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

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Interfacial modular assemblies of eco-friendly metal–phenolic networks (MPNs) are of interest for surface and materials engineering. To date, most MPNs are 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) on a water-soluble substrate (i.e., urea) via the self-assembly of MPNs in a nonaqueous solvent (i.e., acetonitrile). The coordination-driven assembly of the MPN coatings in the nonaqueous 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 FeIII–TA complexes and micrometer-sized FeIII–TA particles formed in solution. The straightforward nature of the present fabrication method in generating thick and robust coatings with high stability in nonaqueous 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.

1. Introduction

Polyphenol compounds, which are naturally abundant and found in most plant families, possess antibacterial, anticarcinogenic, and antioxidant properties.1 Tannic acid (TA) is a specific type of tannin with multidentate chelation properties and is inexpensive and highly biocompatible (Figure S1, Supporting Information).2 Its potential to engage in multiple interactions with different types of solid surfaces makes it useful for the formation of coatings via self-assembly.3 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.4 In general, the catechol/galloyl groups of TA provide multivalent chelating sites for coordination with various metals.5 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.6–9

To date, different MPN assembly methods have been developed, including discrete,4 multistep,6 precomplex,7 electro-triggered,10,11 rust-mediated,12,13 oxidation-mediated,14,15 and liquid–liquid interfacial growth.16,17 Since the introduction of MPNs, there has been a growing interest in their potential applications in areas such as drug delivery,18 theranostics,19 forensics,20 catalysis,21 phototaxis,22 and as conductive materials,23 bioresponsive materials,24,25 and energy storage devices.26,27 In addition, MPN assemblies have been applied as antimicrobial spray coatings for shoe insoles and fruits,28 inks for printing and writing,29 oil–water separation membrane materials,30,31 and hair dyes.32 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\textsubscript{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.\cite{31,7} 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.\cite{1,10,31} Furthermore, fundamental studies on the mechanism of MPN formation on watersoluble substrates in nonaqueous 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\textsuperscript{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 1. In the first step, Fe\textsuperscript{III} and TA precursor solutions in acetonitrile are mixed and the catechol moiety of TA reacts with Fe\textsuperscript{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\textsuperscript{III}–TA
complexes from mono- to bis-, forming stable MPN films directed by the energetically favorable adsorption of catechol groups onto the substrate, and crosslinking of ligands via covalent and coordination bonding. A real-time particle growth analysis suggests that micrometer-sized FeIII–TA particles are generated in solution only after the addition of urea granules, whereas no FeIII–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 nonaqueous media. The FeIII–TA complexes and FeIII–TA particles (dynamic building blocks) adsorb on the urea granules. Meanwhile, the FeIII–TA complexes can bridge the micrometer-sized particles, resulting in a diffusion-driven 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 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.

2. Results and Discussion

2.1. MPN Formation in Acetonitrile

The formation of FeIII–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 1 and Figure S2 (Supporting Information). A summary of the findings obtained are provided in the caption of Figure S2 and Table S1 (Supporting Information). 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, FeIII and TA solutions were mixed in acetonitrile at a stoichiometric ratio of 1.5:1 (the concentration of TA was fixed at 2.3 × 10⁻³ m), allowing the formation of FeIII–TA mono-complexes. The solution was allowed to age for 15 min. The urea granules were then immerssed into the FeIII–TA aged solution, resulting in the spontaneous formation of FeIII–TA particles in solution, followed by MPN film coating on the surface of the urea granules (Movie S1, Supporting Information). 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 FeIII with the TA solution kept the pk₆ of the solution low and prevented TA ionization (as discussed in Figure S3, Supporting Information).[6,31,34]

In aqueous media, typically, FeIII–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.[4] 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.[4,6] However, FeIII–TA complex formation in acetonitrile is markedly different to what occurs in aqueous solution (Movie S1, Supporting Information). First, bis- and/or tris-complexes of FeIII–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 S4, Supporting Information) and the lack of a solution color change to blue/violet in the mixing and solution aging steps. Second, the bis-complexes due to FeIII–TA coordination form only after the addition of urea granules (as discussed in detail below). Third, micrometer-sized FeIII–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 FeIII–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 FeII solution is important, as FeCl₃ is highly prone to hydrolyzation (solubility product constant, Kₛ_p = 6 × 10⁻³⁹), leading to the formation of insoluble Fe(OH)₃.[6]

From the findings discussed above, to further examine the formation of FeIII–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 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 FeIII–TA complexes (Figure 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 FeIII–TA coordination complexes via a reversible reaction (Figure 1c). Acetonitrile with high electron-donor strength can be partially replaced by TA in the FeIII–TA complexes to form 2FeCl₃·FeCl₂·xCH₃CN·yH₂O through the reduction of FeIII to FeII[35–37] leading to the dissociation of mono FeIII–TA complexes.[4,38] The lower reactivity and stability of FeII–TA owing to the dynamic nature of the coordination bond causes this dissociation and the formation of H₂O–FeII complexes over time (Figure S5, Supporting Information).[34,35,39] To monitor the formation of FeII and acetonitrile–FeII interactions in solution after mixing the ligand and metal, 1,10-phenanthroline indicator was added to the FeII–TA solution, and the solution was analyzed via UV–vis spectroscopy (Figure 1d). An absorption band within the range of ≈400–600 nm with λ_max of 512 nm was observed, which is attributed to the formation of FeII–1,10-phenanthroline complexes.[40] The absorption intensity of this band increased with aging time, confirming that FeIII partially converted into FeII during aging of the FeIII–TA solution.

An aging time of 15 min was selected to subsequently evaluate the formation of FeIII–TA particles upon addition of the urea granules in the aged solution using UV–vis spectroscopy. Analysis of the FeIII–TA solution after the addition of urea granules revealed a characteristic LMCT band at ≈565 nm (Figure 2a), confirming the formation of FeIII–TA complexes.[41] The analytical data suggest that several factors
contribute to FeIII–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 FeIII–TA complexes (similar to the role of H₂O in aqueous solution) (Figure S6a, Supporting Information). 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 λmax = 565 nm, typical for FeIII–TA bis-complexes, and a dark blue solution were obtained, highlighting the role of solvent-present hydroxyl groups for adsorbing FeIII 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 S7, Supporting Information). Second, the −NH₂ groups of urea can deprotonate the catechol groups of TA and initiate the formation of coordination complexes (Figure S6b, Supporting Information). 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. The generated NH₃ can facilitate further deprotonation of catechol groups and subsequent FeIII–TA particle formation (Figure S6c, Supporting Information).

Fourier transform infrared spectroscopy and energy-dispersive X-ray spectroscopy (EDX) analyses revealed the presence of amide bonds and nitrogen atoms in the FeIII–TA films (following removal from solution and washing with water) (Figure S8a,b, Supporting Information). Furthermore, the presence of N–Fe bonds was detected via X-ray photoelectron spectroscopy (XPS), confirming coordination bonding between urea and FeIII (Figure S8c, Supporting Information). No urea–TA bonding interactions were detected in the XPS spectrum of FeIII–TA MPNs following removal of the urea granules. Moreover, the role of urea in crosslinking 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 S8d, Supporting Information). Thus, the formation of dipolar bonds between the lone pair of electrons on the nitrogen atoms of urea and FeIII (Figure S8e, Supporting Information) is likely to cause the color change of FeIII solution from yellow to transparent and the immediate formation of FeIII–TA particles after the addition of urea granules (Movie S1, Supporting Information).

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 FeIII–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\textsuperscript{III}–galloyl coordination (Figure 2b).\[26\] In addition, the presence of bands at 1430 cm\textsuperscript{−1} (symmetric) and 1575 cm\textsuperscript{−1} (asymmetric), and the difference between these two bands of 145 cm\textsuperscript{−1} is attributed to the bridging carboxylate functionality.[50] The absence of a peak in the range of 385–410 cm\textsuperscript{−1} suggests that the \(\mu\)-catecholate bridging mode, which is assigned to \(\nu_{\text{Fe-O}}\), is not dominant in the Fe\textsuperscript{III}–TA complexes.[50] This is likely due to the local environment, i.e., acetonitrile, and the existence of dissolved urea, around the Fe\textsuperscript{III} center. The XPS pattern of the MPN capsules featured Fe 2p\textsubscript{3/2} and 2p\textsubscript{1/2} signals at 712 and 726 eV with a separation of \(\approx 14\) eV, indicating that the dominant iron species in the MPN film was Fe\textsuperscript{III} (Figure 2c).[11,51,52] 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 S9, Supporting Information).

The MPN coating process was also monitored by scanning electron microscopy (SEM). Figure 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\textsuperscript{III}–TA particles generated in solution through adsorption onto the urea granules (Figure S10, Supporting Information) confirms the formation of an MPN coating. The MPN film thickness of urea granules@MPN (obtained after coating for 45 min) was \(\approx 10–14\) \(\mu\)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 S11, Supporting Information, and Figure 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\textsuperscript{III}–TA complexes and micrometer-sized particles adsorb on the urea granules throughout the coating process, as well as Fe\textsuperscript{III}–TA complex-bridged micrometer-sized Fe\textsuperscript{III}–TA particles. Furthermore, SEM images confirmed that MPNs could be coated onto urea granules in acetonitrile when anhydrous FeCl\textsubscript{3} precursor was used instead of FeCl\textsubscript{3}·6H\textsubscript{2}O (Figure S12, Supporting Information). The surface morphology of urea granules@MPN prepared with anhydrous FeCl\textsubscript{3} was similar to that prepared with FeCl\textsubscript{3}·6H\textsubscript{2}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 S13, Supporting Information). 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 \(\approx 400–800\) nm in the UV–vis spectra of the Fe\textsuperscript{III}–TA solutions following addition of the substrates confirmed the formation of Fe\textsuperscript{III}–TA complexes. Fe\textsuperscript{III}–TA complex formation and MPN coating of urea granules were also successfully achieved in a range of other solvents (i.e., isopropanol, tetrahydrofuran, ethyl acetate, and 1,4-dioxane) (Figure S14, Supporting Information), further confirming the versatility of this coating method.

Figure 2. Formation of MPN films on urea granules. a) UV–vis spectrum of Fe\textsuperscript{III}–TA solution in acetonitrile after immersion of urea granules; the highlighted area (500–665 nm) corresponds to the LMCT band of the Fe\textsuperscript{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). 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\textsuperscript{III}–TA solution: d) 0 min (uncoated urea granule); e) 15 min; f) 30 min; and g) 45 min. 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 \(2.3 \times 10^{-3}\) m TA, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min at 25 °C.
2.2. Factors Influencing MPN Formation and Growth

2.2.1. Effect of Solution Aging Time

To investigate the effect of solution aging time on Fe\textsuperscript{III}–TA particle formation and morphology of the MPN films, urea granules were added to TA and Fe\textsuperscript{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\textsuperscript{III}–TA particle growth and the coating time using population distribution measurements of generated Fe\textsuperscript{III}–TA particles in the form of chord length.\[^{53,54}\] As observed in Figure 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\textsuperscript{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 (Figures 2g and 3c,d). The longer solution aging times, as discussed above, resulted in higher Fe\textsuperscript{II}/Fe\textsuperscript{III} ratios in the solution. The assembly kinetics can strongly influence the mode of molecular packing. Thus, the gradual conversion of Fe\textsuperscript{II}–TA into Fe\textsuperscript{III}–TA via oxidation of iron provides additional opportunities for conformational rearrangement and results in the formation of smaller building blocks of Fe\textsuperscript{III}–TA complexes.\[^{14,15}\]

2.2.2. 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 \(7.0 \times 10^{-3} \text{ M}\), while the concentration of TA, solution aging time, and coating process temperature were kept constant at \(2.3 \times 10^{-3} \text{ M}\), 15 min, and 25 °C, respectively. As observed from the FBRM results in Figure S15 (Supporting Information), 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\textsuperscript{III} as the crosslinking agent, led to an increased degree of Fe\textsuperscript{III}–TA complex formation and facilitated MPN coating.

![Figure 3. Influence of solution aging time on Fe\textsuperscript{III}–TA particle formation in acetonitrile after the addition of urea granules into the Fe\textsuperscript{III}–TA solution. a,b) Fe\textsuperscript{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 \(2.3 \times 10^{-3} \text{ M}\) TA and an M:L molar ratio of 1.5:1 at 25 °C.](image-url)
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 FeIII–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 FeIII–TA particle growth in acetonitrile was likely complete for particles smaller than 150 µm.

The higher content of FeIII could induce enhanced deprotonation of the ligands, leading to electrostatic repulsion among TA molecules and the separation of larger complexes into smaller fragments.\[55\] The influence of the M:L molar ratio on the surface morphology is shown schematically in Figure S16a (Supporting Information). SEM (Figure 4a inset and Figure S16b–e, Supporting Information) and atomic force microscopy (AFM) (Figure 4a and Figure S17, Supporting Information) 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 followed by fusion onto the film led to an increase in the surface roughness.\[34\]

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 FeIII species (Figure S18a, Supporting Information). The thickness of the MPN coatings increased from ≈5 to ≈20 µm with increasing M:L molar ratio (Figure 4b and Figure S18b–i, Supporting Information). Accordingly, the total MPN content in the prepared urea granules@MPN increased from 0.27 to 1.54 wt% with an increase in the total count of particles generated at higher FeIII concentrations [Equation (S1), Figure S19, and Table S2, Supporting Information].

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 S20, Supporting Information). 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 °C, which is due to water evaporation (Figure 4c and Figure S21, Supporting Information). The two major mass losses (75 wt% loss in total) occurring above 200 °C is attributed to the degradation of TA.

MPN films prepared with a higher concentration of FeIII experienced a higher resistance to TA decomposition, as indicated by the two mass loss steps shifting to higher temperatures and

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Figure 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). Data are shown as the mean ± standard deviation, and three specimens were analyzed for each sample. Each specimen represents the average of at least five measurements. b) Corresponding thickness profiles of MPN films prepared at different M:L ratios, as measured from the cross-section SEM images. Three specimens were analyzed for each sample (each specimen being the average of at least 20 measurements), with the data shown as the mean ± standard deviation. 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 FeIII 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. Data are shown as the mean ± standard deviation, with three specimens being analyzed for each sample. All data are for systems prepared with a final concentration of 2.3 × 10⁻³ M TA and a solution aging time of 15 min at 25 °C.
the smaller reduction in mass observed after 350 °C. This can be attributed to the increased likelihood of cross-linking of TA with increased iron concentration, resulting in a higher activation energy required to break Fe(III)–TA complexes and a subsequent increase in thermal stability.[6] 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 °C—the extent of degradation at 250 °C decreased, whereas that at 320 °C increased as the M:L ratio increased (Figure S21, Supporting Information). The degradation at 250 °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 4d), whereas the degradation at 320 °C corresponds to the decomposition of benzene diol and the ester groups connected to glucose.[57,58] 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 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 4e and Figure S22, Supporting Information). 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 ≈1:9.1, ≈2.3:1, and ≈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 4e).

2.2.3. 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 × 10⁻³ m, 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 4e and Figure S22, Supporting Information). 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 ≈1:9.1, ≈2.3:1, and ≈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 4e).
while fixing the $\text{Fe}^{\text{III}}$-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 $\text{Fe}^{\text{III}}$–TA particles at the lower TA concentration of $1.1 \times 10^{-3}$ M was slower than that at the higher TA concentrations of 4.7 and $2.35 \times 10^{-3}$ M (Figure 5a–c), and most of the $\text{Fe}^{\text{III}}$–TA particles did not adsorb onto the urea granules. The lack of sufficient crosslinking significantly reduced the adsorption properties of the formed particles and most of the urea granules remained uncoated even after 10 h following the 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 $4.7 \times 10^{-3}$ M, further increases in the TA precursor concentration ($>4.7 \times 10^{-3}$ M) resulted in a sharp decrease in the total number of generated particles within the 100–200 μm size range (Figure 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 5a–c, insets) due to the increased degree of adsorption within the film, which occurs at higher precursor concentrations. Moreover, excess $\text{Fe}^{\text{III}}$ induced aggregation of the complexes, resulting in increased roughness.[5] The film thickness initially increased as the concentration of TA increased, reaching a maximum of $\approx 18$ μm at $4.7 \times 10^{-3}$ M before decreasing with further increases in TA concentration (Figure 5e and Figure S23, Supporting Information). At high TA concentrations ($>4.7 \times 10^{-3}$ M), the affinity of the $\text{Fe}^{\text{III}}$–TA particles to adsorb at the interface of a previously adsorbed MPN layer decreased as a result of steric hindrance among preformed $\text{Fe}^{\text{III}}$–TA particles in solution.[6] 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 $4.7 \times 10^{-3}$ M of TA, which coincides with the maximum MPN film thickness obtained (Figure 5f).

### 2.2.4. Effect of MPN Deposition Cycles

X-ray micro-computed tomography (micro-CT) was used to obtain cross-sectional images and 3D 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 6a–f). The cross-sectional images (Figure 6c,d) and computed analysis (Figure 6e,f and Table S3, Supporting Information) show that repeated film deposition processes increased the film thickness from $\approx 14$ μm (first deposition) to $\approx 40$ μm after the tenth deposition cycle. These results were consistent with the film thickness measured from the SEM cross-sectional images (Figure S24, Supporting Information). 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.[59-61]

### 2.2.5. Effect of Temperature

In contrast to the formation of MPNs in aqueous media, whereby temperature has minimal impact,[7] elevating the temperature to 60 °C for nonaqueous 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 $\approx 82$ °C). Increasing the temperature from 25 to 60 °C resulted in an increase in the film thickness from 12 to 23 μm (Figure 6g and Figure S25, Supporting Information) and a reduction

![Figure 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 first and tenth 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 $\approx 1500$ 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). Data are shown as the mean ± standard deviation, and three specimens were analyzed for each sample. Each specimen represents the average of at least 20 measurements. Scale bars in all micro-CT images are 1 mm. All data are for systems prepared with a final TA concentration of $2.3 \times 10^{-3}$ M, an M:L molar ratio of 1.5:1, and a solution aging time of 15 min.](image-url)
in the MPN coating time from 40 to 5 min (Figures S15b and S26a,b, Supporting Information). The higher solid–liquid interface affinity at the higher coating temperature can increase the kinetics of the coating process (Figure S26a,b, Supporting Information). The formation of fewer FeIII–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 MPN film structure during its initial formation stage (Figure S26c,d, Supporting Information). 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 S26e,f, Supporting Information). The mass of residual materials after 400 °C (attributed to iron metal) increased slightly (Figure S26f, Supporting Information) due to increased solubility of iron in acetonitrile at >25 °C.

2.3. Release Profile of Urea from Urea Granules@MPN Samples

The release profiles of urea from the urea granules@MPN samples in water (Figure 7 and Figure S27, Supporting Information) were estimated via the colorimetric method (Scheme S1, Supporting Information) by calculating the cumulative dissolution of urea granules versus time [Equation (S2), Supporting Information]. 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 S27a, Supporting Information). 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 S27b, Supporting Information). 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 × 10⁻³ m led to a slower release of urea, with the release time increasing to 240 min. Further increases in the TA concentration to 11.7 and 23.5 × 10⁻³ m led to a faster urea release that was complete within 180 and 120 min, respectively (Figure S27c, Supporting Information). These results may likely be due to the reduced thickness of the films prepared at 11.7 and 23.5 × 10⁻³ m.

The MPN deposition cycle also influenced the release profile of the urea granules@MPN samples. As observed from Figure 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 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 S26d, Supporting Information; Figure 6g inset; and Figure S28, Supporting Information), the “spikes” that form on the external surface of the film may provide an air cushion between the microdents and water molecules (similar to what occurs in hydrophobic surface materials). Recent studies have shown that air pockets are trapped underneath the water in the valleys between the bulges (Figure S25d and as discussed in Figure S28, Supporting Information); this reduces the contact area between water molecules and the external surface of the film, reducing water permeation. 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 S27d, Supporting Information). 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.[49] 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.[55] 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 S29a–c, Supporting Information). 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 S29d,e, Supporting Information). 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.

3. 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 MPNs 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 films. 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 MPNs. Overall, our results provide insights into MPN coatings 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.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

coordination chemistry, metal–organic materials, MPNs, self-assembly, surface coatings

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