spectrophotometric method for the determination of urea in blood and urine, *Journal of Clinical Pathology*, 1961, **14**, 202.
172. Rahim, M.A., et al., Coordination-Driven Multistep Assembly of Metal–Polyphenol Films and Capsules, *Chemistry of Materials*, 2014, **26**, 1645-1653.
173. Free, C.M., et al., Expanding ocean food production under climate change, *Nature*, 2022, **605**, 490-496.
174. Chen, Q.-L., et al., Potential of indigenous crop microbiomes for sustainable agriculture, *Nature Food*, 2021, **2**, 233-240.
175. Zhang, X., et al., Societal benefits of halving agricultural ammonia emissions in China far exceed the abatement costs, *Nature Communications*, 2020, **11**, 4357.
176. Zhang, W., et al., Biodegradable Urea–Formaldehyde/PBS and Its Ternary Nanocomposite Prepared by a Novel and Scalable Reactive Extrusion Process for Slow-Release Applications in Agriculture, *Journal of Agricultural and Food Chemistry*, 2020, **68**, 4595-4606.
177. Song, J., et al., Novel Semi-IPN Nanocomposites with Functions of both Nutrient Slow-Release and Water Retention. 1. Microscopic Structure, Water Absorbency, and Degradation Performance, *Journal of Agricultural and Food Chemistry*, 2019, **67**, 7587-7597.
178. Ye, H.M., et al., Degradable polyester/urea inclusion complex applied as a facile and environment-friendly strategy for slow-release fertilizer: Performance and mechanism, *Chemical Engineering Journal*, 2020, **381**, 122704.
179. Dhiman, A., et al., Polymer Based Engineered Materials for Sustainable Agriculture, *ACS Agricultural Science & Technology*, 2022, **2**, 693–711.
180. Szcześniak, B., et al., Mechanochemical synthesis of highly porous materials, *Materials Horizons*, 2020, **7**, 1457-1473.
181. Wang, G.W., Mechanochemical organic synthesis, *Chemical Society Reviews*, 2013, **42**, 7668-7700.
182. Friščić, T., et al., Real-time and in situ monitoring of mechanochemical milling reactions, *Nature Chemistry*, 2013, **5**, 66-73.
183. Ayoub, G., et al., Rational Synthesis of Mixed-Metal Microporous Metal–Organic Frameworks with Controlled Composition Using Mechanochemistry, *Chemistry of Materials*, 2019, **31**, 5494-5501.
184. Zheng, Q., et al., Unique supramolecular complex of diclofenac: structural robustness, crystal-to-crystal solvent exchange, and mechanochemical synthesis, *Chemical Communications*, 2019, **55**, 7639-7642.
185. De Bellis, J., et al., Mechanochemical Synthesis of Supported Bimetallic Catalysts, *Chemistry of Materials*, 2021, **33**, 2037-2045.
186. Rainer, D.N., et al., New avenues for mechanochemistry in zeolite science, *Dalton Transactions*, 2021, **50**, 8995-9009.
187. Tan, D., et al., Main group mechanochemistry: from curiosity to established protocols, *Chemical Society Reviews*, 2019, **48**, 2274-2292.
188. Chen, Y., et al., Mechanochemical tools for polymer materials, *Chemical Society Reviews*, 2021, **50**, 4100-4140.
189. Emmerling, S.T., et al., In situ monitoring of mechanochemical covalent organic framework formation reveals templating effect of liquid additive, *Chem*, 2021, **7**, 1639-1652.
190. Fiss, B.G., et al., Mechanochemical methods for the transfer of electrons and exchange of ions: inorganic reactivity from nanoparticles to organometallics, *Chemical Society Reviews*, 2021, **50**, 8279-8318.

191. Yuan, Y., et al., Ambient Temperature Graphitization Based on Mechanochemical Synthesis, *Angewandte Chemie International Edition*, 2020, **59**, 21935-21939.
192. Yang, C., et al., Mechanochemical Synthesis of γ -Graphyne with Enhanced Lithium Storage Performance, *Small*, 2019, **15**, 1804710.
193. Casali, L., et al., Novel Dual-Action Plant Fertilizer and Urease Inhibitor: Urea·Catechol Cocrystal. Characterization and Environmental Reactivity, *ACS Sustainable Chemistry & Engineering*, 2019, **7**, 2852-2859.
194. Adassooriya, N.M., et al., Mechanochemistry as an emerging tool for the preparation of sustained release urea cocrystals as a nitrogen source, *CrystEngComm*, 2022, **24**, 1679-1689.
195. Bakshi, S., et al., Enhancing Biochar as Scaffolding for Slow Release of Nitrogen Fertilizer, *ACS Sustainable Chemistry & Engineering*, 2021, **9**, 8222-8231.
196. Zheng, B., et al., Mechanochemical Synthesis of Zinc Borate for Use as a Dual-Release B Fertilizer, *ACS Sustainable Chemistry & Engineering*, 2021, **9**, 15995-16004.
197. Honer, K., et al., Reactive Mechanosynthesis of Urea Ionic Cocrystal Fertilizer Materials from Abundant Low Solubility Magnesium- and Calcium-Containing Minerals, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 4680-4687.
198. Sun, M., et al., Hydrophobic octadecylamine-polyphenol film coated slow released urea via one-step spraying co-deposition, *Polymer Testing*, 2020, **91**, 106831.
199. Wang, Y., et al., Spout Fluidized Bed Assisted Preparation of Poly(tannic acid)-Coated Urea Fertilizer, *ACS Omega*, 2020, **5**, 1127-1133.
200. Mazaheri, O., et al., Assembly of Metal–Phenolic Networks on Water-Soluble Substrates in Nonaqueous Media, *Advanced Functional Materials*, 2022, **32**, 2111942.
201. Guo, J., et al., Engineering multifunctional capsules through the assembly of metal-phenolic networks, *Angew Chem Int Ed Engl*, 2014, **53**, 5546-51.
202. Peng, W.-C., et al., Tunability of p- and n-channel TiO_x thin film transistors, *Scientific Reports*, 2018, **8**, 9255.
203. Rahim, M.A., et al., Polyphenol-Induced Adhesive Liquid Metal Inks for Substrate-Independent Direct Pen Writing, *Advanced Functional Materials*, 2021, **31**, 2007336.
204. Espina, A., et al., Analysis of Iron Complexes of Tannic Acid and Other Related Polyphenols as Revealed by Spectroscopic Techniques: Implications in the Identification and Characterization of Iron Gall Inks in Historical Manuscripts, *ACS Omega*, 2022, **7**, 27937-27949.
205. Tanskanen, A., et al., Iron-Terephthalate Coordination Network Thin Films Through In-Situ Atomic/Molecular Layer Deposition, *Scientific Reports*, 2018, **8**, 8976.
206. Zhang, P., et al., Soluble Porous Coordination Polymers by Mechanochemistry: From Metal-Containing Films/Membranes to Active Catalysts for Aerobic Oxidation, *Advanced Materials*, 2015, **27**, 234-239.
207. Bhangu, S.K., et al., Origins of Structural Elasticity in Metal–Phenolic Networks Probed by Super-Resolution Microscopy and Multiscale Simulations, *ACS Nano*, 2022, **16**, 98-110.
208. Elhadj, M.S.Y., et al., Influencing parameters of mechanochemical intercalation of kaolinite with urea, *Applied Clay Science*, 2021, **213**, 106250.
209. Kottegoda, N., et al., Urea-Hydroxyapatite Nanohybrids for Slow Release of Nitrogen, *ACS Nano*, 2017, **11**, 1214-1221.
210. Tsuzuki, S., et al., First-Principles Lattice Energy Calculation of Urea and Hexamine Crystals by a Combination of Periodic DFT and MP2 Two-Body Interaction Energy Calculations, *The Journal of Physical Chemistry B*, 2010, **114**, 6799-6805.

- 211. Youxin, Z., et al., A Bio-Based Hydrogel Derived from Moldy Steamed Bread as Urea-Formaldehyde Loading for Slow-Release and Water-Retention Fertilizers, *ACS Omega*, 2021, **6**, 33462-33469.
- 212. Sarmah, D., et al., Biodegradable superabsorbent hydrogel for water holding in soil and controlled-release fertilizer, *Journal of Applied Polymer Science*, 2020, **137**, 48495.
- 213. Saruchi, et al., Biodegradable hydrogels of tragacanth gum polysaccharide to improve water retention capacity of soil and environment-friendly controlled release of agrochemicals, *International Journal of Biological Macromolecules*, 2019, **132**, 1252-1261.
- 214. Liu, L., et al., Bio-based Large Tablet Controlled-Release Urea: Synthesis, Characterization, and Controlled-Released Mechanisms, *Journal of Agricultural and Food Chemistry*, 2018, **66**, 11265-11272.
- 215. Zhou, T., et al., Synthesis composite hydrogels from inorganic-organic hybrids based on leftover rice for environment-friendly controlled-release urea fertilizers, *Science of the Total Environment*, 2018, **615**, 422-430.
- 216. Olad, A., et al., Water retention and slow release studies of a salep-based hydrogel nanocomposite reinforced with montmorillonite clay, *New Journal of Chemistry*, 2018, **42**, 2758-2766.