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One-Step Assembly of Coordination Complexes for Versatile Film and Particle Engineering

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Abstract: The development of facile and versatile strategies for thin film and particle engineering is of immense scientific interest. However, few methods can conformally coat substrates of different composition, size, shape, and structure. Herein, we report the one-step coating of various interfaces using coordination complexes of natural polyphenols and Fe(III) ions. Film formation is initiated by the adsorption of the polyphenol and directed by pH-dependent, multivalent coordination bonding. Aqueous deposition is performed on a range of planar as well as inorganic, organic, and biological particle templates, demonstrating an extremely rapid technique for producing structurally-diverse, thin films and capsules that can disassemble. The ease, low-cost, and scalability of the assembly process, combined with pH-responsiveness and negligible cytotoxicity, makes these films potential candidates for biomedical and environmental applications.

Main Text: Advances in materials design and application are highly dependent on the development of versatile thin film and particle engineering strategies (1-4). Supramolecular metal-organic thin films have attracted widespread interest due to their diverse properties, which include: (i) stimuli-responsiveness imparted by the dynamic nature of supramolecular coordination bonds; (ii) hybrid physicochemical properties of both metals and organic materials; and (iii) controlled structure and functionality achieved by variation of the molecular building blocks (5, 6). Although metal-organic thin films show potential for sensing, separation processes and catalysis (5, 6), such films are fabricated with multiple, time-consuming steps (7-11). Moreover, biomedical applications of these films have thus far been limited because they are typically unstable in water or are toxic (12).

Herein, we report a simple, rapid, and robust conformal coating method using the one-step assembly of coordination complexes on a range of substrates to prepare various films and particles. The natural polyphenol, tannic acid (TA) and Fe^{III} were chosen as organic ligands and inorganic cross-linkers, respectively. Film deposition occurs upon mixing TA and Fe^{III} in water at ambient temperature. No special equipment is necessary for this method, and the material components are readily and economically available. Moreover, they are generally recognized as safe (GRAS) by the United States Food and Drug Administration. Although the chemical structure of TA is usually given as a decagalloyl glucose (C₇₆H₅₂O₄₆) [fig. S1 (13)], it is actually a mixture of polygalloyl glucose molecules with different numbers of esterified gallic acid (14). Three galloyl groups from TA can react with each Fe^{III} ion to form a stable octahedral complex (15), allowing each TA molecule to react with several Fe^{III} centers to form a cross-linked film. This method is applicable to a wide variety of substrates because of the general surface binding

affinity of TA. When these films are deposited on particles, subsequent dissolution of the templates results in the formation of three-dimensional free-standing films known as hollow capsules, systems that have widespread use in drug and gene delivery, catalysis, biosensing, and as microreactors (16).

We first describe the deposition of Fe^{III}/TA films on planar (Fig. 1A) and particulate (Fig. 1, B to K) polystyrene (PS) templates. The color of the template suspension immediately turned blue upon addition of Fe^{III} and TA solutions (fig. S2). Stirring times (20 sec and 1 h) had no effect on the color or on the resulting film thickness under standard conditions (13), implying that the film formation process was completed instantaneously. Formation of the Fe^{III}/TA films on the PS particles shifted the surface zeta-potential from -27.4 ± 2.8 to -64.0 ± 6.9 mV due to the acidic nature of the galloyl groups in TA. After removing the PS template, we obtained highly uniform microcapsules with a zeta-potential of -64.6 ± 7.3 mV, which was approximately the same value as before template removal.

Differential interference contrast (DIC) microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) images of the Fe^{III}/TA capsules are shown in Fig. 1, B to E. Monodisperse, spherical capsules were readily observed under DIC (Fig. 1B). The permeability of these capsules is molecular weight dependent, and they are essentially impermeable to 2,000 kDa dextran (fig. S3). The presence of Fe in the films was confirmed by energy dispersive X-ray spectroscopy (EDS) (fig. S4) and X-ray photoelectron spectroscopy (XPS) (fig. S5). The capsules observed by AFM, SEM and TEM (Fig. 1, C to E), had folds and creases because these measurements were performed on dried samples. Different-sized templates ($D = 120$ nm, 840 nm, 3.6 μ m, and 10 μ m) can be exploited for capsule preparation (Fig. 1, F to I). Ellipsoidal PS templates, prepared by stretching spherical PS particles above their glass transition temperature, were also used to obtain ellipsoidal capsules (Fig. 1, J and K). From AFM height analysis, the single-wall thickness of the capsules was determined to be half of the minimum height of the collapsed flat regions (10.4 ± 0.6 nm). The Young's modulus (E_Y) of the $D = 3.6$ μ m capsules was estimated to be 1.0 ± 0.2 GPa by AFM force measurements (fig. S6). This E_Y is at the high end of the range observed for layer-by-layer (LbL) polyelectrolyte capsules (10 – 1000 MPa) (17). Several groups have reported LbL capsules fabricated from TA and other polymers (18, 19). For example, LbL capsules of TA/poly(*N*-vinylpyrrolidone) (PVPON) exhibit a bilayer thickness of 1.0 – 2.2 nm depending on the molecular weight of the PVPON (19). The Fe^{III}/TA film, obtained through the one-step assembly, is thicker than four bilayers of TA/PVPON obtained through multi-step LbL assembly, demonstrating the efficiency of the one-step process. Analogous to LbL assembly, the thickness of Fe^{III}/TA films can be further increased by simply repeating the rapid coating procedure (figs. S7 and S8).

The effect of TA and FeCl₃·6H₂O concentrations (hereafter denoted as [TA] and [FeCl₃·6H₂O], respectively) on the resulting film thickness and morphology were investigated by AFM using $D = 3.6$ μ m PS templated capsules. When [TA] was kept constant at 0.40 mg mL⁻¹ (0.24 mM), capsules were obtained over a [FeCl₃·6H₂O] range of 0.06 to 0.20 mg mL⁻¹ (0.22 to 0.74 mM), approximately corresponding to molar ratios of 1:1 to 3:1 between Fe^{III} and TA. The resulting stoichiometries in the capsule walls were determined by XPS (fig. S5) to be Fe^{III}:TA = *ca.* 1:4, 1:3, and 1:2 for feed [FeCl₃·6H₂O] of 0.06, 0.12, and 0.20 mg mL⁻¹, respectively. This demonstrates that the feed concentrations influence the capsule stoichiometries. Above and below [FeCl₃·6H₂O] = 0.06 – 0.20 mg mL⁻¹, aggregated capsules and few capsules were formed, respectively. In the absence of Fe^{III}, no capsules were formed. As [FeCl₃·6H₂O] was increased in

this concentration range, the Fe^{III}/TA film became thicker, from 7.7 ± 0.4 to 11.9 ± 1.2 nm, and exhibited increased roughness (fig. S9). Increasing the amount of Fe^{III} to three molar equivalents of TA resulted in capsules that had a grainy surface because of the excess Fe^{III} (fig. S9A). Values of RMS roughness (300 nm by 300 nm, fold-free flat region) were 1.3 ± 0.1 , 1.6 ± 0.1 and 7.7 ± 0.4 nm for [FeCl₃·6H₂O] of 0.06, 0.10 and 0.20 mg mL⁻¹, respectively. In contrast to these observations based on Fe^{III}, [TA] had minimal impact upon film assembly. Capsules with constant film thickness and roughness were obtained throughout a concentration range of [TA] = 0.10 to 1.80 mg mL⁻¹ (0.06 to 1.06 mM), when [FeCl₃·6H₂O] was fixed at 0.10 mg mL⁻¹ (0.37 mM) (fig. S10). These results suggest that TA was relatively in higher excess than Fe^{III} under these conditions, and that Fe^{III}, and not TA, influenced the film thickness.

To further investigate the mechanism of the Fe^{III}/TA film formation, polyethyleneimine (PEI)-coated PS templates were used for capsule preparation. The PEI coating changed the zeta-potential of the templates from negative (-27.4 ± 2.8 mV) to positive (36.9 ± 5.6 mV). Capsules were still formed with these positively charged templates, indicating that the surface charge is not an important factor for film deposition. We also determined the zeta-potential after incubating the bare PS particles with either TA or FeCl₃. The adsorption of TA reduced the zeta-potential value to -39.4 ± 3.6 mV, while the value was slightly changed after incubation with FeCl₃ (-33.1 ± 4.7 mV). Furthermore, rapid surface-adherence and formation of a TA layer on the template particle surface were confirmed by adsorption experiments (fig. S11). Catechol-functionalized molecules and their derivatives have a high affinity for a wide variety of substrates with different surface charges (4, 20). Thus, it is most likely that the free TA or small Fe^{III}/TA complexes initially adsorb onto the template surface and are subsequently cross-linked by further Fe^{III} complexation. The increase in the cross-linker concentration causes the attraction of more TA to the initially formed films, making them thicker. Film growth is completed when free Fe^{III} in the bulk solution is consumed. Excess Fe^{III} induces aggregation of Fe^{III}/TA complexes in the bulk solution. These small aggregates subsequently bind to the surface, leading to an increased roughness of the capsule films (fig. S12). Unlike thin film formation using dopamine self-polymerization (4), this study relies on the complexation of TA with Fe^{III} through coordination bonds, which allows the films to form rapidly and disassemble in response to pH (see below).

To show the versatility of this method, various planar and particulate substrates including glass, gold (Au), polydimethylsiloxane (PDMS), poly(lactic-co-glycolic acid) (PLGA), melamine-formaldehyde resin (MF), low-molecular-weight PDMS emulsion, silica (SiO₂), aminated SiO₂, cetyltrimethylammonium bromide-capped Au nanoparticles (Au NPs), calcium carbonate (CaCO₃), *Escherichia coli* (*E. coli*), and *Staphylococcus epidermidis* (*S. epidermidis*) with various surface properties (anionic, neutral and cationic) were coated with the Fe^{III}/TA films (Fig. 2). The color and zeta-potential values (Fig. 2, A to D) changed after the coating in all cases, demonstrating that Fe^{III}/TA films can be formed on a wide variety of substrates. Fig. 2E and fig. S13A show protein and rhodamine B loaded CaCO₃ coated with Fe^{III}/TA films, respectively. The replica particles were obtained by filling mesoporous CaCO₃ particles with Fe^{III}/TA complexes and dissolving the CaCO₃ cores (fig. S13, B to E). After the coating, a Fe^{III}/TA shell layer was visible around the Au NP core (Fig. 2, F and G, fig. S13F). Magnetic Fe₃O₄ nanoparticles were encapsulated by coating low-molecular-weight PDMS emulsion templates loaded with Fe₃O₄ nanoparticles (fig. S13G). Subsequent removal of the emulsion by ethanol produced magnetically active Fe^{III}/TA capsules (Fig. 2, H and I).

The coordination between Fe^{III} and TA is pH-dependent, and the obtained capsules exhibit pH-dependent disassembly. The color of the capsule suspension was different at varying pH (Fig. 3A). The suspension was colorless at pH < 2, blue at 3 < pH < 6, and red at pH > 7. This color change is consistent with observations for analogous Fe^{III}/catechol complexes (21, 22), which can be attributed to the transition between the mono-, bis- and tris-complex states (Fig. 3B). At pH 2.0, the Fe^{III}/TA capsules shrunk immediately (fig. S14) and were disassembled afterward. At low pH, most of the hydroxyl groups are protonated, which leads to rapid de-cross-linking and disassembly of the films. Even above pH 3.0, Fe^{III}/TA capsules disassembled. Fig. 3C shows the disassembly kinetics of the Fe^{III}/TA capsules. At pH 3.0, all of the capsules had disassembled in 4 h, while at pH 4.0, 6 days incubation was required to disassemble the majority of the capsules. In contrast, *ca.* 70% and 90% of the capsules still remained intact after 10 days incubation at pH 5.0 and pH 7.4, respectively. The stability constants of Fe^{III}/TA are 1.5×10^5 , 3.4×10^9 , 2.8×10^{17} at pH 2, 5, 8, respectively (23). Additionally, we carried out AFM experiments after incubation at pH 5.0 (fig. S15). The films became thinner (6.0 ± 1.4 nm) and rougher, confirming the gradual disassembly of the Fe^{III}/TA films. Ethylenediaminetetraacetic acid (EDTA) accelerated the disassembly because of its strong affinity for Fe^{III} (Fig. 3C).

The cytotoxicity of Fe^{III}/TA capsules was shown to be negligible (fig. S16). Coupled with their pH-sensitive disassembly profile, Fe^{III}/TA capsules have potential biomedical application, because of the varying pH in different parts of the body, *e.g.* blood (pH 7.4), stomach (pH 1.0 – 3.0), duodenum (pH 4.8 – 8.2), *etc.* (24). Iron tannate has been historically recognized as an ink (25) and a corrosion-resistant layer for steel (15). It had also been used for dyeing teeth black, and consequently preventing cavities, in the old Japanese custom called ‘Ohaguro’ (26). The general applicability of this technique was further demonstrated by using different metals and another polyphenol (figs. S17 and S18). The simple preparation and biologically relevant physicochemical properties of the metal-polyphenol films provide a platform for the engineering and assembly of advanced materials for potential use in a range of applications.

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Figure Captions

Fig. 1. Film formation. Fe^{III}/TA films prepared on PS substrates with various shapes (planar, spherical and ellipsoidal) and sizes ($D = 120 \text{ nm} - 10 \text{ }\mu\text{m}$). (A) Photograph of PS slides before (top) and after (bottom) Fe^{III}/TA coating. (B–K) Microscopy images of Fe^{III}/TA capsules. DIC (B,I,J), AFM (C), TEM (E,F,G,K), SEM (D), and fluorescent microscopy (H) images.

Fig. 2. Fe^{III}/TA coating on various substrates. (A–C) Photograph of planar substrates before (upper) and after (lower) Fe^{III}/TA coating. Glass (A), Au (B), PDMS (C). (D) Zeta potential values of particulate substrates in water before and after the Fe^{III}/TA coating. The results are average values with standard deviations (mean \pm S.D.). (E) A confocal laser scanning microscopy image of protein-loaded CaCO₃ particles (red) coated with Fe^{III}/TA films (green) (F,G) TEM images of Au NPs non-coated (F) and coated (G) with Fe^{III}/TA films. (H,I) Photographs of Fe^{III}/TA capsules loaded with Fe₃O₄ nanoparticles dispersed in water before (H) and after (I) applying a magnet.

Fig. 3. pH-responsive disassembly of Fe^{III}/TA capsules. (A) UV-Vis absorption spectra of spherical Fe^{III}/TA capsule dispersions ($D = 3.6 \text{ }\mu\text{m}$, $4.0 \times 10^7 \text{ capsules mL}^{-1}$) at various pH. Inset is a photograph of the capsule dispersions at the indicated pH. (B) pH-dependent transition of dominant Fe^{III}/TA complexation state. R represents the remainder of the TA molecule. (C) Plot of remaining capsule population (%) against time. The results are average values with standard deviations from three independent measurements (mean \pm S.D.).