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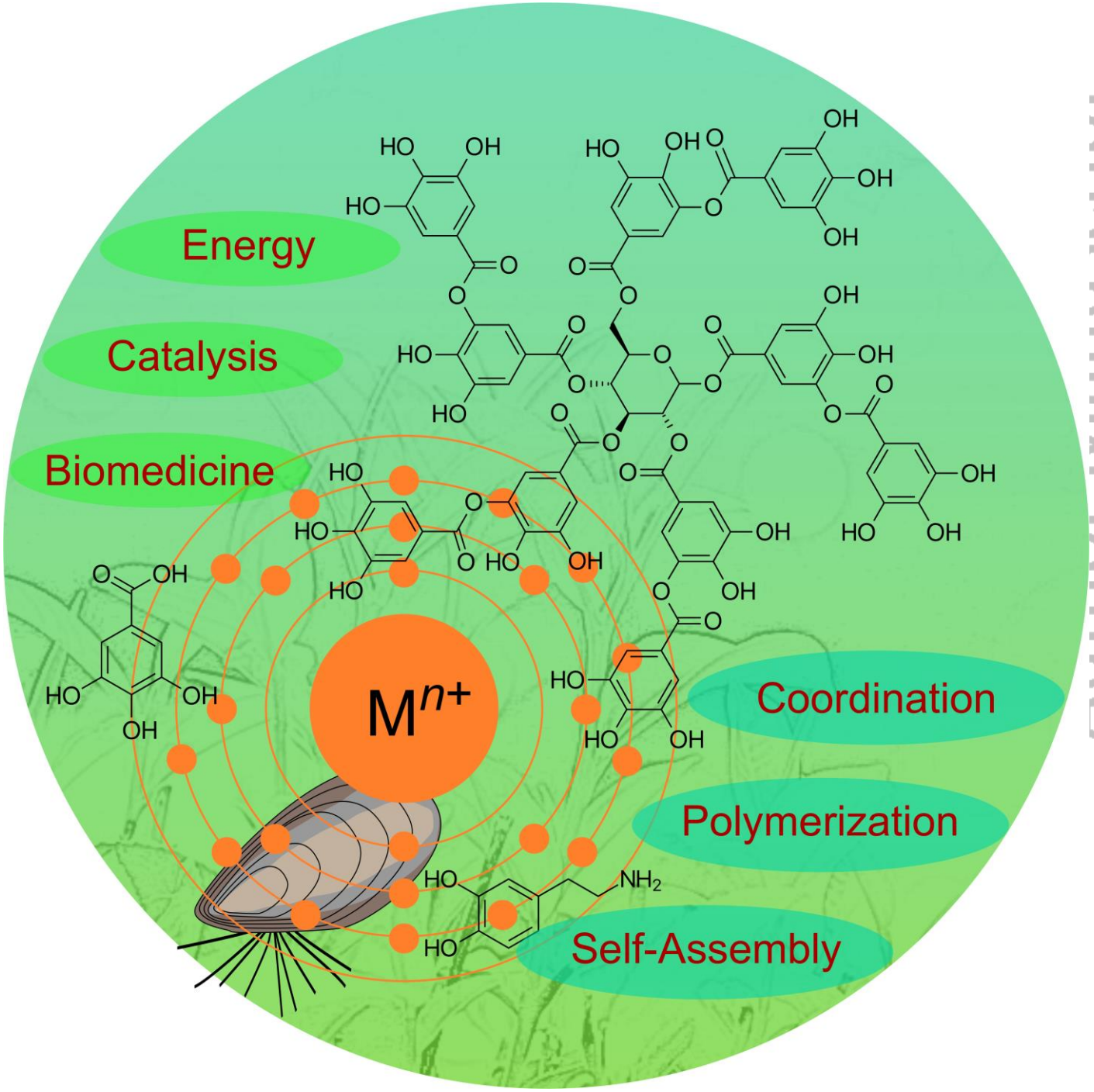
Phenolic Building Blocks for the Assembly of Functional Materials

Md. Arifur Rahim, Samantha L. Kristufek, Shuaijun Pan, Joseph J. Richardson, and Frank Caruso*



Phenolic materials have long been known for their use in inks, wood coatings, and leather tanning. However, recently there has been a renewed interest in engineering advanced materials from phenolic building blocks. The intrinsic properties of phenolic compounds, such as metal chelation, hydrogen bonding, pH responsiveness, redox potentials, radical scavenging, polymerization, and light absorbance, have made them a distinct class of structural motifs for the synthesis of functional materials. Materials prepared from phenolic compounds often retain many of these useful properties with synergistic effects in applications ranging from catalysis to biomedicine. The present review provides an overview of the diverse functional materials that can be prepared from phenolic building blocks, bridging the various fields currently studying and using phenolic compounds. Natural and synthetic phenolic compounds are first discussed, followed by the assembly of functional materials. The engineered phenolic materials are grouped under three broad categories: thin films (e.g., metal–phenolic networks and polydopamine); particles (e.g., metal–organic frameworks and superstructures); and bulk materials (e.g., gels). Applications of phenolic-based materials are then presented, focusing mainly on mechanical (e.g., adhesives), biological (e.g., drug delivery), and environmental and energy (e.g., separation and catalysis) applications. Several examples of their emerging applications are also included. Finally, potential routes for the continued integration of disparate fields using phenolic building blocks and fundamental questions still requiring investigation are highlighted, and an outlook of the field is provided.

1. Introduction

Phenolic compounds display diverse functions in a variety of natural systems, ranging from bacteria and fungi to plants and animals.[1,2] Largely found as secondary plant metabolites, these compounds not only play a pivotal role in plants' defense mechanisms, but also exhibit a wide range of properties including pigmentation and flavoring of plants and food products, protein complexation, metal coordination, and radical scavenging.[1,3-6] For example, flavonoids, a major subclass of polyphenols, are primarily responsible for the colors (from non-chlorophyll origin) of fruits, flowers, and vegetables, and protect plants against the sun's ultraviolet (UV) radiation by preventing UV-induced tissue damage.[7-10] Furthermore, the antioxidant activity of dietary phenolics is generally attributed to their ability to scavenge reactive oxygen species (ROS) and regulate certain metal coordination interactions that inhibit metal ions from generating ROS.[5]

In addition, other living organisms use phenolic moieties to perform various complex tasks. Investigations into the mechanism of microbial iron transport have revealed that bacteria employ siderophores, such as enterobactin (a triscatechol derivative), to accumulate iron and subsequently facilitate cellular iron transport. Another prominent example is the protein-based adhesives produced by several marine organisms.[11-13] Mussels can attach their soft invertebrate body to various surfaces underwater by secreting mussel foot proteins that form byssal threads. Sandcastle worms construct protective shells by assembling sand grains with a proteinaceous glue.[13,14] Both the mussel byssus and sandcastle glue are known to be heavily decorated with catecholamine functional groups (i.e., 3,4-dihydroxyphenyl-L-alanine (DOPA)).[12,13]

Over the last two decades, the progress in understanding these natural systems and the underlying diverse chemistry of phenolic compounds have spurred tremendous interest in the use of phenolic building blocks within the scientific community, leading to numerous major breakthroughs in the fields of chemistry and materials science. For example, the discovery in 1981, that catechol-containing proteins are responsible for the adhesion of mussels,[15] led to a surge in synthetic mussel-inspired materials with over 8,000 articles published in that field to date. Simultaneously, a wide variety of functional materials have also been developed taking inspiration from other natural products such as plant-derived phenolics.[16] While the various synergistic interactions of catechol- and gallol-containing phenolic compounds are still being studied,[17] they have been used in the design of various synthetic materials including conformal coatings,[18] particles,[16] gels,[19] elastomers,[20] and adhesives.[21]. The field has moved so rapidly that it is difficult to even claim inspiration from nature anymore, as the chemicals and materials have integrated with the everyday lexicon of science.

Owing to the natural abundance of phenolic compounds and their varied applications as writing inks, tanned leather, and protective coatings for teeth, phenolic-based materials lie at the intersection of chemistry, material sciences, biology, and engineering.[1,22] Therefore, a near limitless number of functional phenolic materials can be engineered. However, a comprehensive review is implausible owing to the large amount of activity surrounding these compounds. The present review is instead an overview of functional materials that can be engineered from phenolic building blocks, in an attempt to bridge the gaps among the currently disparate fields using phenolics to fabricate materials. After an overview of naturally abundant phenolic building blocks commonly used for the preparation of functional materials and a summary of their diverse interactions, a brief introduction on the chemistry surrounding synthetic phenolic derivatives is provided, as these compounds have allowed for numerous advances in the field of functional materials. Using the natural phenolic lignin or its synthetic derivatives has been a prominent approach for designing functional materials. However, given the extensive number of reviews on this building block,[23-26] this will not be discussed herein. The polymerization chemistry surrounding molecules with catechol and gallol groups is not always straightforward. Thus, Section 2.1, which is devoted to synthetic phenolic derivatives, can help guide researchers to the most relevant studies and methodologies. The phenolic-based functional materials discussed in the present review are grouped into three broad categories—thin films (Section 3), particles (Section 4), and bulk materials (Section 5)—which cover a broad range of

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synthetic materials from soft to hard and one-dimensional to three-dimensional structures, with applications ranging from nanotechnology to macromolecular science. Section 3 covers films prepared from metal–phenolic network (MPN) assembly, layer-by-layer (LbL) assembly, and via oxidative self-polymerization (e.g., polydopamine (PDA)), thus representing surface-confined or surface-initiated materials from phenolic building blocks with tunable thicknesses ranging from several nanometers to hundreds of nanometers. Section 4 covers capsules, crystalline particles, nanoparticles, micelles, and superstructures, all of which are commonly formed in solution as discrete materials, ranging in size from tens of nanometers to tens of micrometers. Section 5 covers gels, plastics, and elastomers, which can be formed via diverse techniques, typically resulting in macroscopic materials of arbitrary size and dimensionality. Following the overview of these three major categories of phenolic-based functional materials, their applications in various established and emerging fields including adhesives, stretchable and self-healing materials, drug delivery, sensing, sporulation, separation, catalysis, antioxidant and antimicrobial coatings, micronutrient delivery, and drug crystallization are discussed. We conclude the review by highlighting where continued integration of separate phenolic-focused fields could yield fruitful breakthroughs, and we provide some possible future directions of interest for researchers studying phenolics and phenolic-based materials.

Md. Arifur Rahim received his Bachelor's degree in Applied Chemistry and Chemical Engineering from University of Dhaka and his Master's degree in Nanoscience and Technology from Chonbuk National University. He completed his Ph.D. in 2016, working on metal–phenolic thin films and gels under the supervision of Frank Caruso at The University of Melbourne. Since then he has been working as a postdoctoral fellow in Frank Caruso's group exploring various applications of metal–phenolic materials.

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2. Phenolic Building Blocks

Phenolic compounds are widely distributed in nature and constitute a major class of phytochemicals.[27] More than 8,000 phenolic compounds of the polyphenol family have been identified and are divided into two major groups based on their chemical structures: flavonoids and non-flavonoids.[28] In addition to plant-based phenolic compounds, catecholamines, such as dopamine and melanin, are found in many living organisms.[13,15] Some of the common phenolic compounds extracted from natural sources and used as building blocks for functional materials synthesis are shown in Figure 1a–d. While significant research has focused on using natural building blocks, such as dopamine and tannic acid (TA), to form functional materials,[16,29] the synthesis of synthetic phenolics and phenolic polymers allows for a near limitless variety of functionalities to be incorporated into phenolic-based materials. Some of the common synthetic polymers are shown in Figure 1e–i.

Synthetic phenolic polymers offer a wide range of functionalities, as a large number of non-phenolic side groups, such as *co*-blocks, spacers, and reactive groups, can be incorporated. Catechol and gallol groups are regularly included in linear and dendritic polymers through a variety of synthetic routes. Although, careful choice of synthesis parameters, such as monomer type, polymerization route, reaction condition, is necessary owing to the reactivity of phenolic moieties. Early synthetic phenolic polymers involved the reaction between commercially available polymers and DOPA,[30] and from that seminal report, the field has evolved into synthesizing polymers containing catechols and gallols. Phenolic synthetic polymers have been prepared through different routes, including functional initiators,[31-33] post-polymerization,[34,35] and incorporation within the backbone, where the latter approach is the main focus of this section. Other useful synthetic techniques are also briefly mentioned.

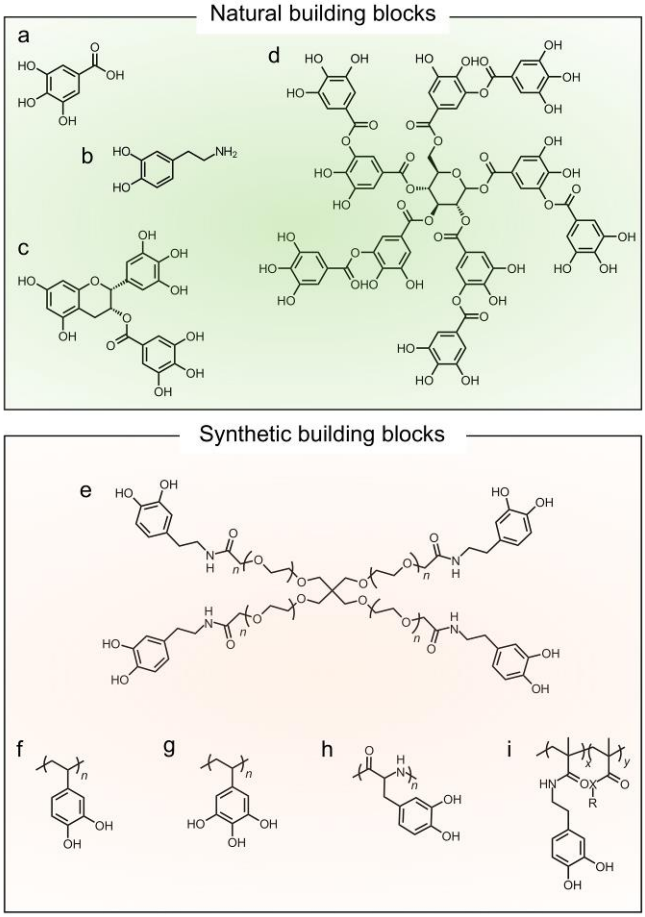

Figure 1. Examples of some common phenolic building blocks used for the preparation of functional materials. Examples of natural building blocks: (a) gallic acid, (b) dopamine, (c) epigallocatechin gallate, and (d) tannic acid. Examples of synthetic building blocks: (e) PEG–catechol, (f,h,i) polycatechols, and (g) polygallol.

One of the simplest routes for functionalizing polymers with phenolic moieties is through the use of dopamine. Dopamine itself can be used to prepare functional materials[29] (as discussed at length below). However, owing to the presence of its terminal amine, dopamine can also be coupled to diverse chemical moieties using simple conjugation strategies. The phenolic molecular toolbox extends to various reactions that have been used to modify commercially available synthetic and natural polymers. One of the most common strategies has been the functionalization of different polyethylene glycol (PEG) structures through common amide coupling reactions with various catechol-containing compounds including DOPA,[30] 3,4-dihydroxyhydrocinnamic acid,[36] and dopamine.[37] Other synthetic polymers such as poly(acrylic acid)[38] and polyethyleneimine[39] have been conjugated with catechol- and gallol-based compounds. In addition to the functionalization of synthetic polymers, naturally occurring polymers such as chitosan[40] and hyaluronic acid[41,42] have been functionalized with catechol functional groups. Together, these simple chemical reactions allow for the rapid development of advanced materials. However, when specific functionalities need to be incorporated, the polymers often have to be synthesized from simple building blocks, likely necessitating the use of phenolic monomers.

As DOPA is an amino acid containing a catechol, it can be combined with the widely available library of amino acid comonomers to allow for additional functionality to be incorporated during polymerization. Amino acid monomers can be synthesized to form *N*-carboxyanhydride (NCA) compounds followed by ring-opening polymerizations of various monomer combinations. Anderson et al.[43] synthesized a random copolymer of DOPA and N^5-(2-hydroxyethyl)-L-glutamine where the amount of DOPA was varied to study the effect on the adhesive and cohesive properties of the polymer.[43] Inspired by the sandcastle glue, DOPA-NCA was incorporated into two polypeptides with opposite charges, and when mixed together tunable coacervates formed, depending on the mixing ratios and conditions.[44]

One common monomer containing catechol is dopamine methacrylamide (DMA), which can be synthesized from dopamine and a methacrylate-containing compound. DMA has been copolymerized with various comonomers such as aminoethylmethacrylamide[45] and 2-methoxyethyl acrylate[46] to allow for DNA immobilization and adhesion under wet conditions, respectively. The polymerization conditions for DMA have allowed for the incorporation of monomers with additional functionality either through copolymerization or the formation of block copolymers. Recent examples include fluorine-containing, poly(2,2,3,3,3-pentafluoropropyl acrylate), grafted brushes for antifouling applications,[47] and the incorporation of glycopolymer-based monomers to mimic the immunogenic properties of natural pathogens.[48] Additionally, host–guest chemistry can be incorporated into DMA systems with an adamantyl comonomer, allowing for reversible adhesion.[21]

Using protecting groups is a commonly used synthetic strategy when preparing synthetic phenolic polymers, as catechols can scavenge radicals and thereby limit polymerization and induce side reactions. Studies on the synthesis of protected monomers have focused on both accessibility and ease of protecting group removal post-polymerization. For example, an acetonide protecting group shows promise and limited degradation upon deprotection.[49] Although protecting group chemistry is generally the most commonly explored strategy, controlled polymerization with DMA has been achieved in specific instances.[47,50]

To extend the scope of catechol- and gallol-containing synthetic polymers beyond dopamine-based compounds, a range of other polymers and monomers have been explored. One well-studied monomer is the commercially available, styric compound, 3,4-dimethoxystyrene. Using this monomer, poly[(3,4-dihydroxystyrene)-*co*-styrene] was synthesized, and its adhesive properties were studied under various conditions.[51,52] A homopolymer of 3,4-dimethoxystyrene[53] was accessed through reversible addition–fragmentation chain-transfer (RAFT) polymerization, and upon demethylation, the free catechol moieties were investigated for their metal binding capacity, which was independent of molecular weight. Commercially available phenolic monomers have therefore allowed for the rapid access of functional polymers. However, it has been recently demonstrated that RAFT-prepared gallol-containing polymers have superior free-radical scavenging ability over catechol polymers.[54] This finding demonstrates the trade-offs between synthesizing the required monomer from simple building blocks and the use of a commercially available monomer that can be readily polymerized.

The synthesis of novel phenolic monomers has also been crucial for expanding the scope of functional phenolic materials. One well-studied monomer, triethylsilane-protected eugenol acrylate (TES-EA), can be prepared in three steps from eugenol. TES-EA has been copolymerized with four other monomers to form a polymeric mussel foot protein analog[55] or assembled as a *co*-block for further complexation and quaternization with chitosan.[56] In another recent example of synthesized phenolic monomers, linear polymeric antioxidants were prepared with complex catechol- and gallol-like functional groups, which allowed for control over a variety of material properties such as hydrophobicity.[57]

Though an array of synthetic monomers and polymers have been synthesized, with near endless possibilities for future structures, other factors beyond simply the addition of phenolic moieties need to be considered. Specifically, numerous fundamental studies have begun to explore the structure–function relationships between the components of synthetic phenolic polymers. For example, a fundamental study on the polarity of the backbone of a synthesized polymer containing catechol moieties has shown additional complexity in the synthesis because the polarity changes specific functional properties of the polymer such as underwater adhesion.[58] Other investigations into redox-active catechol-containing polymers have shown that changing the catechol-containing monomer as well as the comonomer can have performance effects for electrochemical energy storage.[59] Switching from catechol to gallol moieties has also been observed to change the properties of materials, for example, the underwater adhesion of a polymer can be increased sevenfold.[60] These studies demonstrate a few examples of the structure–function relationships of the various components within phenolic polymers, highlighting the importance of these relationships for designing future materials. Collectively, a variety of routes of different complexity and versatility exist for synthesizing phenolic polymers, and many high-performance functional materials can be engineered by combining the attributes of phenolics with carefully designed polymers.

3. Thin Films

Phenolic compounds tend to be universally adherent and therefore are suitable for use as building blocks in constructing thin films on diverse substrates.[16] Three general approaches have been developed to date using phenolic compounds for thin film formation: MPN assembly,[16] LbL assembly,[61] and one-pot synthesis of PDA coatings.[29] MPNs are formed rapidly through a combination of metal–phenolic coordination bonds and adherence between the phenolic materials and the substrate. Alternatively, LbL-assembled films are constructed by first adhering a phenolic to the substrate, followed by sequential buildup of metal ions or polymers, and phenolics. PDA-based materials are prepared from the self-polymerization of dopamine under mild conditions on a substrate. Choice of the deposition methods and materials allows for control over the physicochemical properties of the resultant thin films.[62] For example, when TA and iron ions are assembled into MPNs, they have different disassembly kinetics than when they are assembled into LbL films.[63] The following sections focus on these three approaches for assembling phenolic thin films and highlight some of the different building blocks and substrates applicable for preparing phenolic thin films, as well as the physicochemical differences arising from the different assembly mechanisms.

3.1. Metal–Phenolic Network Assembly

The recent introduction of MPNs has expanded the scope of phenolic thin films to a variety of different materials, applications, and deposition techniques, as highlighted in recent reviews.[22,64] The present section provides a general overview of the methodologies, building blocks, substrates, and technologies that have to date been used for forming MPNs (Figure 2a–h). MPNs have originally been constructed from metal ions, such as Fe^{III} or Al^{III}, coordinated with multidentate phenolic ligands, such as TA and epigallocatechin gallate (EGCG).[16] The deposition process is independent of the substrate—silica, gold, iron oxide, emulsions, and even bacteria could be coated in a matter of seconds after mixing the metal ions and phenolic building blocks. Generally, the pH is raised to stabilize the complexes in the tris complex form after mixing the building blocks, with acidic environments leading to slow disassembly of the MPNs.[16] Other substrates such as lignin,[65] collagen,[66] yeast (Figure 2e–h),[67] adherent mammalian cells, and red blood cells have been used as substrates, with unique applications, such as sporulation or reduced immune responses, demonstrating the wide utility of these materials.[62,68,69]

The toolbox of applicable building blocks rapidly expanded after the introduction of MPNs. Different metals have been explored to yield both novel applications for MPN films and to control the physicochemical properties of the films (Figure 2i). Applications such as fluorescence imaging, magnetic resonance imaging (MRI), positron emission tomography (PET) imaging, and catalysis were realized by appropriate choice of the incorporated metal, which included Eu^{III}, Gd^{III}, Cu^{II}, and Rh^{III}, for each application, respectively.[70] The choice of metal additionally determined MPN film disassembly at different pH values, with the Al^{III}-based film showing disassembly within a physiological pH range (pH 5–7.4) suitable for drug delivery applications.[71] Additionally, the metalloid-containing molecule diphenylboronic

acid has been used instead of a metal ion to allow for the formation of films that disassemble in the presence of *cis*-diols.[72]

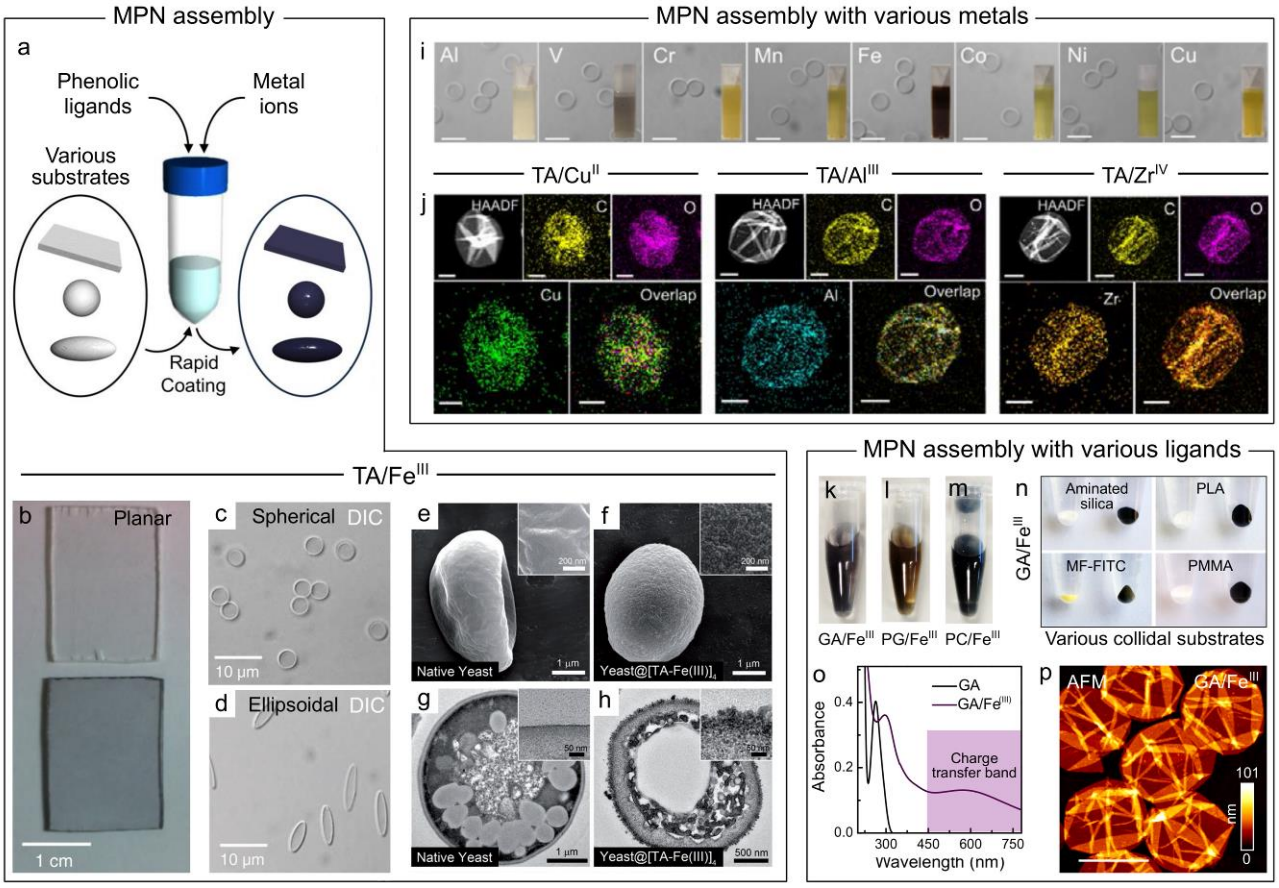

Figure 2. (a) Schematic of MPN assembly. Adapted with permission.[16] Copyright 2013 American Association for the Advancement of Science. TA/Fe^{III} films and capsules synthesized on diverse substrates: (b) planar (photographs), (c) spherical and (d) ellipsoidal (differential interference contrast (DIC) images), and (e–h) yeast cells (scanning electron microscopy images). (b–d) Reproduced with permission.[16] Copyright 2013 American Association for the Advancement of Science. (e–h) Reproduced with permission.[67] Copyright 2016 Wiley-VCH. MPN assembly with various metals: (i) capsules obtained from different TA/M systems (M = Al^{III}, V^{III}, Cr^{III}, Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, and Cu^{II}) (DIC images) and the corresponding (j) high-angle annular dark-field spectra of the capsules. Scale bars are 5 μm in (i) and 1 μm in (j). Reproduced with permission.[70] Copyright 2014 Wiley-VCH. (k–p) MPN assembly with various phenolic ligands: photographs showing the colors of capsule dispersions of GA/Fe^{III} (k), PG/Fe^{III} (l), and PC/Fe^{III} (m) systems, and different colloidal substrates coated with GA/Fe^{III} (n); and (o) absorption spectra of GA and GA/Fe^{III} capsule dispersion and (p) atomic force microscopy (AFM) image showing the morphology of dried GA/Fe^{III} capsules. Reproduced with permission.[75] Copyright 2015 American Chemical Society.

A wide variety of synthetic and biological phenolic ligands have also been used, including flavonoids, tea infusions, and single-ring phenolic moieties.[73-75] Small phenolic ligands, namely gallic acid (GA), pyrogallol (PG), and pyrocatechol (PC), were used to demonstrate that at least one vicinal diol group is necessary for MPN film formation (Figure 2k–p).[75] The choice of phenolic ligand (small or multidentate ligands) used for deposition strongly influences the final disassembly kinetics of MPN films.[75]

Additionally, hybrid synthetic analogs including PEG–DOPA polymers,[76] HA–DOPA polymers,[77] or TA modified with peptides[78] can be used to form MPNs, thereby allowing for new functionalities and applications to be realized.

Early MPN studies used solution-based batch processing for the formation of MPNs.[16,70,71] Since then, other approaches commonly used for the formation of LbL films and capsules have been used. Specifically, spray assembly has been used for the formation of MPNs; the technique readily affords the coating of large substrates such as fruits or shoe inserts (Figure 3a,b).[79] This is an important development for the application of MPNs, as spraying can be incorporated into industrial supply chains to allow for continuous processing. Similarly, the continuous processing of MPN capsules has recently been demonstrated using microfluidics (Figure 3c–f). Although, careful choice of solvents for both the phenolic ligand and metal ions was crucial owing to the fast kinetics of the coordination complexation.[80]

In previous studies,[16,70,75] MPN film formation has been observed to proceed in discrete steps, ~10 nm increments, where interfacial assembly ceases beyond a finite time (<60 s). This limitation has been addressed in recent studies where it has been shown that the assembly process for MPNs can be modulated from discrete to continuous by using solid-state metal precursors such as rusted nails (Figure 3g–m).[81] This

continuous assembly method has not only yielded the thinnest MPN films (~5 nm) to date, but also produced high-quality multiligand MPN capsules from crude phenolic extracts such as green tea infusions.[82] Another recently demonstrated continuous MPN assembly method used an electro-triggered assembly approach, where a mixture of TA and

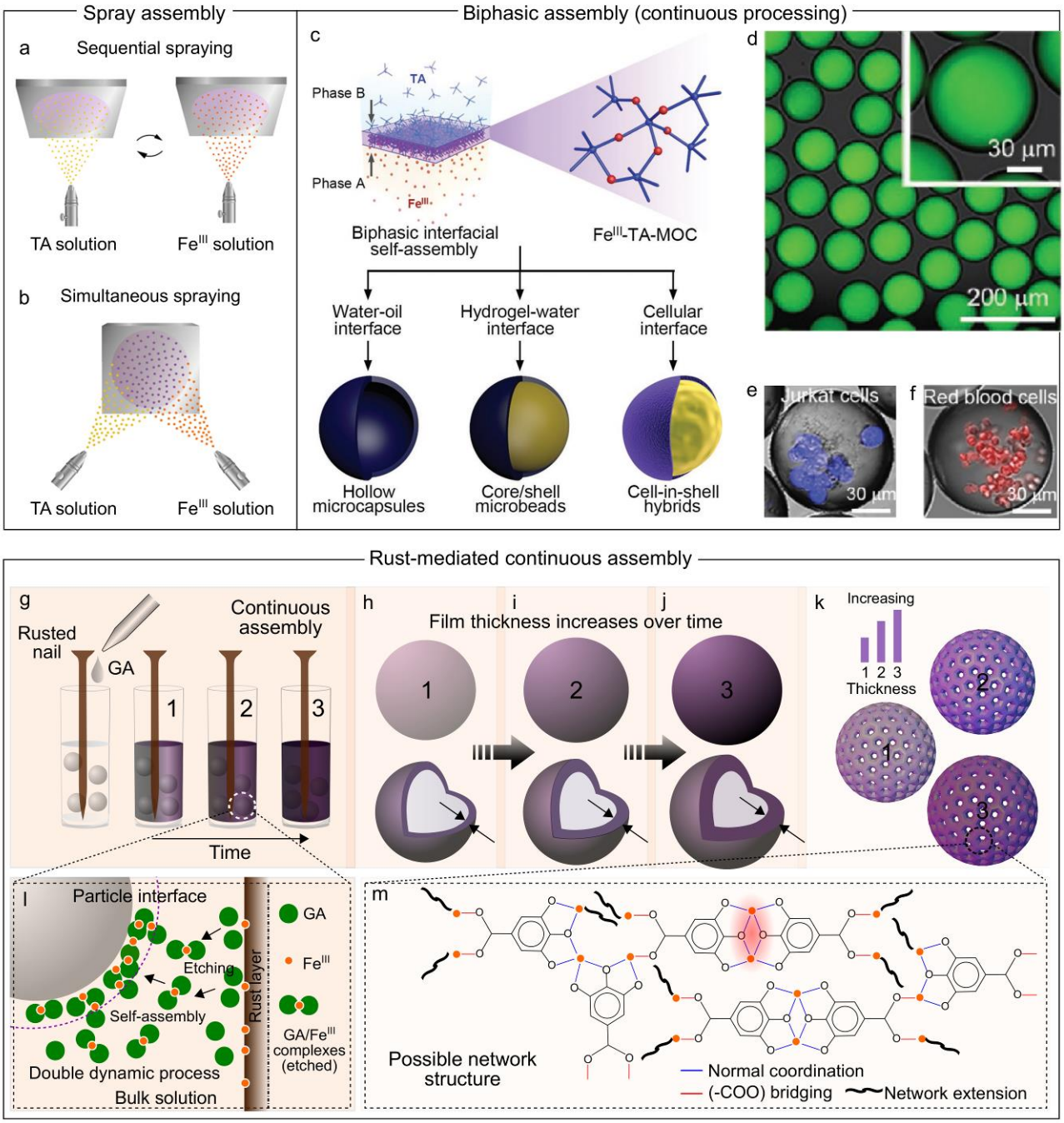

Figure 3. Schematic representations of different methods for MPN assembly. (a,b) Spray coating (sequential and simultaneous) assembly method. Reproduced with permission.[79] Copyright 2017 Springer Nature. (c–f) Biphasic assembly for continuous processing: schematic of method (c); dextran–fluorescein isothiocyanate (d); and cells-encapsulated microcapsules in solution (e,f). Reproduced with permission.[80] Copyright 2016 Wiley-VCH. (g–k) Rust-mediated continuous assembly method, (l) interfacial interactions, and (m) possible network structure of assembled films obtained using this method. Reproduced with permission.[81] Copyright 2017 Wiley-VCH.

Fe^{II} were incubated in the presence of an electrode.[83] Fe^{II} was electrically converted in situ into Fe^{III}, thereby allowing for the continuous growth of MPNs on the electrode modulated by the metal–ligand ratio, and the intensity and duration of the applied current.

Experiments on the growth behavior of MPNs have recently been conducted using precursor solutions of various ionic strengths; the results have shown that salts can shield the chelation complex and thereby enable the formation of thicker

and rougher films.[84] Additionally, the redox properties of MPNs have been elucidated in a recent electrochemical study.[82] Though many previous studies have provided useful insights into various aspects of MPN assembly,[16,75,81] more fundamental studies are required to elucidate the kinetic and thermodynamic aspects. The structure–function relationship of MPNs, when assembled from different

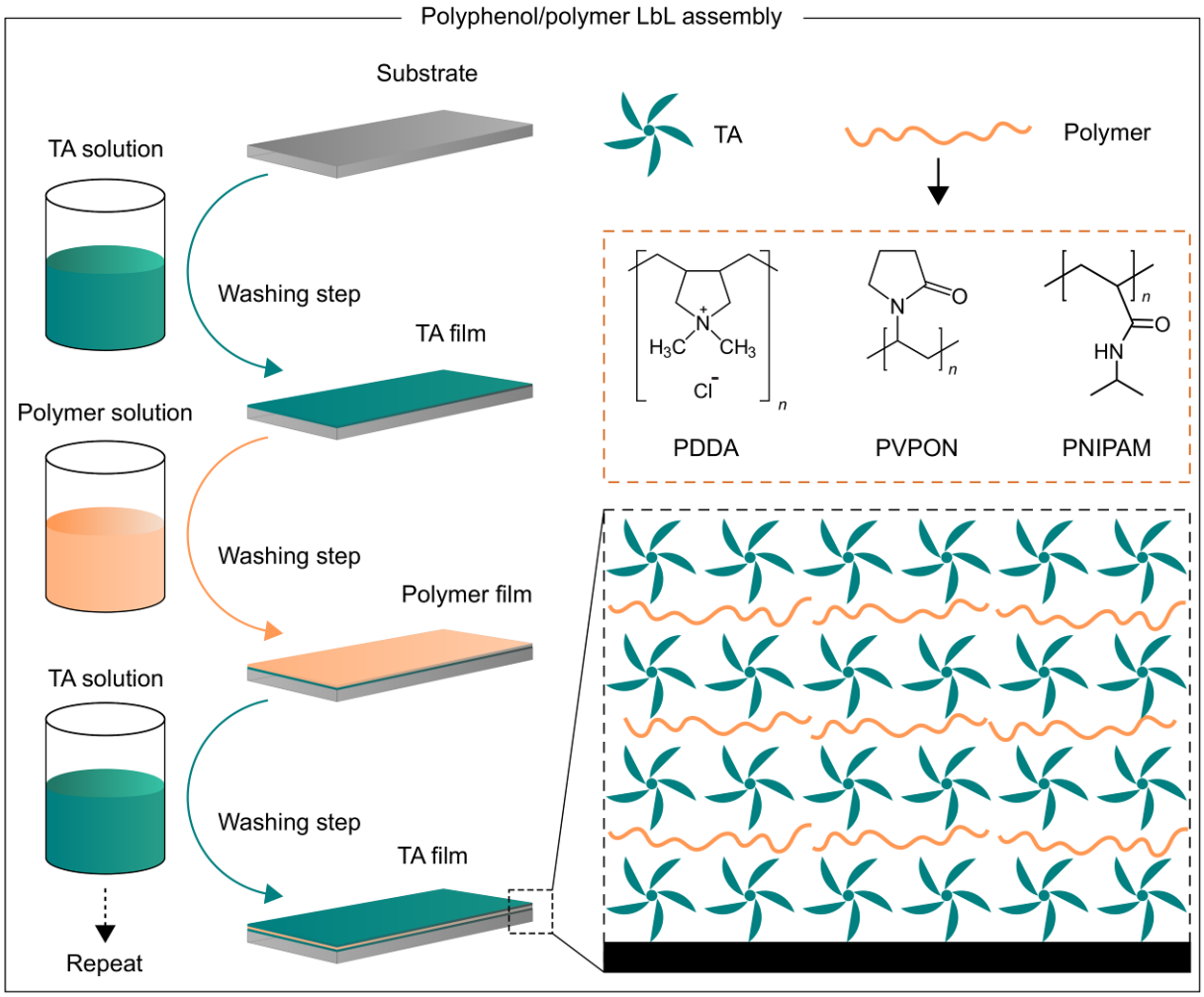

Figure 4. Illustration of the general method for LbL assembly of TA with different polymers such as poly(dimethyldiallylamide) (PDDA), poly(vinylpyrrolidone) (PVPON), and poly(*N*-isopropylacrylamide) (PNIPAM).

phenolic building blocks, is another aspect that needs to be investigated toward establishing design principles for future MPNs. Finally, it is foreseeable that other thin film assembly techniques adopted from LbL assembly, including vacuum filtration or dewetting, could be used to assemble MPNs with unique properties.[85]

3.2. Layer-by-Layer Assembly

TA has been used extensively as a building block for LbL film formation owing to its ability to form hydrogen bonds and electrostatically interact with a wide range of biological and synthetic polymers such as chitosan, poly(dimethyldiallylamide) (PDDA), poly(vinylpyrrolidone) (PVPON), and poly(allylamine hydrochloride) (some of these structures are shown in Figure 4).[61] Generally, the pH of the growth solutions has a significant influence on the growth behavior and mechanical properties (e.g., permeability) of the resulting films, as the degree of protonation or deprotonation of the phenolic moieties varies with pH.[86] Thermoresponsive polymers, such as poly(*N*-isopropylacrylamide) (PNIPAM), can be used with TA to engineer unique temperature and pH bi-responsive thin films.[87] A more recent development has been the modification of synthetic polymers, such as poly(acrylic acid), with catechol groups to allow for multilayer growth with PVPON.[88]

Detailed investigations into the assembly process of TA-containing LbL films have demonstrated a pH dependence on the film growth depending on whether the layer buildup is accomplished through hydrogen bonding or electrostatic interactions.[89] For example, TA and poly(*N*-vinylamide)s display higher affinities for each other at low pH, where the gallol groups of TA are protonated and thus form hydrogen bonds efficiently with the carbonyl groups of poly(*N*-vinylamide)s. Consequently,

a larger mass is deposited for each layer at low pH.[89] PVPON was deposited by LbL assembly with TA through hydrogen bonding. The molecular weight of PVPON played an important role in controlling the permeability of the resultant thin films, with lower molecular weight PVPON yielding films of higher permeability. Furthermore, for a given PVPON molecular weight, the permeability of the TA–PVPON films decreased when the incubation pH was changed from pH 6 to pH 9.[87] Poly(2-ethyl-2-oxazoline) can also be used to form LbL thin films through hydrogen bonding with TA.[90]

Alternatively, thermodynamically stabilized materials, such as micelles,[91] can be assembled into thin films with phenolic compounds without disruption. Similarly, proteins can be used as an intermediary layer for TA-based LbL films,[92] and it has been demonstrated that TA does not inhibit the enzymatic activity of the incorporated enzymes after film growth.[93] These thin films have allowed for a variety of applications to be targeted including wound healing and metal sequestration,[94] due to the antioxidant properties[95] and metal affinity of phenolic compounds, respectively.[91]

More recently, the multilayer assembly of phenolics has also been accomplished using metal ions instead of polymers.[63,96] These films are assembled in a LbL (multistep) process and have different physicochemical properties from MPN films prepared from the same components (i.e., TA and Fe^{III}) such as different disassembly kinetics and permeability.[63] As metal ions and phenolic substrates are soluble in a wide range of solvents, multilayer assembly can be conducted in both organic and aqueous solvents.[63,96] The layer order, that is, whether TA or Fe^{III} is deposited first, has a significant effect on the final film properties, as does post-treatment at different pHs.[97] Investigations are ongoing to elucidate the differences between MPNs and LbL films, and it is likely that the wide range of LbL assembly techniques used for other polymer combinations[85] will be applied to phenolic materials in the near future.

3.3. Oxidative Self-Polymerization Assembly

Adhesive biomaterials produced by marine organisms are known to possess superior mechanical properties (e.g., strength, toughness, and durability) when compared to many synthetic materials.[12,98,99] The exceptional ability of mussels to strongly attach to diverse substrates (Figure 5a), including wet surfaces with high binding strength, has been the focus of extensive research over the past two decades.[98,99] Early investigations into the wet adhesion properties of mussels have shown that DOPA and lysine-enriched proteins at the plaque–substrate interface play critical roles for such robust adhesion of mussels (as mentioned earlier).[12,13,98] Based on these initial observations, in 2007, Lee et al.[29] demonstrated a surface coating technique via dopamine polymerization (Figure 5b–f). The resulting material is known as PDA. Recent reviews have extensively detailed and summarized the numerous PDA studies conducted to date,[100,101] and in the present section, we provide a brief overview of the versatility and functionality of PDA-based materials. In addition, we briefly discuss the plant-derived phenolic building blocks capable of forming films via oxidative self-polymerization such as dopamine.

The distinct advantage of PDA film formation is that it can be achieved on a wide range of substrates, including inorganic, organic, and hydrophobic surfaces, via oxidative self-polymerization of dopamine under mild basic pH conditions (Figure 5b–g).[29,99] Besides planar substrates, PDA coatings can also be applied to various particulate substrates to prepare functional core–shell particles and capsules via core removal (Figure 5g).[102,103] Despite the wide applicability and methodological simplicity of the PDA films, the actual mechanism of PDA formation has remained controversial possibly because of the generation of a series of reaction intermediates during the polymerization reaction and the complex redox process associated in each step.[104] In earlier studies, the formation of PDA was believed to involve a process akin to the pathway of melanin (eumelanin, a natural pigment commonly found in bacteria, fungi, plants, and animals) production in living organisms.[104,105] This is known as the "eumelanin" model of PDA formation where covalent interactions are regarded as the dominant driving force (Figure 5g).[102,104,106] Alternatively, a physical self-assembly pathway has been proposed, wherein a combination of different noncovalent interactions, such as hydrogen bonding, charge transfer, and π–π stacking, contribute to the formation of PDA films.[107]

As the field progressed, various chemical routes, including selective chemical reactions, such as the secondary treatments shown in Figure 5h, have been explored to modify PDA films, yielding materials with alternative functionalities. For example, an anticancer drug, doxorubicin (DOX), was conjugated to PDA capsules through the formation of an acid labile covalent bond on thiolated poly(methacrylic acid) for drug delivery applications.[108] In another example, a potentiometric sensor designed from a polymeric membrane ion-selective electrode was imprinted in the PDA layer for the detection of biological analytes.[109]

PDA surfaces have also been used to conduct various polymerization reactions. For example, atom transfer radical polymerization (ATRP) initiators were immobilized in PDA-coated carbon nanotubes,[110] magnetic nanoparticles,[111] and ordered mesoporous carbon (Figure 5h)[112] to allow for the surface-initiated growth of polymer brushes. PNIPAM polymers were also grown on PDA particles and capsules using activators regenerated by electron transfer ATRP. The inward and outward growth of the polymer chains could be controlled by solvation effects and hydrothermally induced regulation of the pore network of PDA.[113] Polymerization techniques other than ATRP have been exploited, for example, a carbonyl–azide RAFT agent was coupled to the surface of PDA-coated silica particles to perform "grafting from" polymerization reactions.[114]

Owing to the presence of abundant catechol groups, PDA films can display diverse properties including metal chelation and reduction.[2,115] Combining these properties, a multilevel functionalization strategy to construct PDA-based single nanoparticle@metal–organic framework (MOF) core–shell nanohybrid systems has recently been demonstrated (Figure 5i).[116] Besides conformal coatings, dopamine polymerization can lead to the formation of self-assembled PDA nanoparticles under appropriate conditions.[117,118] Inspired by the structural colors produced from the self-assembled melanosomes in avian feathers, Xiao et al.[119] demonstrated the assembly of PDA-

based synthetic melanin nanoparticles to fabricate colored films (Figure 5j–l). These nanoparticles showed a high refractive index and broad optical absorption in the UV–visible range.

In addition to dopamine, plant-derived phenolic compounds have been observed to undergo oxidative self-polymerization at slightly basic pH and form colorless coatings on various substrates (Figure 6a–d).[120] In a pioneering study, Sileika et al.[120] illustrated this phenomenon using plant polyphenols such as EGCG, PG, and TA. The resulting coatings not only showed antibacterial and

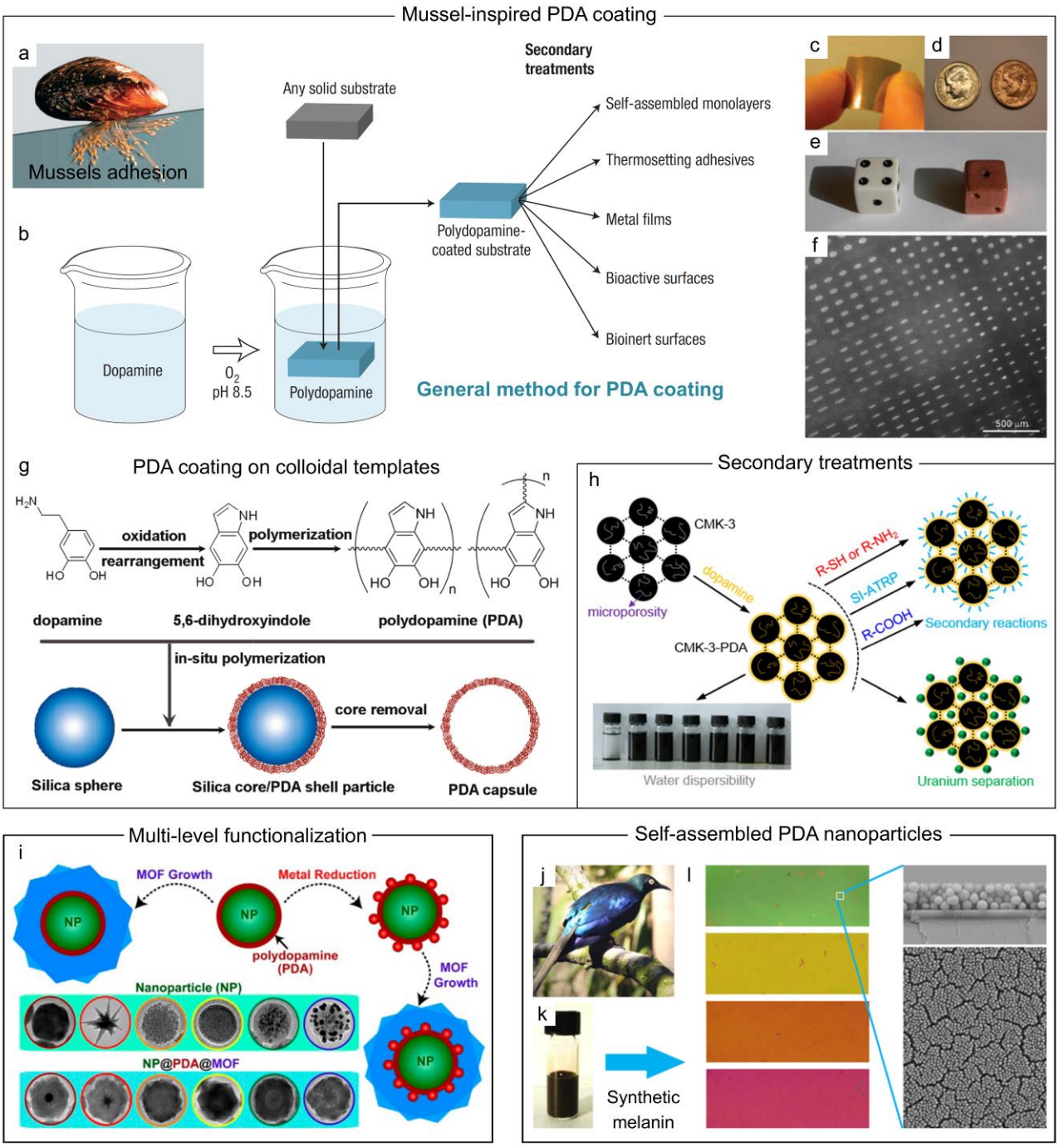

Figure 5. (a) Adhesion of marine mussel *Mytilus californianus* to a surface. Reproduced with permission.[98] Copyright 2011 Annual Reviews. (b) Schematic of mussel-inspired polydopamine (PDA) coating method and subsequent treatment (secondary) to fabricate functional materials. Reproduced with permission.[99] Copyright 2008 Springer Nature. (c–e) PDA coating on different solid substrates and (f) electroless silver metallization of a photoresist-patterned surface coated with PDA. Reproduced with permission.[29] Copyright 2007 American Association for the Advancement of Science. (g) Schematic of PDA coating on colloidal templates and the resulting PDA capsules after template removal. Reproduced with permission.[102] Copyright 2009 American Chemical Society. (h) Illustration of surface modification of ordered mesoporous carbon CMK-3 by PDA chemistry leading to improved water dispersibility, uranium binding ability, and potential for post-functionalization through secondary reactions. Reproduced with permission.[112] Copyright 2016 American Chemical Society. (i) Schematic illustration of the stepwise synthesis of nanoparticle@PDA, nanoparticle@PDA@metal–organic framework (MOF), and metal nanocatalyst-loaded nanoparticle@PDA@MOF core–shell hybrid nanostructures and examples of the as-synthesized structures. Reproduced with permission.[116] Copyright 2015 American Chemical Society. (j–

l) Avian feather-inspired periodic assembly of PDA-based synthetic melanin nanoparticles to fabricate colored films. Reproduced with permission.[119] Copyright 2015 American Chemical Society.

antioxidant properties, but also could be used to modulate the optical properties of inorganic nanoparticles such as gold nanorods (Figure 6d). Many examples have followed, thus affording a large family of plant-derived phenolic compounds to be used for surface modification via oxidative self-polymerization.[121,122] Instead of using basic pH, UV radiation can induce the oxidative self-polymerization of phenolic compounds[123] and has been used to construct patterned thin films (Figure 6e–g).[124] As the field grows through expanding the library of building blocks and different methodologies, a wide variety of new materials and applications are expected to emerge.

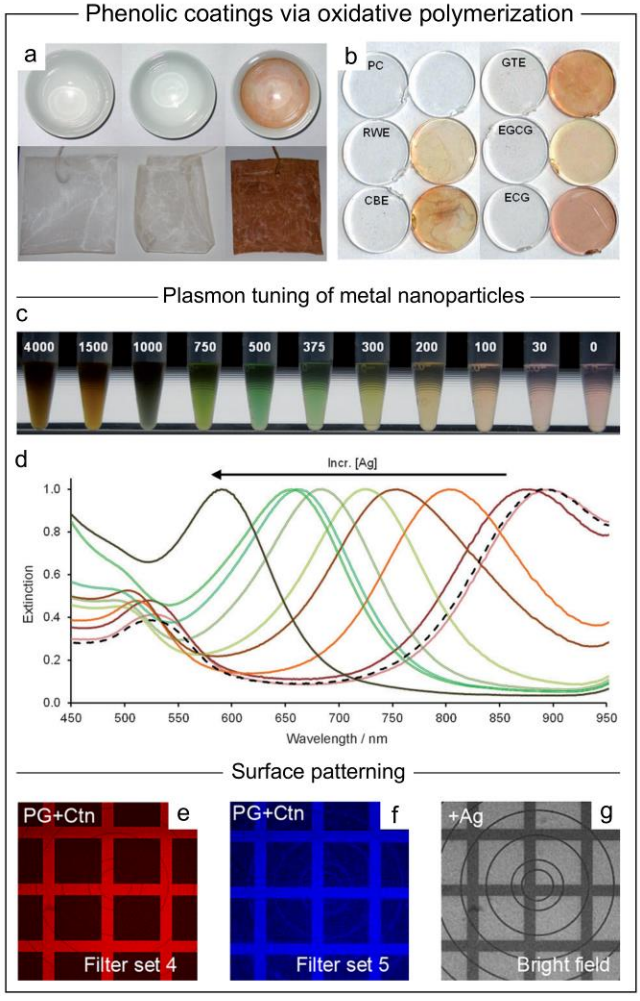

Figure 6. (a) Adherent polyphenol coatings deposit on surfaces exposed to tea infusions. (b) Coatings deposited onto clear polycarbonate (PC) disks using various natural polyphenols. For each pair of disks, the disk on the right has also been treated with aqueous silver nitrate to visualize the coatings. Plasmonic tuning of metal nanoparticles through templated synthesis of core–shell nanorods using plant polyphenol-inspired coatings: (c) blue shift of the longitudinal surface plasmon resonance wavelength as indicated by a color change of the nanorod suspension and (d) normalized optical extinction spectra of Au-pyrogallol (PG)-Ag nanorods, illustrating plasmon tuning through control of the Ag shell thickness. Reproduced with permission.[120] Copyright 2013 Wiley-VCH. Patterning of polyphenol coating by UV irradiation: (e) overlaid pattern formed on the surface by first UV irradiating PG solution through a photomask with circular patterns, followed by washing and rhodamine modification; (f) pattern formed on the surface by UV irradiating the catechin (Ctn) solution through a photomask with square patterns (fluorescence microscopy images were taken using filter sets 4 and 5); and (g) bright-field microscopy image of the silver-modified pattern. Reproduced with permission.[124] Copyright 2018 American Chemical Society.

4. Particles

The diverse chemistry of phenolic moieties has led to the development of a variety of phenolic-based particulate materials including hollow capsules, crystalline particles (such as MOFs), nanoparticles, micelles, and superstructures. Similar to thin films, phenolic particles are most commonly formed by self-assembly from a variety of phenolic building blocks. GA has been traditionally used as a ditopic ligand for MOF synthesis. Although, more recently other natural and synthetic phenolic ligands have been used with a variety of metal ions. Other self-assembled structures include nanoparticles, micelles,[125] vesicles,[126] and brushes,[127] which can be produced by controlling the assembly conditions. Moreover, metal ions can be used to assemble phenolic-coated particles into superstructures.[128] The wide structural diversity in these self-assembled particles has made phenolic building blocks powerful motifs in nanomaterials design, and the present section broadly summarizes the current state of the field.

4.1. Capsules

Capsules are an important class of particle systems that find applications ranging from biomedicine to catalysis.[85] The synthetic strategy for capsule formation generally involves two stages: 1) film formation on colloidal templates and 2) subsequent removal of the templates.[62,85] Phenolic capsules can be prepared by all of the different coating techniques (i.e., MPN, LbL, and PDA assembly) discussed in Section 3. The methodological details for phenolic capsule formation have been recently reviewed[129] and will not be discussed separately in this section.

4.2. Crystalline Particles

The use of phenolic compounds as organic ligands for the formation of crystalline coordination polymers, or MOFs, can be traced back to at least 1991, when Fe^{III}–gallate MOFs were prepared using GA and Fe^{III} salt as precursors.[130] However, unlike carboxylate and imidazole-based ligands, the exploration of phenolic ligands has not flourished in MOF research though the recent upsurge in interest is noticeable.

The synthesis of Fe^{III}–gallate MOFs was reinvestigated using a solvothermal route and extended to other transition metals such as Mg^{II}, Mn^{II}, Co^{II}, and Ni^{II}, and Zr^{IV}.[131-133] The GA-based MOFs are isostructural and composed of infinite chains of corner-sharing MO_6 octahedra (where, M = Zr^{IV}, Fe^{III}, Mn^{II}, Co^{II}, Ni^{II}, Mg^{II}) connected by the gallates (an example is provided in Figure 7a).[131,132] Expanding on GA-based MOF structures, a synthetic digallate ligand can be used to form phenolic Zr^{IV}–MOFs (Figure 7b,c).[134] Both GA- and digallate-based MOFs

show enhanced chemical and hydrolytic stability, owing to the high pK_a of the phenolate groups which strengthens the Zr–O bonds, compared with the typical Zr^{IV}–carboxylate MOFs.[133,134]

Crystalline metal–catecholates are another emerging class of MOFs that use synthetic catechol derivatives, with metals such as Co^{II}, Ni^{II}, Fe^{II}, Ti^{IV}, and V^{IV} (Figure 7d–f).[135,136] Fe–catecholate MOFs show mixed oxidation states of Fe and an ultrahigh proton conductivity comparable to that of Nafion.[136] Ellagic acid has also been used to form crystalline materials with metal ions (in this instance Zn^{II}).[137] Finally, catechol-containing molecules can also be used for the surface functionalization of MOFs, as demonstrated by the use of a gallol-containing lipid molecule to

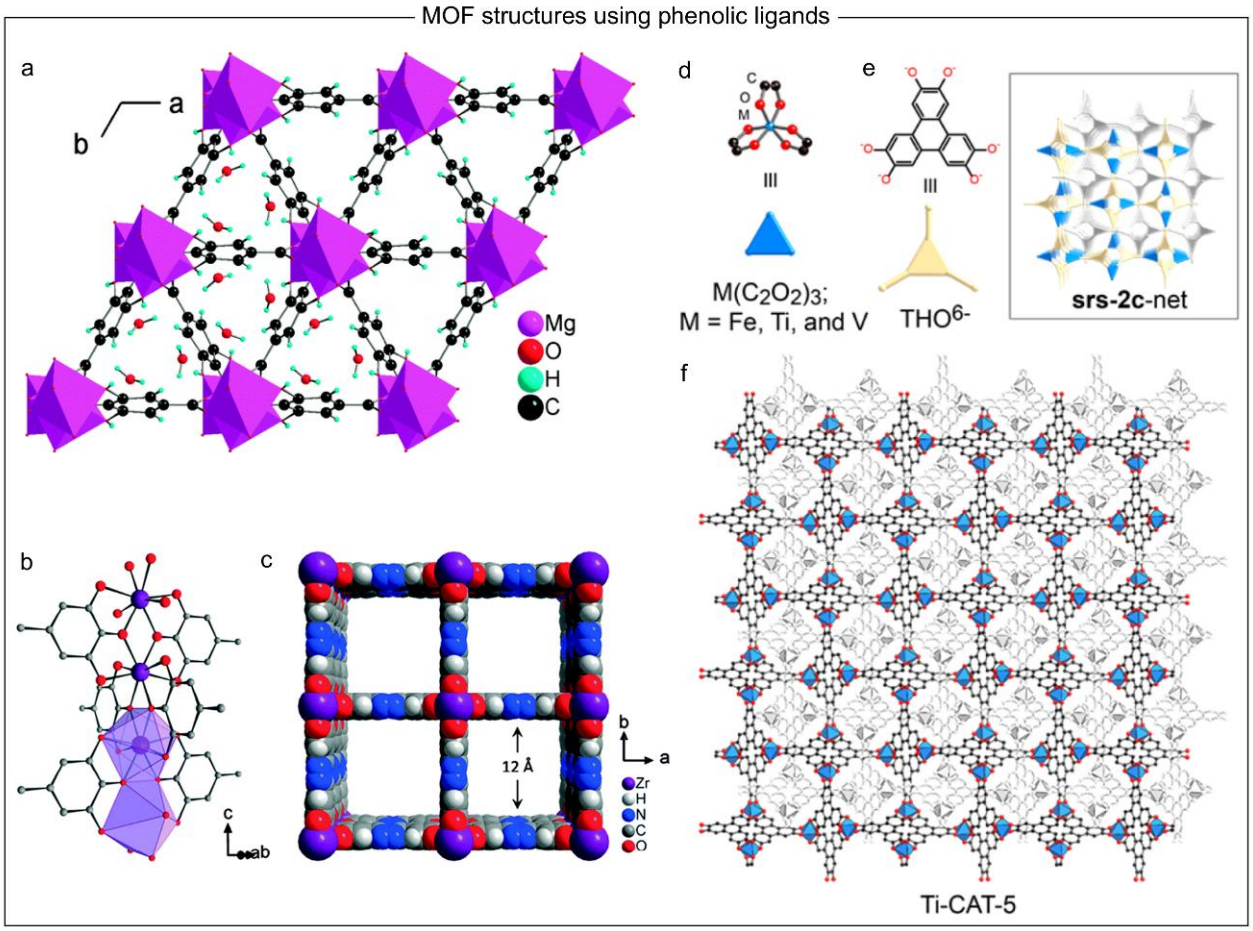

Figure 7. (a) Structural representation of the Mg^{II}–gallate MOFs. Reproduced with permission.[131] Copyright 2014 Wiley-VCH. Structure of Zr^{IV}–gallate MOFs: (b) view of a single chain showing the Zr atoms coordinated by gallol groups and (c) view of the structure along the [001] direction. Reproduced with permission.[134] Copyright 2015 Wiley-VCH. (d,e) Crystalline metal–catecholates frameworks constructed from H_6THO ligand (THO^{6-} = triphenylene-2,3,6,7,10,11-hexakis(olate)) with Fe^{II}, Ti^{IV}, and V^{IV}, and (f) simplified representation of the resulting topology. Reproduced with permission.[136] Copyright 2012 American Chemical Society.

modify the dispersibility of MOF particles.[138]

4.3 Nanoparticles, Micelles, and Superstructures

Self-assembled nanostructures from phenolic compounds can be prepared through various interactions including hydrogen bonding, metal coordination, oxidative self-polymerization, and any combination thereof. Examples of a few of these nanoparticle systems have been provided in Section 3.3 and herein, we highlight some of the recent advances in the field. For instance, Wang et al.[139] reported a self-assembled nanoparticle system with an average size of ~140 nm using TA and a poloxamer, Pluronic F-127. After incorporating ^{89}Zr into the system, the composite particles were used for tumor PET imaging. PEG-modified Pt prodrug nanocomplexes were prepared via metal–phenolic coordination using an emulsion-based process.[140] The resulting particles with an average size of ~100 nm showed a high drug loading capacity and low fouling properties. Another recent study demonstrated a series of metal-loaded PDA nanoparticles via oxidative self-polymerization of metal−dopamine complexes in the presence of free dopamine.[141] Among the various metal-loaded systems investigated, Mn^{III}-loaded PDA nanoparticles showed high spin, low anisotropy, and weak magnetic coupling and therefore, superior relaxivity behavior when compared with Fe^{III}-loaded PDA nanoparticles.[141]

Phenolic–micellar structures can be formed through metal or boron complexation with various catechol derivatives. For example, micelles from telodendrimers with either catechol or

boron functionalities can be assembled using dual-responsive boronate crosslinking.[125] These micelles are pH and diol responsive, and when functionalized with a catechol-based dye exhibit dramatic changes in color.[125] Catechols have been incorporated into linear di-block copolymers, instead of branched dendrimers, and used to incorporate boronic acid-containing drugs, such as bortezomib, to micelles.[142] In an alternative strategy towards pH and diol responsive micelles, block copolymers of either PEG-*b*-catechol or PEG-*b*-phenylboronic acid were synthesized and mixed to form well-defined, stable, core crosslinked polyion complex micelles (Figure 8a).[143] A small molecule polyion complex micelle system has also been developed for drug delivery using EGCG as a crosslinker in the assembly to prevent DOX-induced cardiotoxicity during drug release.[144] Alternatively, metal–catechol coordination can be

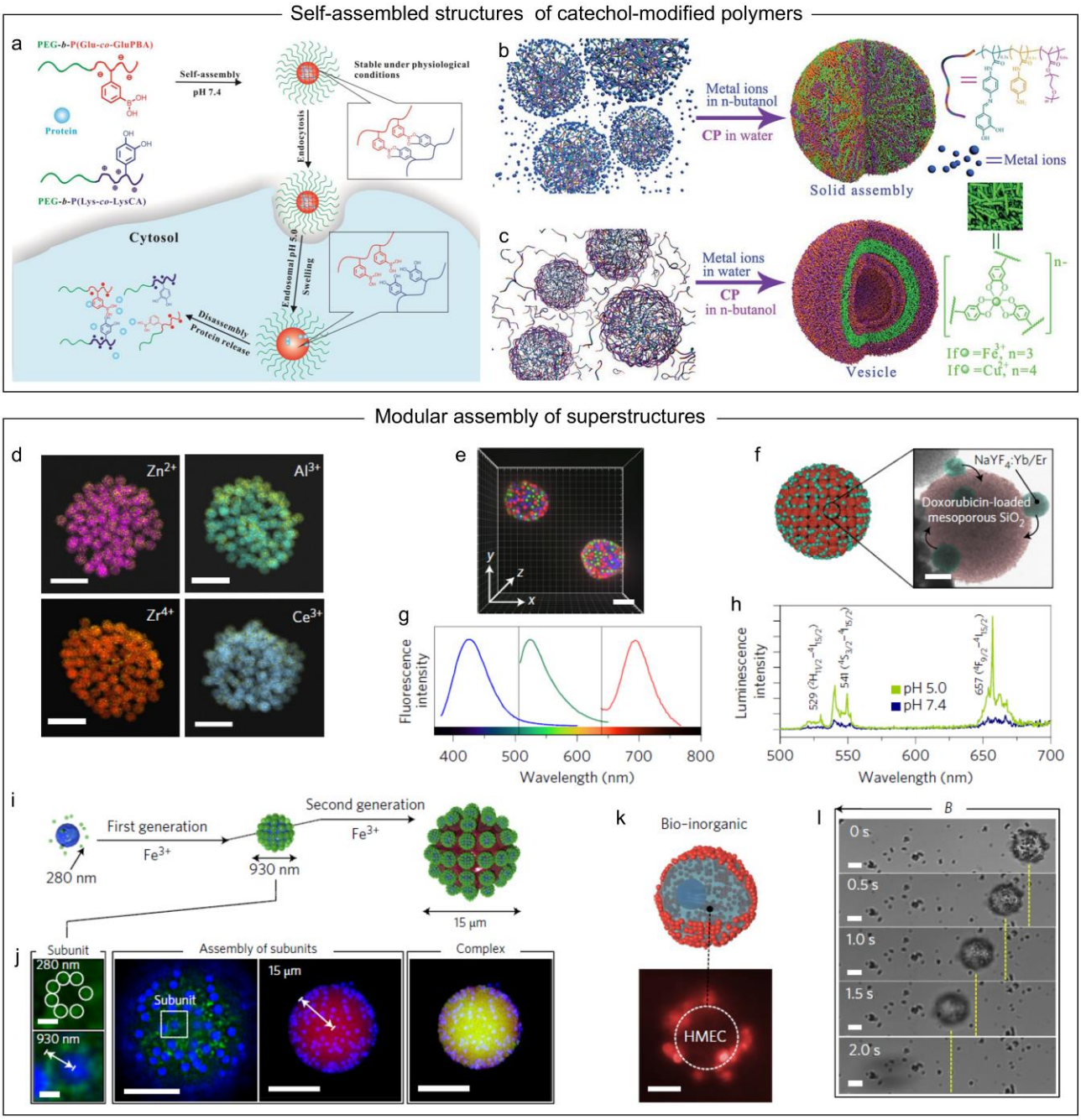

Figure 8. Self-assembled structures of catechol-modified polymers using different crosslinking strategies such as (a) core-crosslinked polyion complex micelles (using catechol–boron complexation), and (b) either solid assemblies or (c) vesicles (using catechol–metal complexation). (a) Reproduced with permission.[143] Copyright 2013 American Chemical Society. (b,c) Reproduced with permission.[126] Copyright 2015 Royal Society of Chemistry. (d–l) Structural tailorability of modular-assembled superstructures using phenolic coatings characterized by various spectroscopic methods. Reproduced with permission.[128] Copyright 2015 Springer Nature.

used to crosslink micelles, allowing for drug loading and pH-responsive release.[140,145] For example, PEG-*b*-PDOPA copolymer can be crosslinked using Fe^{III}–catechol coordination to generate drug-loaded theranostic micelles, which can assemble and disassemble through a change in acidity enabled by the coordination crosslinks.[146]

Block copolymers with a catechol-containing segment can also be used for phenol-specific drug loading. In an example by Chan et al.,[147] DOX was loaded into the core of catechol/imidazole mixed micelles via the organocatalytic Raper–Mason reaction between the amine groups of the drug and the catechol groups of the phenolic polymer. The resulting imine bond was hydrolyzable, demonstrating pH-dependent drug release from the micelles in vitro. These micelles can also be embedded into a hydrogel using strain-promoted alkyne−azide chemistry to form a composite material, further advancing the use of phenolic micelles.[148]

In an elegant synthesis of a norbornene-containing macromonomer with a pendant silyl-protected catechol, bottle brushes were synthesized and crosslinked using ketone functional groups. This design allowed for the presence of free catechols after gel formation, and the catechols could slow the drug release rate from the network when compared to individual micelles.[127] Other macrostructures can be achieved using copolymers of poly(*N*-(4-aminophenyl) methacrylamide-*co*-polyethylene glycol monomethyl ether methacrylate), where post-polymerization functionalization through a Schiff base formation from 3,4-dihydroxybenzaldehyde allowed for assembly with co-solvent mixtures of Fe^{III} or Cu^{II} into either solid particles or vesicles (Figure 8b,c).[126] Very recently, fiber-like self-assembled materials were obtained from TA and poly(2-ethyl-2-oxazoline) using a thin film templating approach followed by rearrangement with acidic buffer.[90]

Metal–phenolic coordination interactions can also be used to bridge nano- and microstructures to form complex superstructures.[128] For example, nanoparticles and microparticles were separately coated with phenolic films (MPNs or PDA), mixed, and then crosslinked with metal ions. Using this approach, a range of particle systems (including living cells) with different functionalities could be assembled into superstructures (Figure 8d–l). A recent study described a different approach to assemble particles into superstructures, using Mo–PDA complex as the binder and curing agent.[149] This strategy has been applied to assemble superstructures from particles with various shapes (e.g., nanospheres, nanocubes, and hollow spheres) in the size range of 10–500 nm. Though the field of phenolic-based superstructures is still in its infancy, it can be envisioned that the use of metal–phenol coordination bonds to form complex hierarchies can pave the way for unique applications of structured assemblies such as synthetic cells or artificial organs.[128]

5. Bulk Materials

In addition to the nano and microsystems discussed in earlier sections, bulk, macroscopic materials, including gels,[30] epoxy networks,[150] polycarbonates,[151] and elastomers,[20] can be engineered from phenolic compounds. Some of these materials have been thoroughly reviewed elsewhere.[98] Thus, the present section briefly covers these phenolic bulk materials, while highlighting the building blocks used in their design and assembly.

5.1. Gels

Gel-based materials represent an important class of soft materials that find applications in diverse fields including tissue engineering, drug delivery, catalysis, pollutant sequestration, filtration, and chemical sensing.[152-158] The driving forces for the assembly of these viscoelastic soft materials can be covalent and noncovalent in nature. Among diverse noncovalent driving forces, metal–ligand coordination has become an attractive route to gel both organic and aqueous solvents, and the resulting materials are commonly known as metallogels.[159-161] The growing interest in metallogel research stems from the prospects of integrating metallic properties (e.g., redox, optoelectronic, and magnetic)[152-154,162,163] into a gel matrix and exploiting the dynamic nature of coordination bonding to design systems with stimuli responsiveness or specific mechanical properties for targeted applications.[152-154,159,164]

Early examples of metallogels using phenolic derivatives have their roots in the field of mussel-inspired chemistry where iron–catechol coordination, in particular, has been the subject of extensive research.[19,161,165,166] To date, the most established approach for such metallogel formation consists of two steps: 1) covalent modification of natural or synthetic polymers with phenolic moieties and 2) gelation of these modified polymers via coordination crosslinking induced by the addition of transition metals.[19,165,167-170] The most widely used combination is PEG modified with catechol functional groups (PEG–catechol) and Fe^{III} ions (Figure 9a–c).[19,165,166] Some of the properties exhibited by these gels include self-healing (Figure 9d) and stimuli responsiveness, thereby illustrating the dynamic and reversible nature of coordination interactions.[19,166,169] Using the differences in pH responsiveness and reversibility of catechol–boron and catechol–Fe^{III} complexes, Lee et al.[171] designed a gel-based actuator system via an ionoprinting approach (Figure 9e–h). Additionally, Li et al.[172] reported a variant of this approach using Fe_3O_4 nanoparticles as crosslinking motifs (instead of using of Fe^{III} ions as crosslinkers) for PEG–catechol. The resulting gels showed remarkably different mechanical properties from their ionic counterparts (e.g., solid-like, yet, reversible hydrogel mechanics), which can be attributed to the dynamics of multiple catechol–Fe^{III} crosslinks formed on the surface of Fe_3O_4 nanoparticles. Furthermore, Hou and Ma[173] demonstrated a supramolecular hydrogel system using photopolymerizable, pre-coordinated catechol–Fe^{III} complexes as multifunctional crosslinkers and acrylamide as a monomer. The resulting dual-crosslinked (i.e., coordination and covalent) gels showed high extensibility and self-healing capacity (Figure 9i–k).

An alternative approach has also been developed where a native polyphenol, a polyelectrolyte, and a transition metal are mixed to form a ternary gel system.[174,175] Krogsgaard et al.[174] used TA, poly(allylamine hydrochloride), and Fe^{III} ions to form one such system ((Figure 9l–n) where both the TA–poly(allylamine hydrochloride) covalent crosslinking via Michael-type or Schiff base reaction and TA–Fe^{III} crosslinking via coordination were essential for gelation to occur.[174] This

approach was later extended to other transition metals and hydrogen bonding (with TA) polymer motifs.[174,175]

Besides metal coordination, polyphenols can form gels with biopolymers or synthetic polymers solely via hydrogen bonding.[176,177] For example, spontaneous gelation of a DNA/TA (named as TNA hydrogel) mixture has been reported by Shin et al., where the gallol groups of TA crosslink the phosphate groups in the DNA backbone via hydrogen bonding (Figure 9o).[177] The TNA hydrogel exhibits adhesiveness, extensibility, and superior in vivo hemostatic ability. Very recently, Hu et al.[178] demonstrated the formation of a hydrogel by adding polyphenols such as EGCG to amyloid fibrils present in the nematic phase. The resulting gels have been observed to be shear thinning and thermostable in the range of 25–90 °C without occurrence of a phase transition. Chen et al.[176] reported a temperature-responsive shape memory gel (Figure 9p) based on hydrogen bonding interactions between TA and poly(vinyl alcohol) (PVA). The TA/PVA hydrogel samples in

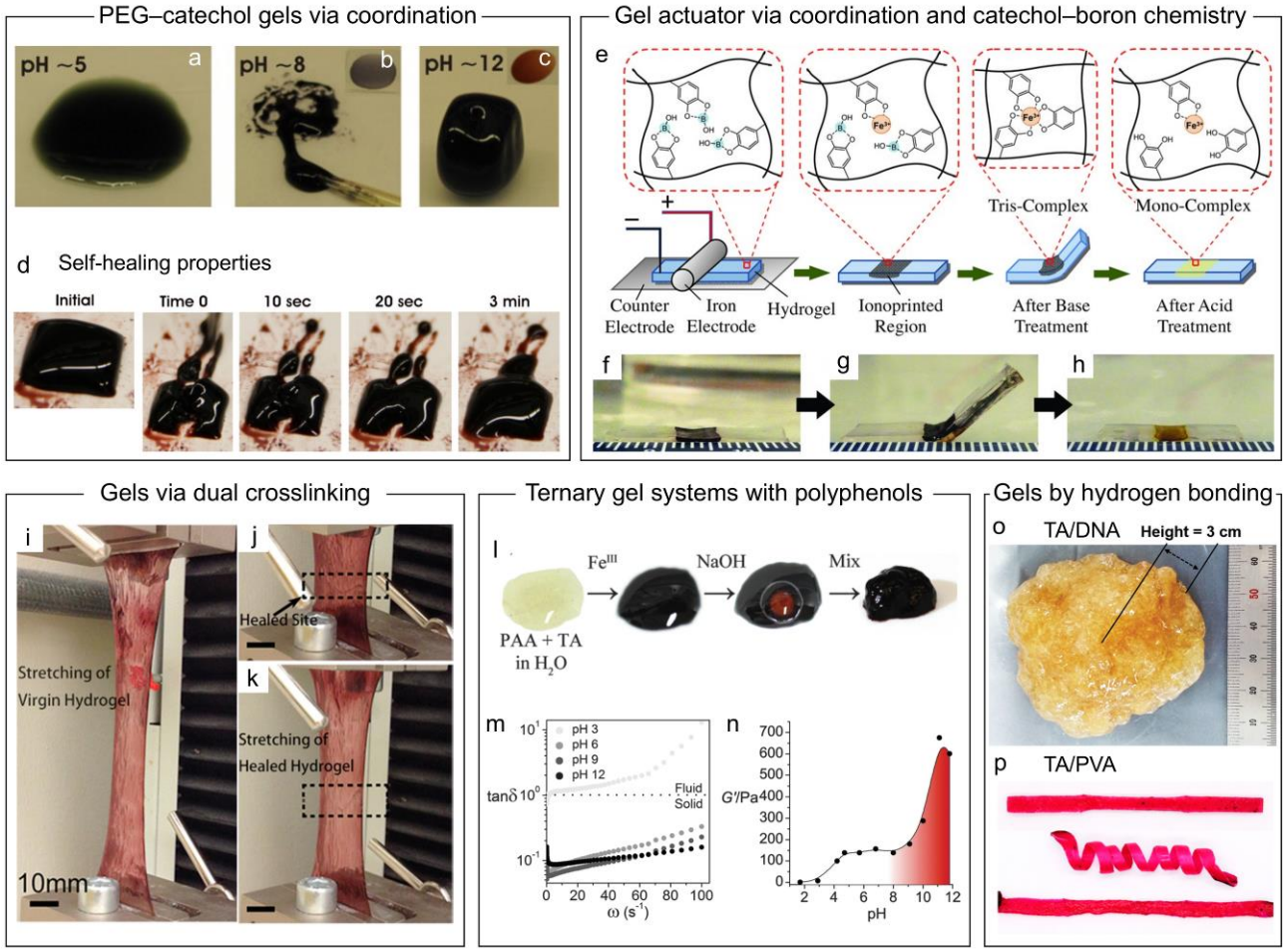

Figure 9. (a–c) Gelation behavior of PEG–catechol with Fe^{III} at different pHs and (d) self-healing properties of the resulting gels. Reproduced with permission.[19] (e–h) Gel actuator fabricated using catechol–boron and catechol–Fe^{III} chemistry via ionoprinting. Reproduced with permission.[171] Copyright 2014 Wiley-VCH. (i–k) High extensibility and fast self-healing property of a photopolymerized (covalent crosslinking) hydrogel using pre-coordinated catechol−Fe^{III} complexes as dynamic crosslinkers. Reproduced with permission.[173] Copyright 2015 American Chemical Society. Ternary gel system (l) using a mixture of poly(allylamine hydrochloride) (PAA), TA, and Fe^{III}, and (m,n) its rheological properties as a function of pH. Reproduced with permission.[174] Copyright 2014 Royal Society of Chemistry. Examples of gels obtained via hydrogen bonding between TA and (o) biopolymer (DNA) or (p) synthetic polymer poly(vinyl alcohol) (PVA). Shape memory property of the TA/PVA gel. (o) Reproduced with permission.[177] Copyright 2015 Wiley-VCH. (p) Reproduced with permission.[176] Copyright 2016 American Chemical Society.

wet or dried conditions, with a deformed or elongated shape, can recover their original shape when immersed in water at 60 °C in a few seconds or at 125 °C in ~2.5 min, respectively.

Despite the progress mentioned above, the direct gelation of native phenolic compounds with transition metals remained elusive until recently, where the combination of TA and group IV transition metals (e.g., Ti^{IV}; Figure 10) was used.[179] Interestingly, this gelation was observed to be specific to this group. TA in combination with transition metals from other groups, e.g., Fe^{III} from group III, resulted in only coacervates or soluble complexes (also observed by Krogsgaard et al.[174]). Considering such specificity, it was hypothesized that the high oxidation state and formal charge of group IV metals in addition to coordination crosslinking could play a critical role in the solvent trapping process, thereby enabling the overall gelation process.[179] The TA–Ti^{IV} metallogels could be formed by a simple mixing process at ambient conditions in various organic and aqueous solvents

(Figure 10a–d) and display a range of properties including optical transparency, self-healing, shape persistence, injectabilty, adhesiveness, and tunable mechanics (examples of these are provided in Figure 10f,g).[179] One of the remarkable features revealed by this system is its robust and adaptive nature that allows in situ co-gelation of diverse additives (Figure 10h) and regulation of other concomitant assembly processes such as the crystallization (Figure 10i) of MOFs.

5.2. Plastics and Elastomers

The study of plastics and elastomers based on phenolic compounds has been ongoing for decades, and herein we highlight some of the more recent examples. Commercially available phenolic compounds, such as bisphenol A (BPA), have been extensively and successfully used as monomers for the industrial synthesis of epoxy resins and polycarbonates. However, there has been recent interest in replacing BPA and similar estrogenic phenolic analogs because of concerns around health risks and the petroleum-based origin of the starting materials.[180] In this context, phenolic compounds from natural origin are of interest.[181,182] Examples include the use of phenolic lipids (e.g., cardanol), phenolic acids (e.g., GA and hydroxybenzoic acid), and polyphenols (e.g., quercetin).[183-187] For polycarbonates, phenolic compounds such as ferulic acid, honokiol, and lignin can be used directly in the polymerization reactions.[151,161,188,189] The toolbox of natural phenolics has therefore allowed for a multitude of structural materials with different properties to act as replacements for conventionally used BPA.

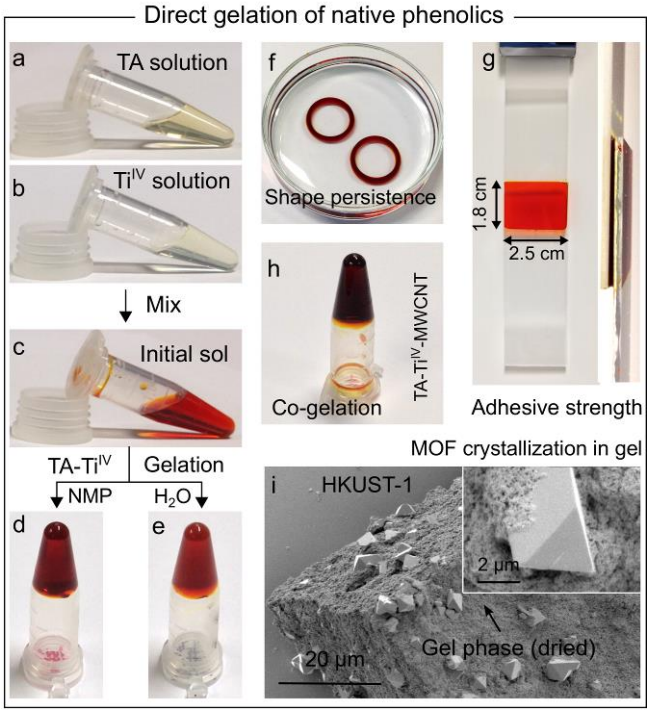

Figure 10. (a–e) Gelation process of TA–Ti^{IV} gel system. (f) Shape persistence and (g) adhesiveness of the TA–Ti^{IV} gel system. (h) Example of in situ co-gelation of multiwalled carbon nanotube (MWCNT) in TA–Ti^{IV} gel system. (i) Crystallization of HKUST-1 (Cu–benzene-1,3,5-tricarboxylate MOFs) in TA–Ti^{IV} gel system. Reproduced with permission.[179] Copyright 2016 Wiley-VCH.

Phenolic elastomers containing catechol and gallol functional groups and their composites are also of interest to fabricate materials with superior mechanical properties.[60,190] For example, Li et al.[190] designed a catechol-functionalized elastomer that showed self-healing properties in seawater via hydrogen bonding and coordination interactions with metal ions (such as Ca^{II} and Mg^{II}) found in seawater. In another approach, catechol-based self-healing elastomers under seawater were synthesized using the reversible boron–catechol chemistry.[191] Recently, Filippidi et al.[20] prepared a high-performance composite elastomer using catechol–Fe^{III} coordination chemistry. The introduction of the reversible coordination crosslinks in the initial epoxy network simultaneously increased the crosslink density and energy dissipation characteristics of the network in the dry state, resulting in a stiff, yet tough elastomer.

6. Applications

Traditionally, phenolic-based materials have been used as pigments, antioxidants, photographic developers, and inks.[70] However, in recent times, their broad range chemical properties and functions have made them useful precursors for constructing a range of smart, advanced materials including stimuli-responsive materials,[192,193] antibacterial and chemical-resistant materials,[194,195] superstructures,[128] unique polymeric materials,[196] DNA origami-based materials,[197] and other nanosystems.[198,199] Moreover, natural polyphenols have recently been shown to provide enhanced blood circulation after complexation with proteins.[200] The present section focuses on recent scientific advances regarding applications of materials composed of phenolic building blocks.

6.1. Mechanical Applications

6.1.1. Adhesives

Nature often serves as an inspiration to scientists to engineer novel adhesives, and one commonly referenced example deals with the phenolic-based adhesive of mussels. Pioneering investigations have revealed that the byssal adhesion property of mussels arises from the abundance of phenolic amino acids in the adhesive protein, DOPA,[15] and their synergistic interplay with lysine residues.[17] Mussels have the ability to permanently stick to nearly any available surface, even in the most turbulent intertidal zones (Figure 11a).[18] Unlike mussels, which maintain permanent adhesion in wet and dry states, many natural reversible adhesives, such as gecko feet, lose adhesion when exposed to water.[18] Combining the robust wet/dry adhesion of marine mussels and the reversibility of the foot hair structures of geckos (Figure 11a), a reversible wet/dry adhesive was designed.[18] This system displayed excellent performance over 1,000 adhesion tests both in dry and wet states. Another hybrid adhesive was fabricated from mussel foot proteins and amyloidogenic proteins (a major subunit of amyloid curli fibers produced by *Escherichia coli*). These two compounds can be assembled together into higher-order hierarchical structures with a high underwater adhesion energy (20.9 mJ m^{-2}).[201]

Alternatively, conjugating phenolic moieties to stimuli-responsive polymers allows for the fabrication of wet adhesives with reversible triggered adhesion, which can be useful as a sealant for fetal membrane repair.[202] In another strategy, the thermoresponsive polymer, PNIPAM, was introduced into catechol-containing polymers via host–guest chemistry.[21] Owing to the conformational transition of PNIPAM around its lower critical solution temperature (LCST), the adhesive exhibits tunable interfacial forces. At temperatures lower than the LCST (e.g., 25 °C), the hydrophilic PNIPAM chains form a swelling layer with water molecules, thus preventing adhesion. In contrast, at temperatures greater than the LCST (e.g., 40 °C), the PNIPAM chains transition into the hydrophobic state, thus exposing the adhesive groups. In addition to these selected examples, adhesives for tissue engineering applications have been discussed in a recent review.[203]

6.1.2. Materials with Superior Mechanical Properties

Phenolic materials have been engineered with a wide range of mechanical properties. For example, drawing inspiration from the excellent mechanical properties displayed by squid beaks,[204]

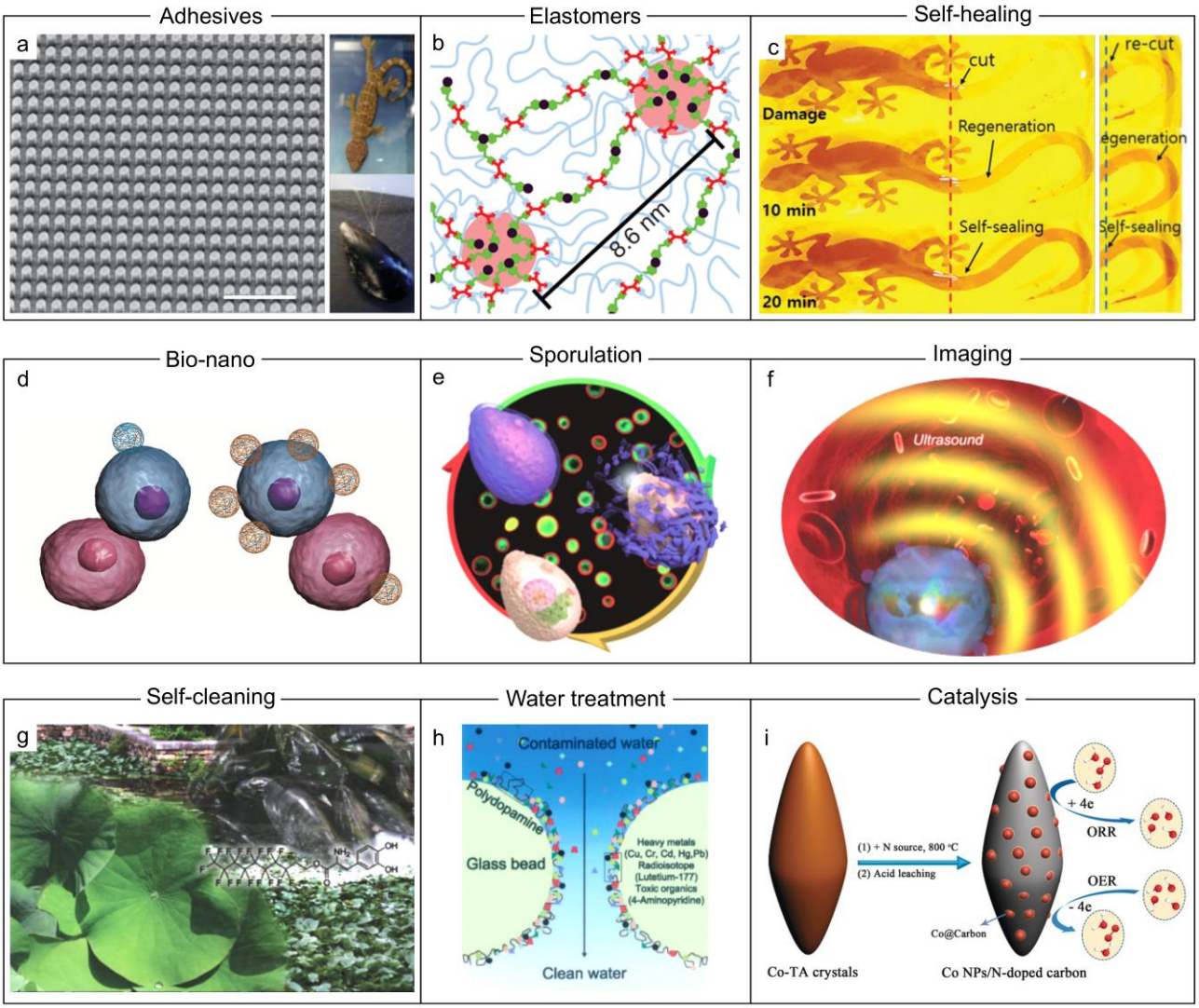

Figure 11. Diverse applications of phenolic materials. (a) Biomimetic adhesive inspired by mussel and gecko. Reproduced with permission.[18] Copyright 2007 Springer Nature. (b) Elastomer toughening by metal–catechol crosslinks. Reproduced with permission.[20] Copyright 2017 American Association for the Advancement of Science. (c) Biologically inspired regenerative self-healing and self-sealing films. Reproduced with permission.[206] Copyright 2016 Wiley-VCH. (d) Drug carriers with tunable cellular adhesion and targeting performance. Reproduced with permission.[77] Copyright 2016 American Chemical Society. (e) Single-cell encapsulation and artificial sporulation. Reproduced with permission.[67] Copyright 2014 Wiley-VCH. (f) Ultrasound imaging application of metal–phenolic particles. Reproduced with permission.[212] Copyright 2015 Wiley-VCH. (g) Mussel-inspired coating for self-cleaning applications. Reproduced with permission.[214] Copyright 2014 Royal Society of Chemistry. (h) Detoxification of water by polydopamine. Reproduced with permission.[219] Copyright 2012 Wiley-VCH. (i) Metal–polyphenol crystals and the derived composites for catalytic applications. Reproduced with permission.[222] Copyright 2016 Wiley-VCH.

scientists have designed stiff and compliant phenolic materials. A catechol crosslinking method that has been used is metal complexation, where inorganic ions (e.g., Fe^{III}) are used to generate desired mechanical properties (e.g., high hardness, extensibility,[205] and gelation).[81] For example, iron–catechol crosslinking can be used to enhance the toughness of elastomers (Figure 11b)[20] owing to the sacrificial, reversible coordination bonds of metal–phenolic chemistry. In another approach, interface-assisted formation of self-healing and self-sealing films was achieved, using a range of phenolic ligands,[206] as polyphenols preferentially form at the air–water interface where phenolic ligands oxidize and polymerize given sufficient oxygen (Figure 11c). Upon damage, the films can easily self-heal upon regeneration at the air–water interface. Alternatively, metalloid-based systems (e.g., boron–catechol complexation) can be used to form self-healing materials.[191]

6.2. Biological Applications

6.2.1. Drug Delivery

In recent years, particles and hollow capsules fabricated from MPNs have been engineered for drug delivery using a variety of assembly methods.[63,70,71,76,77,80,140,207] A notable advantage of MPN-based systems is that the incorporated therapeutic cargo can be released through changes in pH, with the incorporated metal determining the pH of disassembly.[16,70,71] As tumor sites have a lower local pH than healthy tissues, as well as different intracellular and extracellular pH, these MPN-based systems may have potential for use in anticancer therapy. In addition to pH changes, controlled release has been achieved by UV light.[208] An example of a photo-responsive release system consisted of TA–Cu^{II} coordination networks coated on a mesoporous silica core loaded with photoacid generators and therapeutic cargo. Upon UV irradiation, the photoacid was generated, which degraded the coordination coatings and released the cargo. Additionally, the surface chemistry of drug delivery vehicles has
been engineered to show tunable targeting and stealth behavior using phenolic building blocks (Figure 11d).[77]

6.2.2. Sensing and Imaging

Dopamine-modified quantum dots were first used as cell-based biosensors to investigate the interplay between cell labeling and redox states.[209] A non-conductive nanocoating of polyphenols was used as a molecular-imprinting nanosensor for the recognition of proteins with ultrahigh sensitivity.[210] This system not only showed specific recognition for human ferritin and papillomavirus, but also responded to the conformational changes of proteins such as calmodulin. GA-based self-assembled nanodots obtained via iron coordination were used in the enhancement of tumor-imaging sensitivity and the promotion of renal clearance.[211] The incorporation of metal ions in MPNs has enabled their use as imaging agents in biological applications through PET, MRI, ultrasound (Figure 11f), and fluorescence imaging.[70,212]

6.2.3. Artificial Sporulation

The TA–Fe^{III} MPN system has been used for single-cell encapsulation (Figure 11e).[16,67,147] After coating yeast cells with MPNs, cell division was suppressed, but could be fully restored upon disassembly of the coatings.[67] The MPN coatings could protect the yeast cells from multiple external aggressors such as UV-C irradiation and lytic enzymes, which mimics the sporulation process in nature.[67]

6.3. Energy and Environmental Applications

6.3.1. Controlled Wetting and Self-Cleaning

Conformal coatings prepared from PDA and MPNs are also of interest to modify the wetting properties of various surfaces. Superhydrophobic particles were engineered by attaching silver nanoparticles to silica particles with PDA as bridging coatings, followed by reaction with thiol to lower the surface energy.[213] The resultant particles were super repellent to water owing to the satellite composite structure and low surface energy. Superhydrophobic self-cleaning coatings have also been obtained in a single dip-coating step using a perfluorinated dopamine derivative (Figure 11g).[214] Moreover, antifouling phenolic coatings were prepared using catechol-containing polymers or thiol-containing peptides–dopamine conjugates.[76,215,216]

6.3.2. Separations

Oil–water separation is important for environmental remediation and a wide range of industrial applications.[217] TA–Fe^{III} MPN coatings have been used to fabricate multifunctional filtration membranes.[218] MPN-coated poly(ether sulfone) membranes exhibited high water flux and antifouling properties against proteins and cells, demonstrating potential applications in water purification.[218] Owing to the high binding affinity of catechol to metals, catechol-coated substrates could also be used in environmental remediation for the removal of heavy metals (Figure 11h)[219] and organic contaminants.[220] Additionally, films embedded with PDA-modified nanoparticles could be used for CO_2 separation.[221]

6.3.3. Catalysis

The ability to chelate a variety of metals makes phenolic materials ideal candidates in catalytic reactions. Crystalline cobalt–polyphenol MOFs can be used as a high-performance catalyst for oxygen reduction and oxygen evolution reactions (Figure 11i).[222] Catalytic applications of MPNs include the Suzuki–Miyaura coupling reaction in water,[223] the Fenton reaction,[65] the photocatalytic degradation of organic dyes (thermally treated MPNs),[66] and the hydrogenation of quinoline,[70] and as radical and ROS scavengers.[54,73,224]

6.4. Emerging Applications

In addition to the applications mentioned above, phenolic materials have recently been explored for some interesting emerging applications using their adhesive, antibacterial, antioxidant, astringent, and metal chelating properties. For example, Ma et al.[225] studied the astringent effect of phenolics,

originating from protein-mediated lubrication failure, and engineered a tongue-like polyacrylamide hydrogel that exhibited high polyphenol sensitivity. Using this property, a scientific strategy has been demonstrated to efficiently catch fishes (the epidermal layer of fishes is rich in various biologically active proteins) with a TA-modified glove (Figure 12a–c). A physical mixture of TA and PEG have been shown to have superior mucoadhesive properties originating from the pH-dependent intermolecular interactions between TA and mucin.[226] Park et al. demonstrated that TA-based MPNs could be used as edible coatings to preserve the post-harvest shelf life of perishable fruits (Figure 12d,e).[79] Meurer et al. designed a biohybrid microgel particle system containing catechol moieties to deliver micronutrients (e.g., Fe^{III}) as a foliar fertilizer system.[227] The TA–Ti^{IV} metallogel system has recently been used as a medium for the controlled crystallization of active pharmaceutical ingredients (APIs), which is critical in optimizing the processing and performance of drug formulations.[228] The method for API crystallization in the TA–Ti^{IV} metallogel is shown in Figure 12g,h. The gel-grown API crystals were observed to be significantly different in size, morphology, and polymorphism when compared with those grown in controls without the gelators (Figure 12i,j). Additionally, the size and morphology of the API crystals could be tailored by altering the reaction parameters and gel composition.

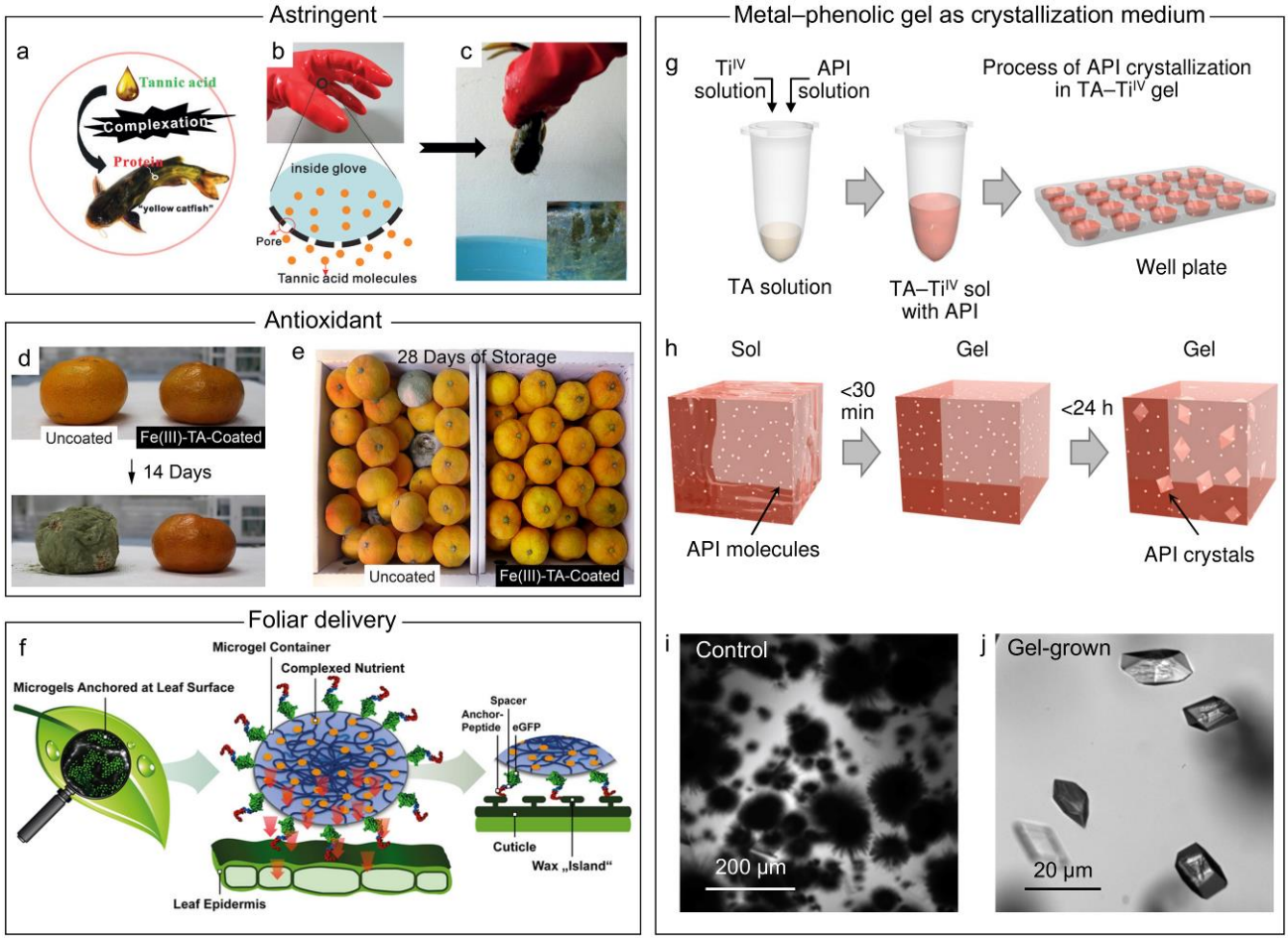

Figure 12. Emerging applications of phenolic-based materials. (a) Responsiveness of a fish to TA owing to astringency. (b) Schematic and (c) photograph of fish capture using a TA-modified glove. Reproduced with permission.[225] Copyright 2016 Wiley-VCH. (d,e) Spray-coated MPNs on fruits showing antioxidant activity. Reproduced with permission.[79] Copyright 2017 Springer Nature. (f) Schematic of microgel-based fertilizers for specific attachment to leaf surfaces and controlled foliar delivery of nutrients to plants. Reproduced with permission.[227] Copyright 2017 Wiley-VCH. (g) Illustration of the crystallization of an active pharmaceutical ingredient (API) in the TA–Ti^{IV} gel system. (h) Sol–gel transition and subsequent crystallization of the API in the gels. Optical microscopy images showing piroxicam crystallization in (i) solution (without the gelators) and (j) TA–Ti^{IV} gel. Reproduced with permission.[228] Copyright 2018 Wiley-VCH.

7. Summary and Outlook

The ubiquity of phenolic compounds and their facile combination with synthetic and biopolymers have allowed for the engineering of a wide variety of functional materials. Phenolic materials can be assembled across a wide range of length scales (in the nanometer to centimeter range) for a variety of applications. The three broad classes of phenolic materials described in the present review, namely films, particles, and bulk materials, overlap in some instances, but act as robust categories for classifying past phenolic literature studies. Films are classified by being surface-confined and encompass MPN films, LbL films, PDA films, and other self-polymerized films. If film formation is performed on nano- or microparticles, film-coated particles are

obtained. Phenolic-based particles encompass diverse materials ranging from MOFs to micelles and superstructures. Finally, bulk materials, such as gels and elastomers, represent some of the most established phenolic materials in the literature.

We highlight that the building blocks play a key role on the final material properties, and that a wide variety of attractive and stabilizing forces, such as electrostatic, hydrogen bonding, and metal chelation, can be used to form functional phenolic materials. Moreover, building blocks of similar types can be blended together to allow for emergent properties. The extensive research studies on phenolic materials, arising separately from mussel-inspired chemistry and phytochemistry, are starting to merge into a single cohesive and productive field. Therefore, the present review has aimed to collate knowledge from seemingly unrelated fields and research topics that share the use of phenolics as the point of similarity so that researchers can find inspiration from outside traditional avenues.

There are also challenges to overcome to advance this important field of research. For example, the assembly of MPN- and PDA-based materials is poorly understood at the molecular level, in part due to the amorphous nature of these materials. As a result, many of the biomimetic materials are yet to replicate the performance of living systems such as mussel's underwater adhesion. Fundamentals into the structure–function relationship and synergistic impact of the organic–inorganic components of MPNs assembled from different combinations of metals and phenolic building blocks are also critical aspects that need to be addressed.

Moving forward, the use of strategically designed, multi-component phenolic composites will be important for next-generation applications. The synergistic combination of various phenolic materials and methods used in disparate fields is expected to yield unique materials with emergent properties. For example, the coating of phenolic gels with phenolic thin films could allow for capsule-like structures with phenol or metal gradients and a defined distribution of high and low modulus regions. Additionally, the combination of amorphous and crystalline materials (such as gel–MOF composites)[179] could allow for the fabrication of unique composites with synergistic functions.

Beyond the use of catechol- and gallol-containing building blocks, expansion into other phenolic compounds, such as phenolic lipids, would allow for the generation of a broad range of materials as well as the possible generation of emergent properties. Moving tangential to phenolics, the amino acid histidine is responsible for significant functional metal chelation in biological systems,[229] where histidine–metal complexes have recently begun to emerge for constructing functional materials and sensors.[230] Finally, a deeper understanding into the physical and chemical interactions of phenolic materials is necessary for designing materials with even better performance, which requires interdisciplinary collaborations between chemists, materials scientists, engineers, and biologists. Along these lines, advanced analytical techniques and computational chemistry will play pivotal roles in rationalizing design principles for the preparation of advanced phenolic materials.

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Keywords: coordination chemistry • functional materials • material science • phenolics • self-assembly

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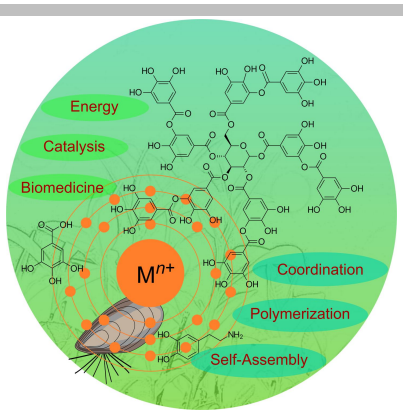
Layout 1:

REVIEW

Phenolics on the rise: This Review provides an overview of recent advances in the preparation of functional materials using phenolic building blocks, namely thin films, particles, and bulk materials. Their diverse applications, ranging from biomedicine to catalysis, are also highlighted. This review will help integrate various disciplines using phenolics and serve as a guide for future materials development.



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