Biomaterials Technology for AgroFood Resilience

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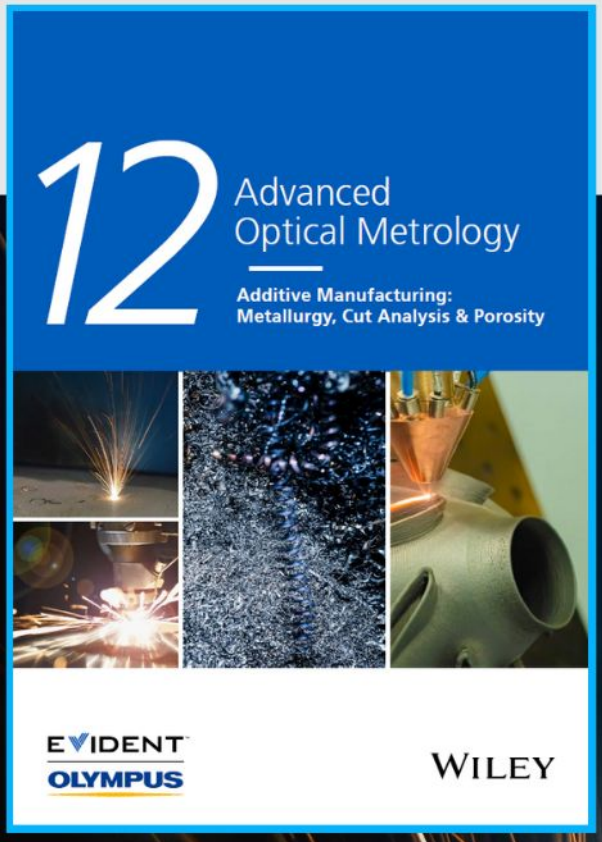

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Biomaterials Technology for AgroFood Resilience

*Hui Sun, Yunteng Cao, Doyoon Kim, and Benedetto Marelli**

This review article highlights recent advances in designing biomaterials to be interfaced with food and plants, with the goal of enhancing the resilience of the AgroFood infrastructure by boosting crop production, mitigating environmental impact, and reducing losses along the supply chain. Special attention is given to innovations in biomaterial-based approaches and platforms for 1) seed enhancement through encapsulation, preservation, and controlled release of payloads (e.g., plant growth-promoting microbes) to the seeds and their rhizosphere; 2) precision delivery of multi-scale payloads to targeted plant tissues, organelles, and vasculature; 3) edible food coatings that regulate gas exchanges and provide antimicrobial properties to extend the shelf life of perishable food; and 4) food spoilage detection based on different sensor/reporter systems. Within each domain, biomaterials design principles, emerging micro-/nanofabrication strategies, and the advantages and disadvantages of different delivery/preservation/sensing platforms are introduced and critically discussed. Views of future requirements, aims, and trends are also given based on the opportunities and challenges of applying biomaterials in the AgroFood system.

1. Introduction

Food is the single, most important determinant of human health. Nonetheless, the ability to provide sufficient, safe, and nutritious food to the global population, which is projected to reach 9.7 billion by 2050,[1] is becoming a major challenge for the AgroFood infrastructure. Currently, more than 800 million people are living in conditions of food insecurity and climate change is exacerbating the biotic and abiotic stressors that negatively affect crop yield and quality.[2–5] The need to mitigate environmental impacts of current agricultural practices and to minimize crop losses caused by transboundary pests and diseases also coincides with the required increase in crop productivity to feed the ever-growing population.[6] To this date, overapplication of fertilizers and pesticides is still a widely adopted agricultural practice to increase crop yield, due to the low efficiency in agrochemical delivery and utilization. Thereby, innovations in more precise and efficient application platforms that minimize agrochemical waste and runoff are urgently needed. Additionally, the current crisis of food loss and waste necessitates more efforts to sustainably boost food production. The Food and Agriculture Organization (FAO) of the United Nations has estimated that 30–40% of the food produced for human consumption worldwide is annually lost or wasted from farm to fork.[7] Food loss and waste in fact heavily impact the environment—25% of the worldwide freshwater consumption is used to produce food that is never eaten.[8–10] Besides, global food loss and waste generate annually 4.4 $GtCO_2$ eq, which corresponds to circa 8% of the total anthropogenic greenhouse gas (GHG) emissions. This means that the contribution of food wastage emissions to global warming is almost equivalent to that of global road transport emissions and that food loss is the largest producer of GHG after China and US.[11,12]

To address these challenges, new technologies are emerging to sustainably produce more food with less inputs (water and agrochemicals) and to minimize food waste from farm to fork.[13] Particularly interesting is the case of precision agriculture,[14] where robotics, geolocalization, smart sensors, and big data analysis are increasingly employed to optimize resources and to avoid significant crop loss due to extreme weather conditions. The potential benefits of biomaterials-based innovation in agriculture and food production, however, remain underexplored.

Biomaterials are commonly defined as "a substance that has been engineered to take a form which, alone or as part of a complex system, is used to direct, by control of interactions with components of living systems, the course of any therapeutic or diagnostic procedure, in human or veterinary medicine."[15] Although its definition has been evolving over the years, the scope of biomaterials remains largely within the healthcare domain that is associated with human or veterinary medicine. With this review, we aim to expand the current perception and scope of biomaterials by demonstrating how they can be engineered to interface with food and plants, to ultimately boost food security. In this respect, biomaterials design principles adopted in the medical field for drug delivery, gene therapy, and nanotechnology-based sensing and diagnostics serve as an inspiration and guidance for new applications in the AgroFood system. We believe that biomaterials can provide huge technological opportunities to enhance food security while minimizing environmental impacts, by enabling

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202201930.

DOI: 10.1002/adfm.202201930

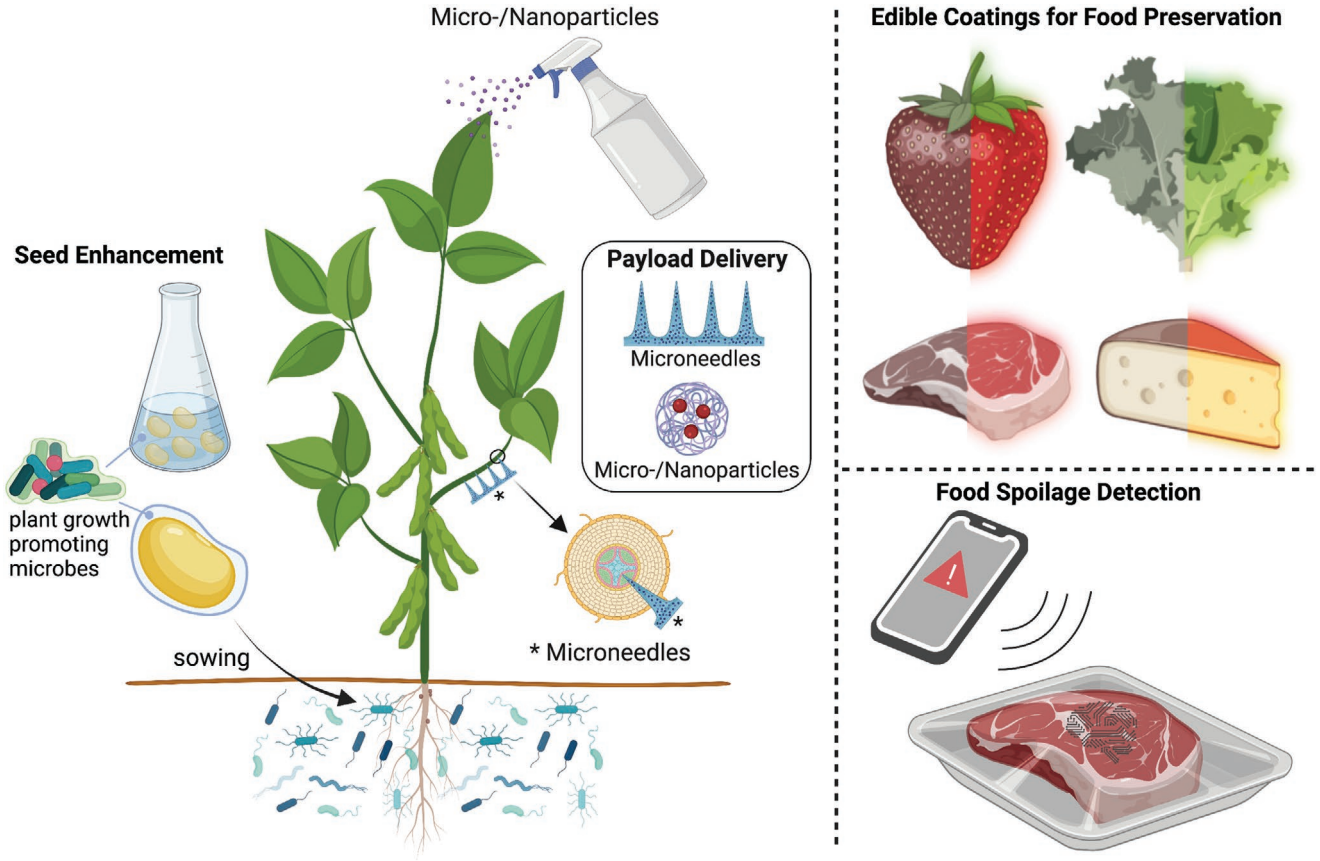

Figure 1. Applications of biomaterials-based approaches and platforms in the agriculture and food industry.

new means to manage crop production, as well as food handling and quality. Specifically, we dedicate our focus to four aspects where we believe biomaterials-based approaches and platforms can make a real impact (**Figure 1**): 1) seed enhancement technology through the development of advanced seed coatings that combine biodegradation with encapsulation, preservation, and controlled release of payloads (particularly plant growth-promoting microbes) to the seeds and their rhizosphere; 2) precision delivery of multi-scale payloads to targeted plant tissues and organelles through microneedles- and nanoparticles-based platforms; 3) edible food coatings with regulated gas barrier and antimicrobial properties to extend the shelf life of perishable food and reduce food waste; and 4) food spoilage detection. Together, these new applications of biomaterials provide disruptive innovations with a big impact on sustainable farming, food security, and food safety, which will in turn strengthen human health and thereby circle back to biomaterials' traditional mission of improving the quality of life.

2. Sustainable Agriculture

Over exploitation of arable lands and unrestricted application of fertilizers and pesticides have traditionally been used in agriculture to meet global food demand but have also severely degraded arable soils, polluted water systems, and escalated climate change through diminishing biodiversity and excessive greenhouse gas emission. Negative environmental consequences caused by unsustainable agricultural practices are now flattening the yield curves for many crops, making food production more and more difficult to catch up with the demand of a growing world population. Moving forward, innovations in AgriTech are needed to make agriculture more efficient, resilient, and sustainable, with the goal of maximizing crop productivity while minimizing inputs, especially under challenging environments. Currently, information technology, big data analysis, and biotechnology are having a tremendous impact on sustainable agriculture, while materials-based innovation is still under development and has been generally overlooked. In this section, we focus on the most recent advancements on material-based innovation for sustainable agriculture, by discussing recent approaches to apply biomaterials in seed enhancement and precision payload delivery in plants, while exploring their design and efficacy.

2.1. Engineering Seed Microenvironment

Seeds are the agricultural products with the most value-added as they represent the sources of food production. Access to high-quality seeds plays a pivotal role in boosting crop yields and supporting global food security. To this end, multiple seed enhancement technologies have been developed,[16,17] with the goal of fortifying seeds against physical damage and pathogen infection, ensuring sufficient nutrients uptake, imparting tolerance to various biotic/abiotic stressors, breaking seeds' dormancy and promoting germination and subsequent seedling

growth. Besides, to address the overuse of synthetic fertilizers and pesticides and to mitigate their detrimental effects on our environment, biofertilizers have been increasingly employed in efforts to engineer the seed microenvironment,[18,19] which can greatly enhance the sustainability and health of soil without compromising crop yields. Biofertilizers, also known as plant growth-promoting rhizobacteria (PGPR), contain living microorganisms that can colonize the rhizosphere or the interior of plants, promote growth by increasing nutrient supply to the host plant, and provide protection against abiotic and biotic stresses. In this subsection, we introduce recent advances in the efforts to use biomaterials to engineer the seed microenvironment through seed priming and seed coating, as well as the incorporation of nanotechnology/nanofabrication in seed enhancement technologies.

2.1.1. Seed Priming

Seed priming is an extensively studied presowing seed treatment that allows for controlled hydration of seeds to imbibe water and to begin some pre-germination metabolism without actual occurrence of germination and radicle emergence.[20] Depending on the priming media used to soak the seeds, seed priming is categorized into multiple types—hydropriming, osmopriming, halopriming, hormonal priming, solid matrix priming, biopriming, and the emerging nanopriming.[21] Hydropriming refers to soaking seeds in tap water with or without aeration followed by air dry,[22,23] which is the simplest and most commonly used presowing treatment by farmers. Osmopriming involves soaking seeds in aerated solutions of low water potential that contain polyethylene glycol (PEG), mannitol, or $CaCl_2$, etc. to control water imbibition in seeds, which is particularly preferred for improving germination in cereal crops under drought stress.[24–26] Halopriming is a process where seeds are pretreated in salt (e.g., NaCl) solutions before sowing, which generally imparts tolerance against soil salinity to seed germination and subsequent seedling emergence.[27–29] Hormonal priming includes soaking seeds in aerated solutions of plant growth regulators such as ascorbic acid, salicylic acid, gibberellic acid, abscisic acid, and cytokinins, which has shown beneficial effects on seeds grown in saline soils[30–32] and under extreme temperatures.[33,34] In solid matrix priming, seeds are mixed with a solid matrix carrier (e.g., vermiculite, clay, sand, and sodium polypropionate gel) that is moderately moistened and that generate matrix forces to slow down water uptake by seeds.[35] It is generally more effective than osmopriming in regulating seed pregermination because the process is designed to mimic a natural seedbed environment and gas exchange between the seeds and the environment is minimally inhibited. Besides, solid matrix priming can be easily combined with other priming methods,[36,37] further promoting seed enhancement, especially in large-seeded crops.

Biopriming integrates seed hydration and a biological treatment by adding living bacterial inoculum to the priming media.[38] The interaction of beneficial microbes with seeds and crops has been studied extensively, however their implementation in the field is limited. Biopriming serves as one of the approaches to apply PGPR in sustainable agriculture practices,[39] which can help increase nutrient availability to crops, mitigate certain biotic and abiotic stresses, and manage plant diseases, thereby reducing the amount of synthetic fertilizers and pesticides needed.

PGPR can assist plants' nutrient acquisition through nitrogen (N) fixation, phosphorus (P) and potassium (K) solubilization, and micronutrients (Fe, Zn, etc.) supply.[40] Nitrogen-fixing bacteria utilize a substantial amount of energy (either self-sustained or from their host) to convert atmospheric nitrogen into available forms for plants.[41] In the case of symbiotic nitrogen fixation in legumes, this is represented by formation of root nodules through legume-*rhizobium* interaction.[42] Common bean (*Phaseolus vulgaris*) seeds primed with *Rhizobium tropici* showed higher germination rate, enhanced seedling development, more articulated roots and better adapted physiological activities in saline environments when compared to untreated controls.[43] For non-legume crops, free-living nitrogen fixers such as *Azospirillum* and *Azotobacter* are commonly used in seed priming.[18] Phosphorus- and potassium-solubilizing microorganisms function mainly by secreting metabolites (mostly organic acids) that can transform insoluble P- and K-bearing minerals into solubilized and accessible forms for plant uptake, through a series of chelation, exchange reaction, acidification, and dissolution processes.[44] Okra (*Abelmoschus esculentus*) seeds primed with P- and K-solubilizing *Enterobacter* spp. exhibited improved germination, seedling growth, leaf surface area and chlorophyll index that resulted from a significant increase in P and K uptake (>89%) as compared to uninoculated controls.[45]

Besides facilitating nutrient supply to crops, PGPR can also impart crop tolerance against abiotic and biotic stresses by producing phytohormones,[46] which influence seed germination, development of root systems and vascular tissues, shoot elongation, flowering, and overall plant growth. It has been reported that more than 80% of rhizobacteria (including *Azotbacter*, *Bacillus*, *Enterobacter*, *Pseudomonas*, and *Rhizobium*) are able to synthesize and release indole acetic acid (IAA) under abiotic stresses such as saline and water deficit conditions,[47,48] which plays a crucial role in ensuring sufficient IAA levels during root development and shoot biomass production. Another example is cytokinin-producing PGPR which is not only important for promoting crop growth under abiotic stresses but is also effective biocontrol agents against multiple pathogens and pests.[40] When dealing with biotic stresses (e.g., crop disease management), consortia of PGPR are generally believed to be more effective than single inoculants.[44] PGPR employs a number of mechanisms to combat biotic stresses, including direct mechanisms such as production of antibiotics that antagonize the pathogen, defense enzymes (e.g., 1-aminocyclopropane1-carboxylate (ACC) deaminase), and secondary metabolites (e.g., hydrogen cyanide), as well as indirect mechanisms such as induced systemic resistance (ISR) and competition for nutrients and niche space.[49–51] Single PGPR strains or a consortium of *Trichoderma, Pseudomonas, Bacillus* and *Rhizobium* have been used in a wide range of crops to mitigate various plant diseases through biopriming of seeds.[38]

Seed nanopriming is an emerging technique that incorporates nanomaterials, mostly nanoparticles, in the priming media. The nanoparticles used in seed priming are mainly of metallic, biogenic metallic, and biopolymeric nature, which can be categorized into two groups—active nanoparticles and nanocarriers with sustained release.[52] Active nanoparticles

refer to those that can cause a biological effect on their own, by acting as a plant-growth stimulant or an antipathogen agent, etc. Examples of active nanoparticles are mainly metallic nanoparticles including those produced using biogenic processes, which are normally smaller than 100 nm. These nanoparticles are usually made from metals that play essential roles in plant metabolism and biofortification,[53] including iron, zinc, manganese, and copper, etc. Studies have shown that seed priming with metallic nanoparticles can help relieve crop stress caused by saline conditions,[54–56] drought,[57] and nutrient deficiency.[58]

Nanocarriers with the sustained release are mainly composed of biopolymeric nanoparticles made from polysaccharides,[59] proteins,[60] and lipids.[61] When used in seed priming, the nanocarriers can be loaded with various substances including micronutrients,[62,63] pesticides,[64] and plant growth regulators[65,66] for different purposes. As biopolymeric nanoparticles are normally larger than 100 nm,[67] their uptake by the seeds is relatively rare compared to metallic nanoparticles. Instead, most of the biopolymeric nanoparticles are retained on the seed surface after priming and they function mainly through slow release of active compounds to modify plant metabolism and to combat pathogens. Examples of such nanocarrier systems include chitosan nanoparticles containing copper and zinc which induced higher activities of hydrolytic enzymes and proteases in maize seeds, promoting germination and subsequent seedling growth;[68] gibberellic acid-loaded lignin, chitosan and alginate nanoparticles which were able to improve not only germination and initial seedling establishment but also fruit production for arugula and tomato seeds;[69,70] and thiamine-bearing chitosan nanoparticles which stimulated a 10-fold increase of auxin levels in chickpea seedlings and boosted the development of secondary roots.[71] Effects such as increased solubility, protection against degradation and enhanced physical-chemical properties of the active compounds when encapsulated in nanocarrier systems can help reduce their required amount and thereby minimize their phytotoxicity.

2.1.2. Seed Coating

Although seed priming possesses great opportunities for making agricultural practices more sustainable, it also faces some challenges related to preservation of bioactive ingredients, seed storage after priming and large-scale implementation in the field. To address these challenges, other seed enhancement technologies have been developed, with the most commonly used being seed coatings. Seed coating is a practice that involves application of exogenous materials onto seed surface to modify its properties and/or to deliver bioactive ingredients.[72] Currently, the industrial standard is to use a thin film (less than 5% of seed weight) for seed coating, which is usually obtained from a film-forming polymer suspension applied via a fluidized bed or a rotary coater.[17] Other commonly used coating application techniques include dip-coating and spray coating. A typical suspension for seed coating is composed of binders, fillers, and active ingredients.[73] Binders are polymeric materials that possess film-forming properties and that can stick to the seed surface after drying while carrying the active ingredients. Active ingredients include a wide range of substances—protectants, tracers, nutrients, symbionts, and plant growth regulators etc. Virtually every ingredient used in the seed priming discussed above can also be incorporated into seed coatings. Fillers are mostly inert powdered substances used in seed encrusting and pelleting to increase seed weight and size and are rarely used in film coatings.

Seed coating materials are selected based on their 1) stability, resilience, and durability; 2) mechanical flexibility and tribological properties; 3) adhesiveness to seed surface and dust-off; 4) ability to modulate gas and water exchanges; and 5) effectiveness in compartmentalization, preservation and sustained release of active ingredients. With these considerations in mind and in an effort to reduce the use of petroleum-based polymers, biopolymers have gained increasing popularity as seed coating materials due to their biodegradability, good film-forming properties, and being nontoxic and ecofriendly. Among others, cellulose and its derivatives,[74] chitosan,[75,76] starch,[77] alginate,[78] gum arabic,[79] gelatin,[80] and soy protein[81] are some of the biopolymers that have been widely used in seed coatings for targeted delivery of active ingredients. More recently, the use of silk fibroin—a structural protein extracted from *Bombyx mori* cocoons in the design of functional seed coatings has opened up new possibilities for sustainable agriculture on marginal lands.[43,82,83]

A recent example showcases the use of silk fibroin in combination with trehalose as seed coatings that encapsulate, preserve, and deliver *Rhizobium tropici* to *Phaseolus vulgaris* seeds upon sowing,[82] which effectively boosted germination and seedling growth in saline soils (**Figure 2**a–d). Such biomaterial formulation for seed coatings synergistically employs the film-forming, payload encapsulation, preservation, and tunable biodegradation capabilities of silk fibroin and the ability of trehalose to support survival of rhizobacteria during desiccation and resuscitation. Statistically significant improvement in both germination rate and seedling growth of coated seeds was observed, as compared to uncoated controls (Figure 2b). Coated seeds grew into seedlings that were taller and possessed longer and more articulated roots in comparison to uncoated controls (Figure 2c), especially when planted in saline soil. Nodule formation assessed by visual inspection and fluorescence microscopy confirmed successful root colonization by the rhizobacteria (Figure 2d). A follow-up study compared the performance of *Phaseolus vulgaris* seeds coated by a thin film of silk fibroin, trehalose, and *Rhizobium tropici* to seeds primed with *Rhizobium tropici* and trehalose, respectively.[43] The results showed that coated seeds exhibited the highest germination rate in soils of increasing salinity and more articulated roots were developed from coated seeds compared to primed seeds and untreated controls.

A second iteration of a biomaterials-based seed coating technology was inspired by the mucilage-producing seeds (e.g., chia and basil) to combat drought conditions. A two-layered biopolymer-based seed coating was developed to enhance germination and impart water-stress tolerance to seeds grown in semi-arid soils.[83] In this study, *Phaseolus vulgaris* seeds were coated with a silk/trehalose inner layer containing rhizobacteria and a pectin/carboxymethylcellulose (CMC) outer layer that re-swells into hydrogels upon sowing (Figure 2e). The mucilage-mimicking pectin/CMC hydrogels acted as a water jacket surrounding the

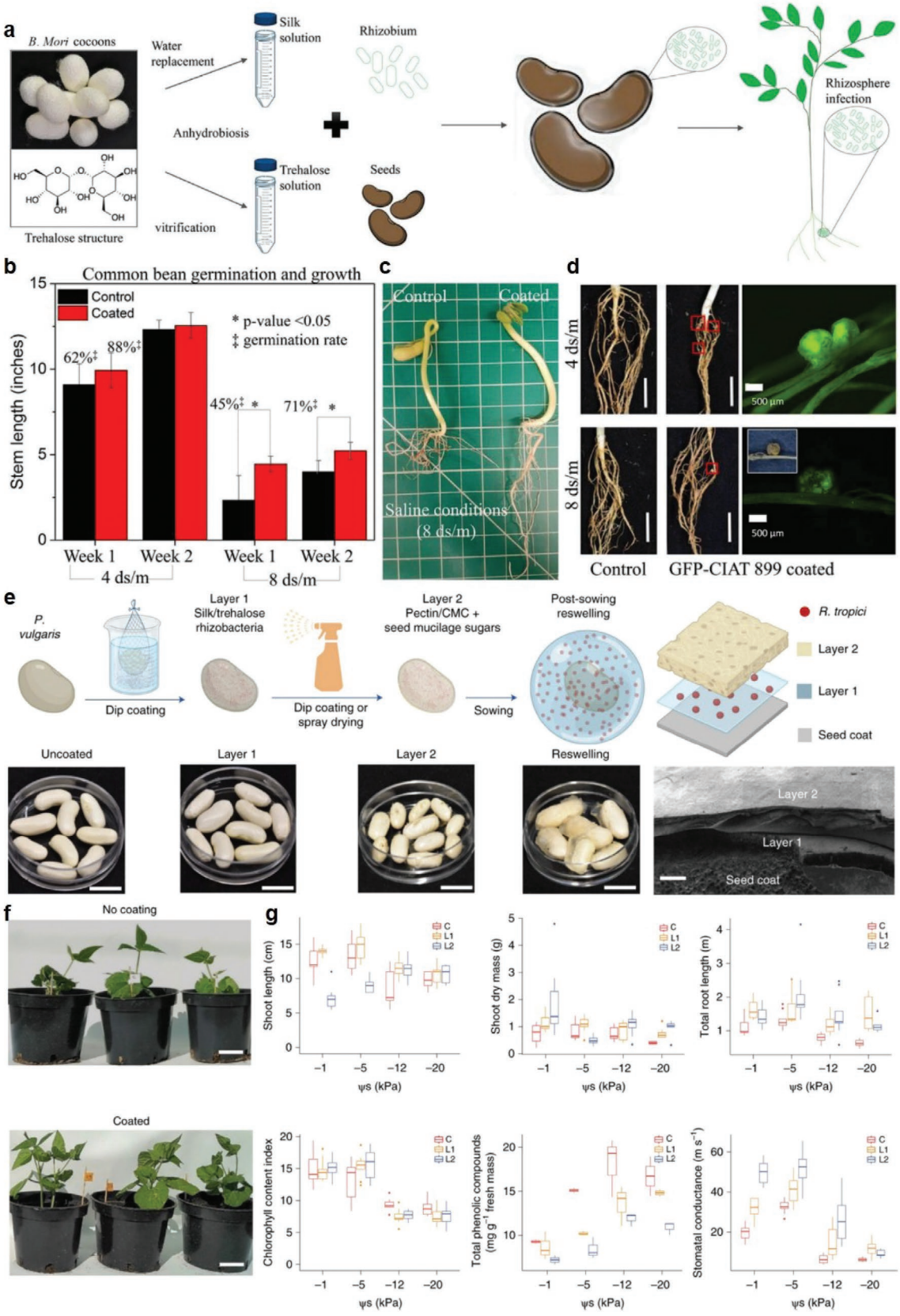

Figure 2. Seed coatings to enhance germination under abiotic stresses. a) Schematic of the seed coating process to encapsulate, preserve and deliver *Rhizobium tropici* to *Phaseolus vulgaris* seeds. b) Germination rate and stem growth over a 2-week period under nonsaline (4 ds m^{-1}) and saline (8 ds m^{-1})

seeds and created a germination-promoting microenvironment by retaining water, facilitating rhizobacteria resuscitation, and regulating nutrient supply. Higher germination rate, better root and shoot development, and enhanced plant establishment were observed from coated seeds grown in semi-arid, sandy soils of decreasing water potential (ψ_S) (Figure 2f,g). Plant physiological activities and defense responses to increased water-stress conditions were investigated by measurements of chlorophyll content, total phenolic compounds, and stomatal conductance (Figure 2g). The decrease in the amount of total phenolic compounds and the increase in stomatal conductance observed in L2 seeds indicated that the designed two-layer coating effectively equipped seeds with better water-stress tolerance so that the seeds feel less stressed in water-deficient conditions.[84,85]

2.1.3. Nanofiber-Based Seed Enhancement

While film-based seed coatings have been dominating the seed enhancement industry due to its ease of application, low cost, and adaptability for large-scale seed treatment, it also possesses a few drawbacks, for example, inhibition in water and gas exchange between seeds and the environment, and limited control over sustained release of encapsulated active ingredients. To address the limitations of conventional seed coatings, nanostructured materials have been explored and used in seed coatings, with one of the most common examples being electrospun nanofibers.[86,87] Electrospinning is a technique that applies an electric field on a highly viscous polymer suspension to produce nanofibers ranging from tens of nanometers to several microns in diameter.[88,89] Their high surface area to volume ratio, controllable porosity, and lack of residual solvents make the electrospun nanofibers good candidates as seed coating materials for preservation and delivery of active ingredients.

As discussed in the previous sections, application of PGPR as biofertilizers in crop production represents a sustainable agriculture practice, as it has the potential to increase crop yields with less inputs (i.e., water, synthetic fertilizers, and pesticides) needed. Commercialization and large-scale implementation of the beneficial bioinoculants in seed enhancement, however, still encounter many obstacles, particularly poor microbial survival, and ineffective colonization of host plants. Thus, seed coating formulations that can provide high microbial density and viability during seed treatment and storage are highly desirable. De Gregorio et al. demonstrated the effectiveness of electrospun polyvinyl alcohol (PVA) nanofibers in immobilizing and delivering rhizobacteria (Pantoea agglomerans ISIB55 and *Burkholderia caribensis* ISIB40) to soybean (Glycine max L.) seeds (**Figure 3**a).[90] The results showed that the PVA nanofiber-based seed coatings maintained sufficient microbial survival on seeds stored up to 30 d and contributed to successful colonization of both rhizobacteria on plant roots (Figure 3b). Coated seeds also presented enhanced germination, root development, dry weight of shoot and leaf numbers compared to microbe-inoculated seeds without nanofiber support. In another study, electrospun composite nanofibers of PVA and polyvinyl pyrrolidone (PVP) loaded with PGPR consortium (*Bacillus subtilis* and *Seratia marcescens*) were applied on canola (*Brassica napus* L.) seeds.[91] Such nanofiber coating was able to maintain microbial viability above a threshold level for 15 d at room temperature and facilitate microbe colonization at the root-soil interface, leading to better germination, seedling growth, leaf area, plant dry biomass, and root system in pot experiments. In vitro studies showed that the PGPR-loaded PVA/PVP nanofiber mats presented antifungal effects against at least three fungi species and phosphate-solubilizing capability, as a result of the presence of viable and functional *Bacillus subtilis* and *Seratia marcescens*. Another potential benefit of nanofiber-based coatings is the possibility for additional control over sustained and localized release of encapsulated active ingredients by regulating the surface area to volume ratio, porosity, and hydrophobicity of the nanofiber mats. This has been demonstrated through the release profile studies of a variety of active ingredients encapsulated in nanofiber-based seed coatings, including pesticides,[92] fertilizers,[93,94] plant growth regulators,[95] and micronutrients.[96]

Although electrospinning represents an effective and low-cost approach to produce polymeric nanofibers in a short period of time, this top-down manufacturing technique is also unfavorable in certain aspects for applications in the agriculture and food industry. As spinnability of a polymer suspension depends critically on its viscosity and surface tension, high polymer concentration (10–30 wt%) and hazardous organic solvents such as formic acid (FA), hexafluoroisopropanol (HFIP), acetone, chloroform, and dichloromethane (DCM) are predominantly used for generating spinning suspension,[87] which are mostly incompatible with biological dopants such as living microorganisms. Besides, the high voltage (typically 10–30 kV) required during electrospinning makes the process energy-intensive and may also pose detrimental effects on certain components involved in the spinning dope. Given these concerns, here we introduce a bottom-up nanofabrication technique named templated crystallization to produce polymeric nanofibers, which was recently developed for structural proteins.

Using silk fibroin as an example, templated crystallization refers to the use of organic templates (specifically, ordered

conditions. c) Photo of seedlings grown from coated and uncoated seeds under saline condition. d) Nodule formation at the roots assessed by visual inspection (scale bars, 1 cm) and fluorescence microscopy. Reproduced with permission.[82] Copyright 2019, National Academy of Sciences. e) Schematic of the two-layered seed coating fabrication process, pictures of seeds after each coating step (scale bars, 10 mm) and a cross-sectional view of coated seeds under SEM (scale bar, 10 μm). f) *Phaseolus vulgaris* plants grown in water-stress regimes from uncoated and coated seeds. Scale bars, 10 cm. g) Plant establishment from control (C), one-layer coated (L1) and two-layer coated (L2) seeds were investigated by measuring shoot length, shoot dry mass, total root length, chlorophyll content index, total phenolic compounds and stomatal conductance, which are plotted as a function of water potential (Ψ_S) levels. Ψ_S = −1 and −5 kPa correspond to healthy soil moisture contents, while Ψ_S = −12 and −20 kPa correspond to mild and severe water-stress conditions, respectively. Reproduced with permission.[83] Copyright 2021, Springer Nature.

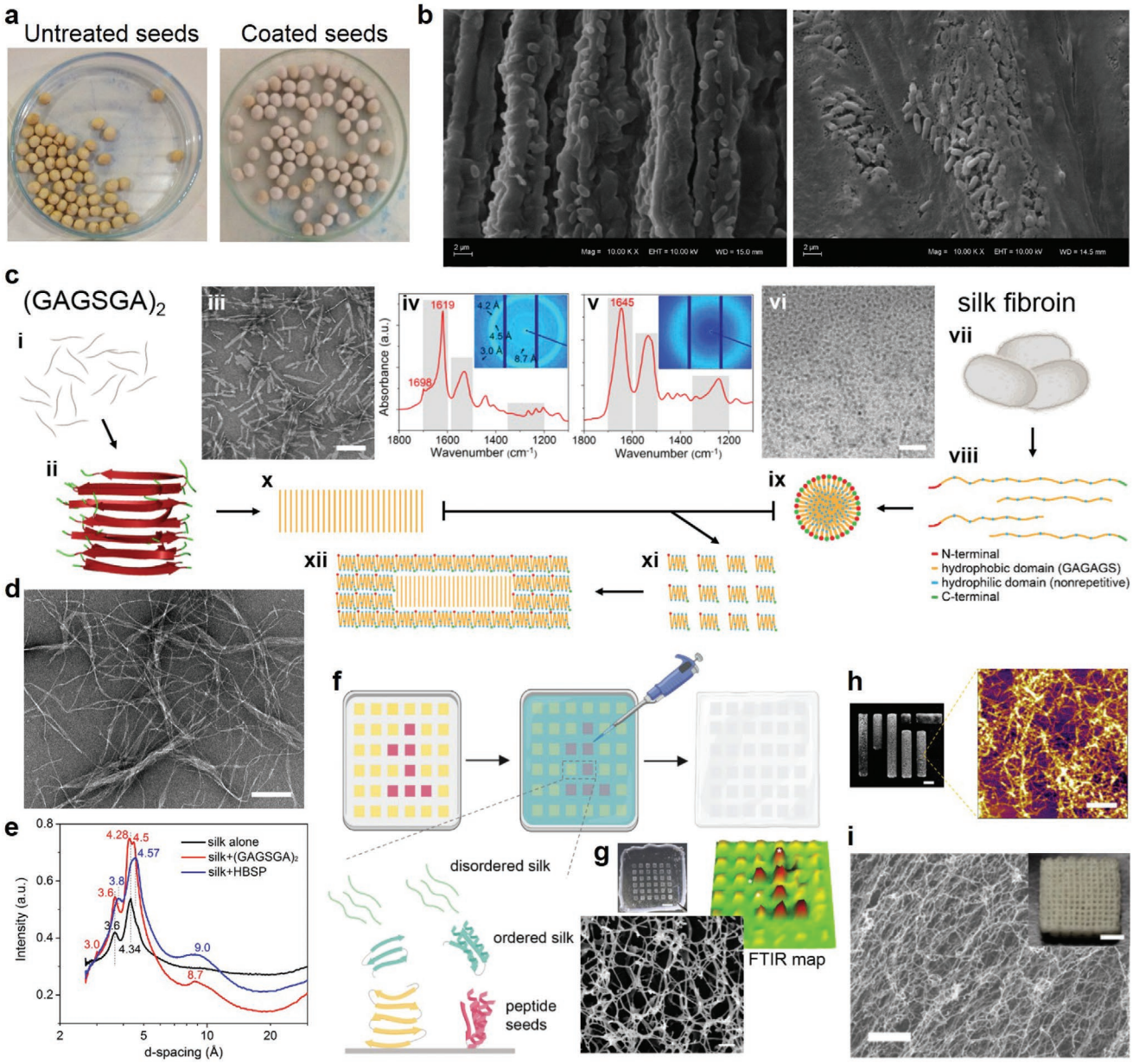

Figure 3. Nanofiber-based seed enhancement and their fabrication. a) Photographs of soybean seeds as received (left) and coated with electrospun PVA nanofibers and rhizobacteria (right). b) Scanning electron micrographs of soybean roots from seeds coated with PVA nanofiber-immobilized ISIB55 (left) and ISIB40 (right). Reproduced with permission.[90] Copyright 2017, Public Library of Science. c) Schematic of the templated crystallization process: A dodecapeptide $(GAGSGA)_2$ self-assembles into nanowhisker-like supramolecular oligomers of a highly ordered β-sheet structure (i–iv), which are used as seeds to drive a phase transformation of silk fibroin (vii, viii) from unordered (v, vi) to ordered conformations (ix,xi), thereby enabling further assembly of the silk fibroin chains into β-sheeted nanofibrils (xii). d) Negative-stain TEM image of silk nanofibrils templated by $(GAGSGA)_2$ seeds. Scale bar, 200 nm. e) Wide-angle X-ray scattering (WAXS) spectra of naturally aged silk and silk templated by different peptides. f) Schematic of the process for epitaxial growth of silk fibroin on substrates modified with different peptide seeds. g) A free-standing patterned silk film (scale bar, 3 mm) fabricated by the process shown in (f) and characterized by SEM (scale bar, 300 nm) and Fourier-transform infrared spectroscopy (FTIR). h) A 2D nanofibrillar mat generated by ink-jet printing. Scale bars, 1 mm (left) and 1 µm (right). i) A 3D construct of silk (scale bar, 5 mm) with aligned nanofibrils at the microscopic scale (scale bar, 200 nm). Reproduced with permission.[97] Copyright 2020, Springer Nature.

peptide assemblies) to drive a phase transformation of silk fibroin from unordered to ordered conformations (Figure 3c), thereby enabling further assembly of the reconfigured silk fibroin chains into higher order structures (e.g., β-sheeted nanofibrils, Figure 3d).[97] Silk polymorphs can be engineered by varying the peptide seeds used, where the silk nanofibrils templated by different peptide seeds depicted different β-sheet contents and intermolecular packing that resulted from the templates' effects (Figure 3e). Through an epitaxial growth process (Figure 3f), a free-standing patterned silk film that was nanostructured and selectively crystallized into different polymorphs was fabricated (Figure 3g), which can potentially be

used for information encryption. Additionally, templated crystallization was employed to develop nanofibrils-based printable inks, where surfaces patterned with 2D nanofibrillar mats were generated by ink-jet printing (Figure 3h) and 3D constructs of customized architecture and controlled anisotropy were produced by extrusion-based 3D printing (Figure 3i). As the templated crystallization is an entirely water-based process and requires minimal energy input, while at the same time allows for materials growth from disordered molecules all the way up to centimeter-scale hierarchically structured forms, we believe that it serves as a promising platform to be used in both seed priming and seed coating.

2.2. Precision Payload Delivery to Plants

Precision delivery of agrochemicals that fulfills plant needs while avoiding run off and side effects to the environment is of great importance in agriculture to ensure high crop yields and at the same time minimize their environmental impacts. Besides, genetic cargos used in plant genetic engineering to introduce new traits, including DNA, RNA and CRISPR-Cas9, must be precisely delivered into plant cells or subcellular organelles in order for them to function properly. In this regard, conventional delivery methods generally suffer from low efficiency, limited cargo types, damage to plant tissues, and specificity to a narrow range of plant species. Development of a more efficient, versatile, and species-independent biomolecule delivery platform is therefore in urgent need. Current efforts for precision delivery to plants can be categorized into two domains—i) precise cargo delivery into targeted tissues/organelles/vasculatures and ii) optimization of cargo release profiles. The former focuses on spatial precision while the latter emphasizes temporal precision (i.e., sustained or on-demand release). Combination of spatial and temporal precision in delivering cargo molecules to plants is also emerging and represents the ultimate goal. In this subsection, biomaterial-based precision delivery platforms for plants are first discussed, followed by an overview of strategies to optimize the release profiles of various agrochemicals.

2.2.1. Biomaterial-Based Precision Delivery Systems

Precision delivery systems refer to solutions facilitating cargo molecules delivery to targeted tissues through several barriers, including cuticle, epidermis, Casparian strip, plant cell wall, and membranes of the cell and organelles. Various strategies have been proposed to overcome tissue barriers, including loss of barrier function by mechanical or enzymatic damage, enhancement of permeability using chemical or electric treatments, developing carriers that can travel through tissue and cellular barriers, and designing devices that can reach target loci. Common delivery practices, such as trunk injection, foliar infiltration, vacuum infiltration, and bombardment, are not discussed here as priority is given to biomaterials-based precision delivery systems (e.g., microneedles and nanomaterials) and the roles of biomaterials to establish a material/plant interface.

Biomaterial-Based Microneedles: Biomaterial-based microneedles have been investigated for decades in biomedicine for transdermal and intradermal drug delivery and vaccination as an easily deployable, rapid, pain-free method to overcome the drug delivery barrier imposed by the skin's outer stratum corneum layer.[98–100] Similar principles are now applied to plants, where the use of microneedles has been recently demonstrated. Although steel microneedles were proposed to increase bark permeability for agrochemical delivery[101] as used for medical applications, polymeric microneedles are now more investigated, given their versatile encapsulation of payloads and materials safety and sustainability. Cao et al. used silk fibroin extracted from *Bombyx mori* cocoons and its derivatives (i.e., proteins) to fabricate microneedles with controlled solubility in plant saps for material delivery and sampling (**Figure 4**a).[102] The authors designed the microneedles according to the target tissue histological analysis. Therefore, they delivered small molecules, proteins, and bacteria to various plant tissues, such as xylem and phloem of tomato plants and leaves and meristem of tobacco, via punching through tissue barriers, including cuticles and epidermis (Figure 4b). This design principle for delivery precision differs from microneedles for transdermal drug delivery systems in medicine where microneedles do not target vasculature as the main motivation for microneedles is low invasiveness, pain free, and ease of application without the need of medical training. However, this design renders microneedles a similar role to steel needles for intravenous injection, which was considered impossible in plants due to anatomical and physiological constraints, such as the dimension of the vasculature and negative pressure in xylem. While trunk injection enables access to the vasculature, it is time-consuming and invasive compared to applying a "sticker." Microneedles can also access meristem, a promising target locus for genetic engineering accessing stem cells, particularly for nonheritable and current generation genetic modification. The authors also showed that biopolymers-based microneedles are mechanically robust for plant tissue injection.

Isomalt, a small molecule made from sugar, was also used for precision delivery in a microneedle-like format. Fiorello et al. developed a microhook array by casting cargos and melted isomalt mixtures for precise delivery to leaf tissues (Figure 4c,d).[103] They presented the small molecule delivery and mobility through the vascular tissue using a fluorescein-loaded isomalt array after injection onto *Vitis labrusca* leaves. Such microhooks can easily lose features under environmental humidity due to the high affinity of isomalt to water, demanding protective post-treatment or specific storage conditions. Note that the high temperature (100 °C) used during fabrication is unsuitable for temperature-sensitive and labile cargos.

Unlike the extensive research done in the biomedical field, using microneedles for precision delivery to plants is emergent, and its versatility is far from being fully unveiled. Combining advanced microneedle fabrication techniques (i.e., drawing, 3D printing, molding, and layer-by-layer fabrication) with rational modification of biomaterials (i.e., formation of micro/nano particles and functionalization of surface groups) will help narrow the research gap. In fact, most reported nanocarriers for plants were first delivered via foliar and vacuum infiltration to plant leaves and explants to circumvent most of the barriers.

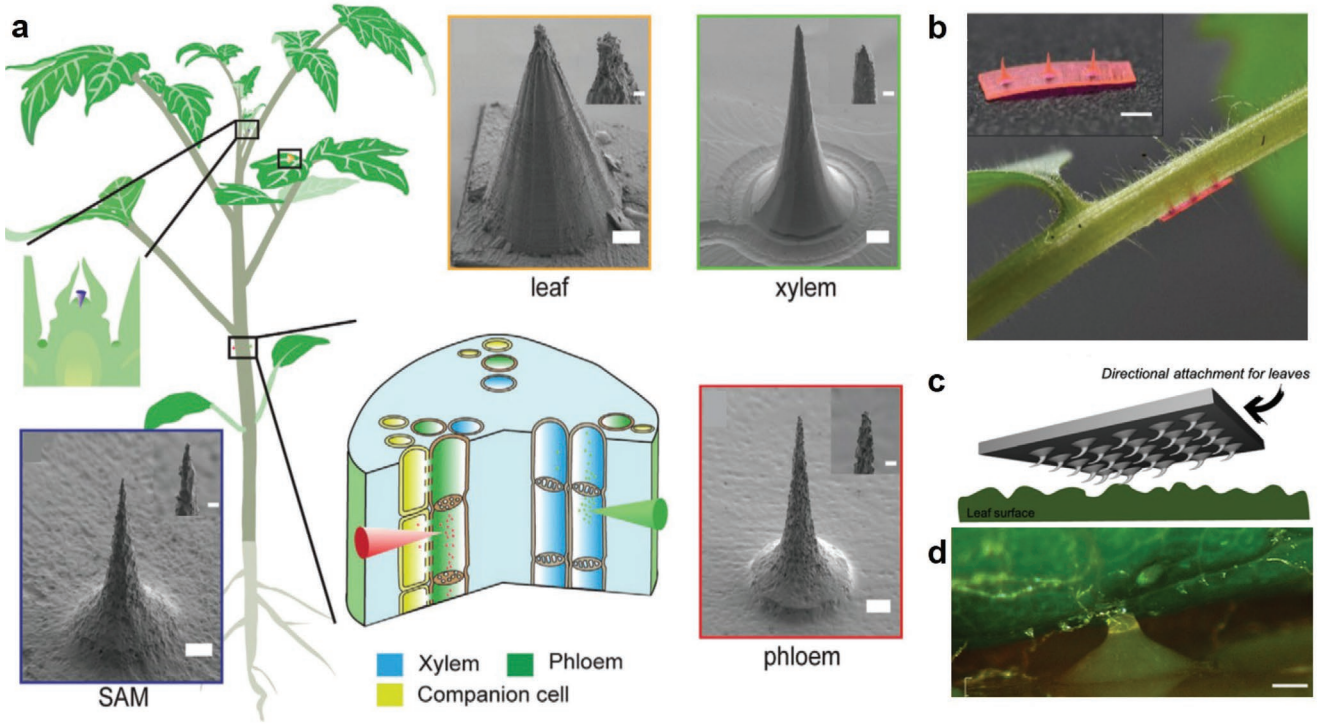

Figure 4. Microneedles for precision delivery. a) Scanning electron micrographs of silk microneedles (scale bar, 100 µm) designed for injection in shoot apical meristem (SAM), leaf, xylem, and phloem. The insets show the corresponding injector tips (scale bar, 20 µm). b) A tomato plant injected in the petiole by an array of microneedles loaded with rhodamine 6G. Scale bar of the top left image, 1 mm. Reproduced with permission.[102] Copyright 2020, Wiley-VCH. c) Microhook-based directional attachment system on leaves. d) Self-dissolving isomalt microhooks loaded with fluorescein interlocking with leaf surface. Scale bar, 200 µm. Reproduced with permission.[103] Copyright 2021, Springer Nature.

However, these laborious practices cannot be used in field and for non-leaf tissues in vivo.

Nanomaterials with Desirable Physiochemical Properties: Nanomaterials provide time-controlled, target-specific, programmed, stimuli-responsive, and multifunctional drug delivery capabilities. Their applications in plant genetic engineering, agrochemical delivery, and consequent environmental impacts have been extensively reviewed.[104–108] Particularly intriguing is the possibility to deliver in vivo cargos (e.g., DNAs, RNAs, proteins, CRISPR/Cas9 complexes) to engineer plants and regulate their metabolic activity. Delivery to intact plant cells in vivo, compared to delivery to isolated protoplasts, is more attractive as it circumvents the laborious and time-consuming regeneration procedure and limitations in plant species.

Size exclusion limit (SEL) is a key design factor for nanomaterials delivery into intact cells and organelles. SEL identifies the upper limit of a molecule size allowing its free transport through a biological membrane. The SEL of cuticle, Casparian strip, and plant cell wall are <10 nm, <1 nm, and 5–20 nm, respectively, even though nanoparticles up to 50 nm were reported to permeate cell wall in plants via unclear mechanisms. Indeed, studies on metallic nanoparticles have demonstrated that most nanoparticles applied via foliar spray are blocked/trapped by the cuticle. For example, >70% of the rod-shaped CeO_2 nanoparticles (≈8 nm) were easily removed after spray,[109] and 20–50 nm CuO nanoparticles aggregated to 230–400 nm agglomerates on lettuce leaf after 2 h,[110] and those reaching plant cells undergo poor dislocation.[107,109,111] Furthermore, the delivery efficiency does not significantly increase for nanoparticles inducing larger pores in cuticles (e.g., TiO_2 nanoparticles damage cuticles probably by photocatalytic properties).[111] Similarly, nanomaterials suffer from low delivery efficiency via root application (≈0.1% or less).[112] Bombardment of biomaterials, including mesoporous silica and gold nanoparticles with large size (around 600 nm in diameter with 10 nm pores), was reported to deliver cargos to plant leaves.[113] However, these are only suitable for superficial tissues with thin barriers because of the particles' limited kinetic energy. Another strategy is exposing nanoparticles to plant cells directly with the assistance of foliar infiltration or via trunk injection. This strategy has been widely deployed to enable nanoparticles to circumvent the permeation through barriers with extremely small SELs, whereby nanoparticles cope with cell wall (SEL 5–20 nm) and membranes of the cell and organelles (SEL > 500 nm).

Preparation and/or modification of nanomaterials with size below the SEL of cell wall is one path to precise delivery for plant, especially those have demonstrated successful delivery to mammalian cells and isolated plant cell protoplasts, for example, metallic/magnetic nanoparticles, carbon-based nanomaterials (e.g., fullerene, carbon nanotube, graphene), silicon-based nanoparticles (e.g., silica nanoparticle, mesoporous silica nanoparticle). These nanomaterials can be directly used for delivery to intact plant cells because they already meet all the SEL requirements. Of particular interest is carbon nanotubes which demonstrated extraordinary performances and versatility

as a nanocarrier for biomolecules delivery to plants owing to their high aspect ratio, exceptional tensile strength, and capability to protect biomolecules from cellular metabolism and degradation, and biocompatibility. Meanwhile, the potential applications of the referred nanomaterials raise safety concerns related to their environmental impacts, translocation and fate in plants and health risks.[114,115] Policy makers are taking precautionary principles that may not be scientifically justified when making regulations. For instance, carbon nanotubes were added to the so-called SIN ("Substitute It Now") list of chemicals as a single substance category.[116]

Natural inorganic materials and polymers have also been fabricated in nanoparticles formats to overcome such concerns and potential regulations due to their intrinsic nontoxicity. For example, Naqvi et al. produced calcium phosphate nanoparticles (size: 15–32 nm and zeta potential: −25.6 mV) to encapsulate a reporter gene and reached a transformation efficiency of ≈80.7%.[117] The self-assembly of DNA molecules through Watson–Crick base pairing allows the construction of various custom-designed 2- and 3D nanostructures with accurately controlled size ranging down to 2.5 nm, well below the SEL of the plant cell walls.[118–120] DNA nanostructures have also been used for drug, DNA, RNA, and protein delivery in animal systems.[121,122] These findings infer that DNA nanostructures may facilitate cargo delivery to intact plant cells. Zhang et al. systematically assessed different DNA nanostructures for their ability to internalize into leaf cells of tobacco, arugula, and watercress (**Figure 5**a).[118] They reconfirmed that structural and mechanical properties (e.g., size, shape, compactness, and stiffness) of DNA nanostructures determine their internalization into intact plant cells, consistent with the results in mammalian cells.[123] Interestingly, they observed an abrupt decline in the internalization efficiencies between the 8.8- and 12.6-nm tetrahedrons, which suggested the SEL of the plant cell wall was less than 12.6 nm. As a functional molecular model, siRNA was hybridized to DNA nanostructures and delivered to leaves of transgenic mGFP5 *Nicotiana benthamiana*. Efficient gene silencing was achieved, ascertaining DNA nanostructures for cargo delivery to intact plant cells. Later studies found that the magnitude of the zeta potential of nanoparticles is another key factor in determining whether a particle can spontaneously penetrate the lipid membrane of cells and organelles.[124,125] Other natural biomaterials such as proteins,[97] cellulose,[126] and chitin[127] can also assemble into nanocrystals with size below the SEL of the plant cell wall and may be used as nanocarriers. The loading capacity of these nanocarriers however, may be limited due to their ultrasmall size.

Fabricating pure polymeric nanoparticles with a uniform size below the SELs is challenging. Therefore, polymeric biomaterials are used to modify and functionalize other nanomaterials (e.g., silica, metal, carbon nanotubes) that can be easily fabricated and highly monodispersed. Modification of surface charge is one major strategy. For example, polycationic chitosan was used to form complexes with single-walled carbon nanotubes, enabling negatively charged plasmid DNA binding to the nanocarriers via electrostatic interactions.[128] Strano and coworkers proposed a mathematical model of the lipid exchange envelope and penetration (LEEP) mechanism for translocation through lipid bilayers based on their findings that particle size and the zeta potential are pivotal factors determining the particle trap within the organelle.[124] Surprisingly, the sign of the zeta potential has little influence in this process, although the lipid bilayer is negatively charged. In addition, the theory counterintuitively indicates that smaller nanoparticles require larger surface potentials to penetrate the lipid bilayer. Despite its assumptions and not dealing with cell wall, the LEEP model successfully predicted the ability or inability of various nanoparticles to penetrate the chloroplast. Modification of amphiphilicity, porosity, and morphology (aspect ratio) is likely to affect the interactions among cargos, nanoparticles, and cell wall and membranes, yet little has been reported. Still, concerns for safety related to nanomaterials applications in plants and crops and policy barriers are inevitable challenges for the deployment of nanomaterials technologies in drug delivery for plants.

Nanomaterials Decorated with Physiologically Functional Molecules: While many studies focus on relating the physicochemical properties of nanoparticles with their structure and function, the physiological roles of biomolecules and existing material translocation mechanisms in cells and organelles are often neglected. Cell-penetrating peptides (CPPs), typically made with up to 30 amino acids, are the domains responsible for the rapid penetration of such peptides through plasma membrane. They have been used as a powerful tool to translocate and internalize a wide variety of cargos into mammalian cells[129–131] and isolated plant protoplasts,[132–134] despite a lack of understanding of the exact mechanism. Their application is also expanding to payloads delivery to intact plant cells, in vitro and in vivo.

Lakshmanan et al. designed a peptide-based gene carrier consisting of a CPP (Bp100 or Tat_2) fused with a polycation (Figure 5b).[135] The polycationic peptide interacts with negatively charged pDNA to form complexes, while the CPP transports the complexes into plant cells by penetrating the cell walls and plasma membranes. The carrier demonstrated rapid and efficient transient transfections into intact leaf cells of *Nicotiana benthamiana* and *Arabidopsis thaliana*. The fusion peptides demonstrated significantly higher transfection efficiency than the non-fused CPP peptides alone. It is noteworthy that the pDNA–peptide complex is around 300 nm in diameter and negatively charged. The same group also delivered double-stranded RNA into intact leaf cells of *Arabidopsis thaliana*, via this peptide-based gene carrier.[136] The dsRNA–peptide complex is 100–300 nm in diameter and weakly positively charged. Double-stranded DNA[137] introduction into intact *Nicotiana benthamiana* and protein delivery to rice callus[138] and *Arabidopsis thaliana*[139] was also demonstrated. Transfection behavior can be changed and controlled by selecting peptide-based gene carriers with appropriate amino acid sequences. For example, CPP structure and properties were optimized to facilitate DNA release from the polycation polymer via the formation of a bioreducible cyclic domain (Figure 5c).[140] Combination of CPP with other existing carriers to impart/enhance desired properties was also reported. Cas9 ribonucleoprotein complexes[141] and enzymes[142] were successfully delivered to *Arabidopsis thaliana* callus and to the root hair cells of *Arabidopsis thaliana* seedlings via a cell-penetrating peptide–polyion complex vesicle, respectively. An artificial peptide, composed of cationic cell-penetrating and hydrophobic endosomal escape domains and CPP fusion peptide, enabled more efficient transfection of

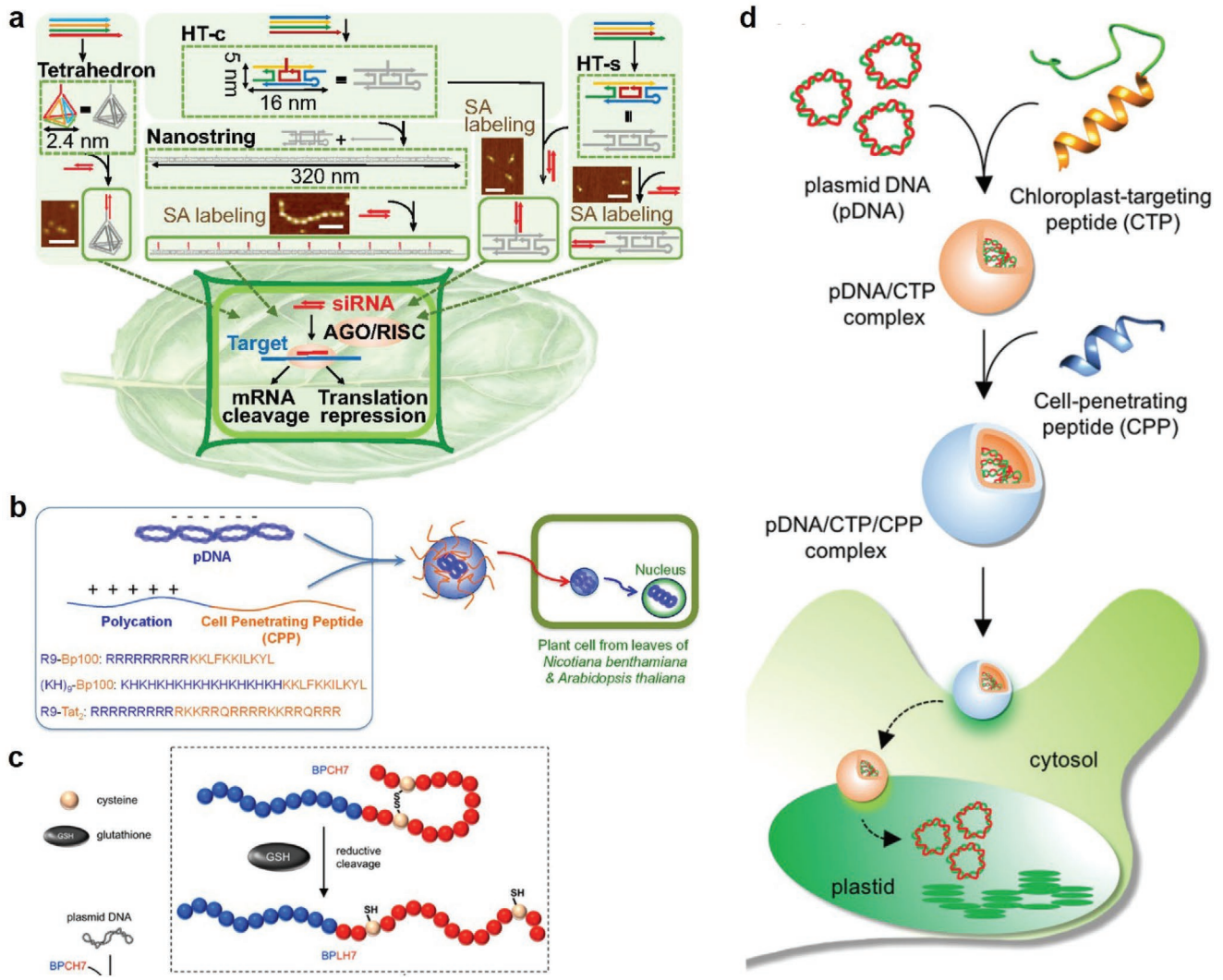

Figure 5. Engineered nanomaterials for precision delivery. a) DNA nanostructure synthesis and plant infiltration. The tetrahedron and HT monomer was synthesized from four single-strand DNA sequences, and the 1D nanostring structure was synthesized by polymerization of HT monomers with the introduction of an initiator strand. The cargo was attached at the apex of the tetrahedron, along the nanostring, and at the side (HT-s) or center (HT-c) of each HT nanostructure, respectively. Insets show AFM images of streptavidin-bound biotinylated HT monomers. DNA nanostructures loaded with cargos are infiltrated into the transgenic mGFP5 Nb plant leaves for downstream studies. Scale bars, 100 nm. Reproduced with permission.[118] Copyright 2019, National Academy of Sciences. b) Peptide-based gene delivery to intact plant cells. The negatively charged pDNA and designed peptides formed complexes via electrostatic interaction. The pDNA complexes penetrated through the cell wall and the cell membrane after foliar infiltration and genes on pDNA were expressed throughout the cell. Reproduced with permission.[135] Copyright 2012, American Chemical Society. c) Schematic representation of the Glutathione Reducible Peptide (BPCH7). Reproduced with permission.[140] Copyright 2018, American Chemical Society. d) Schematic formulation of the clustered pDNA/CTP/CPP complexes and plastid transformation to a plant cell. Reproduced with permission.[147] Copyright 2019, Wiley-VCH.

callus cells than the CPP fusion peptide alone.[143] Similarly, an endosome-escaping micelle, composed of plasmid DNA condensed with cationic peptides and dually modified with CPP and endosome-disrupting peptides, was reported to avoid endosomal entrapment and subsequent vacuolar degradation of the DNA cargo.[144] These results suggest the feasibility of superposition of functionality by adding components and structures.

CPPs alone enable nonspecific delivery to cytosol, while more precise delivery targeting plastids such as chloroplasts and mitochondria is of great interest owing to the metabolisms occurring in these compartments. Incorporation of organelle-targeting biomolecules has been explored. Hurt et al. have shown that the first 12 amino acids of the yeast cytochrome c oxidase subunit IV pre-sequence were sufficient to direct dihydrofolate reductase into the mitochondrial matrix[145] and can be used as a mitochondria-targeting peptide. Using a combination of this mitochondria-targeting peptide (MTP) and cell-penetrating peptide (CPP), Chuah et al. reported the intracellular delivery of plasmid DNA to the mitochondria of *Arabidopsis thaliana* via negatively charged CPP_{KH}-MTP_{KH}-pDNA with hydrodynamic diameters of 160–280 nm.[146] Remarkable increases in transfection levels were

observed compared to that of MTP_{KH}-pDNA complexes, indicating the critical internalization role of CPPs. The group further developed a peptide-based gene carrier consisting of BP100 and chloroplast-targeting peptides (CTP, KH_9-OEP34) for DNA delivery (Figure 5d).[147] Interestingly, the chloroplast-targeting peptide showed recognition of many plastids instead of exclusive recognition of chloroplast. In addition, dimeric CPP has shown significantly higher gene transfection efficiency than monomeric CPP, probably by enhancing the cell-penetrating power of the carrier peptide. The complexes were positively charged and displayed hydrodynamic diameters above 200 nm. The results from studies using CPP for cargo delivery to intact plant cells seem circumventing the SEL of cell wall through unclear mechanisms. Despite the large hydrodynamic diameters reported, the complexes showed much smaller sizes in AFM results, where the heights were around 10 nm. Therefore, the complexes may deform and reduce size during their travel through the cell wall. It is also possible that some complexes are smaller than SEL as the complexes have a large polydispersity index. The charge of the complexes, either positive or negative, does not seem to block their internalization. Overall, the penetrating mechanism of CPPs through plant cell walls needs to be further investigated.

Incorporating organelle-targeting biomolecules into nanomaterials (e.g., quantum dots, carbon nanotubes) enables more precise delivery compared to those depending on physical factors (i.e., pH difference).[128] Santana et al. combined MTP with quantum dots (as a marker) and β-cyclodextrin (as a molecular basket) to deliver small molecules (i.e., ascorbic acid and methyl viologen) to the chloroplast, achieving tuning of the organelle's oxidative status.[148] However, chronic or high-level uses of Cd-based quantum dots (QDs) in agriculture applications raise food and environmental safety concerns.

In sum, the delivery of cargo molecules into intact plant cells and organelles needs to overcome biological barriers with stringent geometrical, biochemical, and physical properties. To address these requirements, nanostructures have been rationally designed to cross biological membranes and promote internalization in cells and organelles by adopting three main strategies, i.e., i) fabrication of nanoparticles with characteristic dimensions below SEL, ii) engineering of nanoparticles with shapes facilitating internalization, and iii) modification of nanoparticles with physiologically functional molecules. The first strategy focuses on fabricating nanomaterials less than the smallest SEL found in cell walls (≈20 nm). Additionally, nanomaterials with negative charges are preferable since they will not be trapped by the also negatively charged cell wall. The second strategy also considers physicochemical interactions between the nanomaterials and the barriers. Nanomaterials with high aspect ratio, i.e., 1D materials (i.e., nanotubes or rods) and 2D nanosheets, experimentally demonstrated internalization, even if their dimension is larger than the SEL, as shown in the use of corona phase carbon nanotubes for targeted delivery of plasmids. The third strategy focuses on the decoration of the nanomaterial with biomolecules that can favor translocation across the membrane. This strategy is particularly important to circumvent size limit and charge requirements that can be technologically difficult to achieve, at scale.

2.2.2. Optimization of Release Profiles

Controlled release and stimuli-responsive release of agrochemicals are two main strategies for the optimization of drug release profiles. Controlled release refers to the release of agrochemicals, mainly fertilizers, herbicides, and pesticides, over a prolonged period, unlike the conventional burst release approaches. For decades, it has been proposed to administer agrochemicals in a safer, more economical, and efficient way, with the ultimate goals of reducing input resources, mitigating environmental impact, and enhancing safety for growers and consumers.[149–152] Most of the technologies for controlled payload release approximate environmental conditions as constant and neglect critical fluctuating parameters, such as soil biochemical conditions, weather, and plant life cycle stages. These variables may however be used to design stimuli-responsive release technologies that employ triggers, such as pH, enzyme, and temperature, to dynamically control precise administration of agrochemicals.

As used for medical applications, carriers for controlled release of agrochemicals have been developed from a variety of materials, ranging from inorganic materials, such as sulfur and silica, to organic materials, such as lipids, proteins, synthetic and natural polymers, with varying sizes, surface physicochemical properties, and architectures. However, these agrochemical carriers must comply with unique requirements that arise from large-scale in-field applications and the sustainability of the economy and the ecosystem. Additionally, environmentally friendly, and safer materials are preferred by policymakers due to public awareness of environmental sustainability. Such requirements hinder the wide application of commonly studied materials, such as toxic heavy metal-based QDs and non-degradable synthetic polymers,[153] despite their outstanding performance. Degradable biomaterials, including biopolymers and their derivatives, such as chitosan, cellulose, lignin, and starch, have been explored as carriers for the controlled release of agrochemicals due to their desirable features, such as low toxicity, circular life, ease of functionalization, and large availability. This section describes degradable biomaterials-based strategies for controlled release and stimuli-responsive release of agrochemicals.

Controlled Release: Macronutrient fertilizers (nitrogen, phosphorus, and potassium) are the largest used agrochemical (demand was estimated to be 184 million tons in 2015 and is forecast to reach 201 million tons in 2020).[154] They are deployed mostly via poorly effective soil application, causing circa 30–50% of runoff with detrimental effects on the environment, resource management, and soil health. Controlled release of nutrients in soil/plant systems that synchronizes the release of macronutrients from fertilizers and their uptake into plants is an effective method to increase fertilizer usage efficiency.[152,155] The European Standardization Committee Task Force recommends the criteria that no more than 75% of the nutrients should be released within 28 d.[156] Urea is the most widely used fertilizer and as such has been explored as a fertilizer model for controlled release studies. The strategy of controlled release is based on the reduction of water and urea permeability by surface coating or strongly binding urea with a substrate.

Early studies of controlled release of fertilizers, also known as slow-release fertilizers, utilized inorganic materials with/without modification and showed limited capability in controlling the nutrient release.[152,157–161] Polymeric coating dramatically extended the release time by forming a release barrier or strongly binding fertilizers on carriers.[162,163] However, environmental concerns are raised by non-degradable polymers. Recent regulations, such as the European Union's *Directive on Single-Use Plastics* and *Limitation in the use of Intentionally Added MicroPlastics in Products*,[164,165] will ban certain use of nondegradable plastics, driving the research focus to degradable polymers, particularly natural polymers (e.g., starch, cellulose, chitin, lignin) that are low cost, abundant (several million tons per year), and suitable for large-scale production. Despite the efforts to optimize the performances of natural polymers as a coating material, few studies have met the criteria and a high loading capacity (>95%). For instance, the hydrophilic nature of starch prevents it from being a suitable coating material for urea, regardless of the combination with other materials and modification of starch.[166–169] Chemical modification of cellulose by reaction with its hydroxy groups was also deployed, and the relationship between release rate and structure of cellulose-based materials was discussed,[170] but the results did not meet the criteria.[171] While Faez and co-workers reported potassium-containing microspheres based on chitosan and montmorillonite clay that sustained K^+ release for more than 55 days and maintained a relatively constant concentration of potassium in the soil, the high polymer content (>46%) make the solution of difficult commercialization.[172] However, many hydrophilic polymers showed excellent release properties when used as superabsorbent polymers at the nanoscale, including starch, alginate,[173] and cellulose derivatives.[174]

Owing to their superior performances as adhesives, coatings, and sealants, biobased polyurethanes,[175] a greener alternative to fossil-based polyurethanes, have also been explored as carriers for the controlled release of fertilizers. Soybean oil,[176,177] castor oil,[162,176,178] palm oil,[179] and corn stover[180] were reported as the raw materials to extract polyol for the synthesis of biobased polyurethanes for coating urea. The uniform coating of urea by biobased polyurethanes significantly prolonged the 75% release duration, from 35 to 80 d. Despite their superior performances, the degradation profiles of these biobased polyurethanes in soil have not been investigated yet.

Micronutrients, phytohormones, and pesticides usually have distinct properties from macronutrients and are required at much lower amounts (micronutrients <0.01% dry weight of plants, phytohormones, and pesticides $<10 \times 10^{-6}$ M). In addition, deficiency of micronutrients results in physiological and metabolic disorders, and excess of micronutrients causes toxicity,[181,182] which technically necessitates controlled release to deliver the precise dosage. Furthermore, targeted delivery using biomaterials formats (coatings, particles, fibers, sheets) that foster deployment close to the plant tissues as opposed to the wide application through foliar spray or soil applications should be favored. Metal and metal oxide nanoparticles are common micronutrient sources, while other biomaterials are incorporated as surface modification, coating, matrix, etc., to control release profile and/or as carriers to facilitate plant uptake and translocation. Martins et al. immobilized ZnO nanoparticles onto biopolymers (microcrystalline cellulose, chitosan, and alginate) to form composites for micronutrient delivery.[183] ZnO nanoparticles/alginate beads showed a lower but enough Zn release for the maize growth while avoiding the early-stage Zn toxicity caused by conventional Zn supplies. While researchers have also explored the application of carbon-based materials, including graphene, graphene oxide, CNTs, and carbon nanofibers (CNFs), as carriers for nutrient nanoparticles due to limited plant toxicity and uptake by plants,[184] the regulatory restriction may apply as previously mentioned.

Controlled release of phytohormones was achieved via strong binding to matrix or encapsulation. Yang et al. developed inclusion complexes of GA_3 with cyclodextrins derivative (HP-β-CD) that showed slow release of GA_3 due to the binding ability of the HP-β-CD.[185] Alginate/chitosan and chitosan/tripolyphosphate nanoparticles containing gibberellic acid (GA_3) were reported for seed priming of *Solanum lycopersicum*.[70]

Controlled release of toxic agrochemicals (e.g., pesticides, herbicides) was employed as an effective strategy to reduce toxicity and side environmental effects compared to a burst release. For example, Grillo et al. prepared chitosan-based nanoparticles to encapsulate paraquat (1,1′-dimethyl-4,4′-bipyridinium dichloride), a fast-acting nonselective contact herbicide.[186] These nanoparticles showed preserved herbicidal activity but reduced toxicity compared to the pure compound. Similarly, calcium alginate nanocarriers were suggested as a promising and safe candidate for sustained and slow release of cypermethrin, which may decrease the use of cypermethrin and mitigate related environmental pollution.[187] Functional biomolecules embedded in degradable nanomaterials for disease control were also investigated. Mitter et al. loaded designed dsRNA into non-toxic, degradable, layered double hydroxide clay nanosheets to target pepper mild mottle virus (PMMoV) and cucumber mosaic virus (CMV).[188] Clay nanosheets were slowly degraded into biocompatible residues by atmospheric CO_2 and moisture, releasing dsRNA in a controlled manner over 30 d. The results showed dsRNA uptake into plant cells and silencing of homologous RNA. Liu et al. developed a gene silencing method for efficiently preventing Tomato yellow leaf curl virus (TYLCV) infection in tomato plants by combining artificial microRNA and clay nanosheets.[189]

Stimuli-Responsive Release: The on-demand release of agrochemicals to fulfill real-time plants' nutritional needs and engineer their response to stressors can be achieved via stimuli-responsive release, which uses pH, temperature, ionic strength, light, enzyme, or magnetic fields, as triggers for cargo deployment.[190,191] Multistimuli-responsive systems were also reported. For example, Hou et al. designed macrospheres loaded with salicylic acid, whose release could be triggered in the presence of hydrogen peroxide (oxidant) and cellulase (enzyme).[192] A novel pH and redox dual-responsive cellulose-based nanogel was also reported.[193] Yang et al. constructed a smart plant hormone delivery system for gibberellic acid based on metal-organic frameworks (MOFs) and supramolecular nanovalves that exhibited multistimuli-responsive release under external stimuli including pH, temperature, and competitive agent spermine.[194] Using plants' environment or response to stressors as triggering principles comes with many limitations. Plants have a limited impact on their local environment, especially at

the early stage of stress. Stimuli that can trigger the release of cargo molecules should leverage changes in plant physiology and metabolism, such as physicochemical properties of sap, hormones, and signaling molecules in the vasculature and the release of volatile organic compounds. Extensive investigations of plant responses to various abiotic and biotic stresses have been carried out. Physiologically associated signs of biotic and abiotic stresses were found and have been used in plant sensors and plant wearables for plant monitoring and diagnosis, as we previously reviewed.[195] However, changes in plant physiological indicators and metabolic activity can be associated with several abiotic stressors. So far, only a few studies have shown a successful development of in planta stimuli-responsive release that can mitigate the emergence of such stressors. Major challenges are, in fact, associated with the causality of the stimulus since several stressors or needs may induce the same triggering signal.

The straightforward causation between the appearance of specific biomolecules and biotic stressors (i.e., pathogen infections) makes disease control the pioneer field for stimuli-responsive release. For example, bacterial and fungal pathogens will secret specific enzymes and/or toxins in hosts that do not exist in healthy plants. These secretions can be considered as a fingerprint of infection and used as a stimulus due to their uniqueness. Lignin, one major component of the plant cell wall, is a target for some lignin-degrading enzymes (e.g., laccases and peroxidases) and has been investigated as infection-responsive nanocarriers for disease control. Fischer et al. presented enzyme-responsive lignin nanocarriers encapsulating fungicide against fungal trunk infections of grapevine plants (**Figure 6**a).[196] Drug-loaded lignin nanocarriers were delivered to grapevine plants by trunk injection. Only upon Esca infection, lignin-degrading enzymes secreted by the Esca-associated fungi, degrade the lignin substrate and release the fungicide to kill fungi. These infection-responsive nanocarriers enabled selective, on-demand drug release for plants. Trichoderma spores were also encapsulated in nanoparticles to enable an enzyme-responsive biofungicides (Figure 6b–d).[197] The spores displayed germination selectively triggered by the pathogenic fungi in vitro, which antagonized the pathogenic fungi and finally supplanted the pathogen. Beckers et al. further explored the fate of polymeric nanocarriers in several plant models, including grapevine, apple, and peach, regarding the chemical composition, size, surface charge, or surfactant of the nanocarriers.[198]

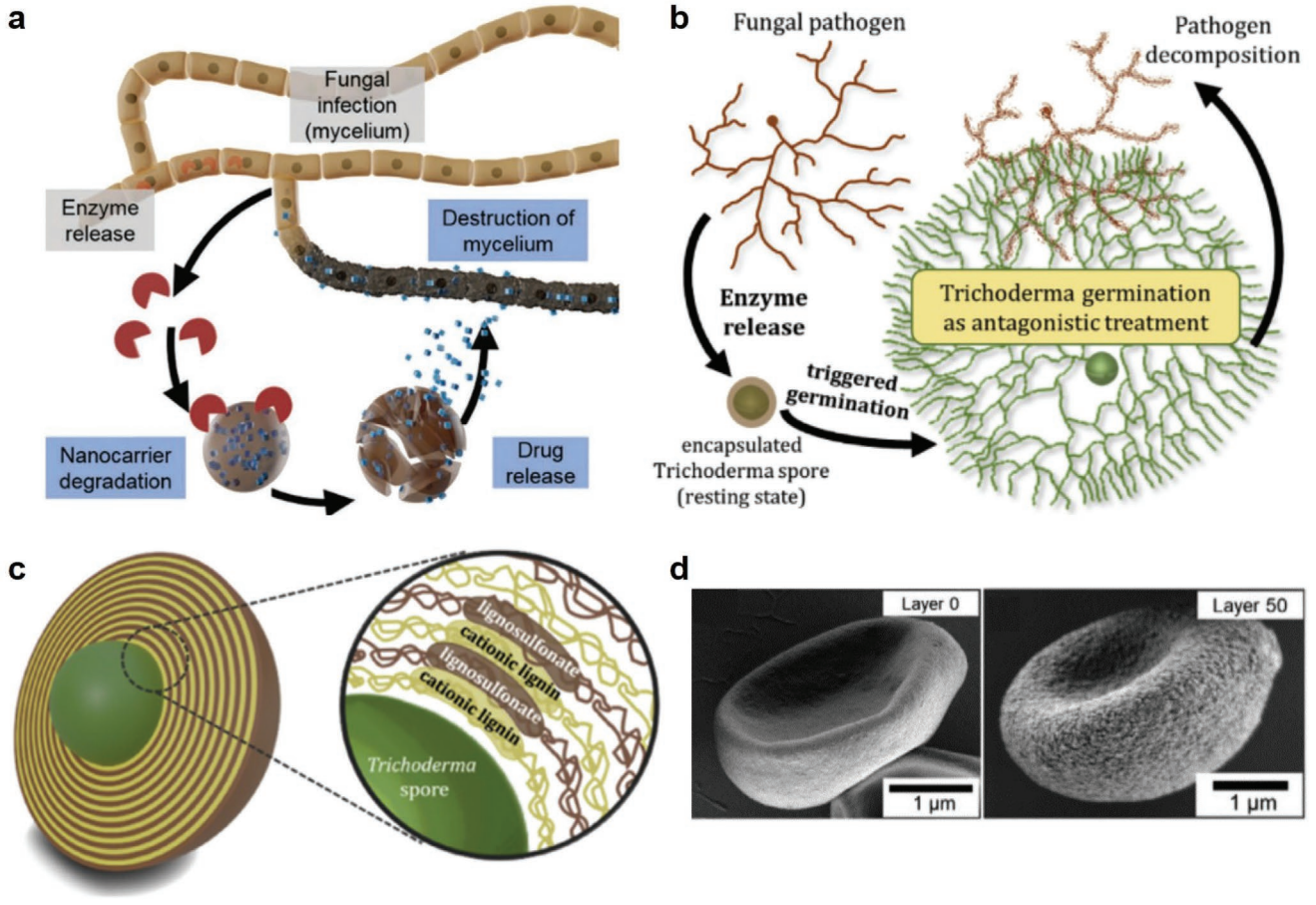

Figure 6. Delivery systems with stimuli-responsive release for disease control. a) Schematic of the mechanism of lignin nanocarriers. Fungicide-loaded lignin nanocarriers release the drug only when the Esca fungi secrete lignin-degrading enzymes. Reproduced with permission.[196] Copyright 2019, Wiley-VCH. b) Conceptual illustration of *Trichoderma* spores delivery as a biological control agent. c) Schematic of the structure of a coated *Trichoderma* spore where the coating is composed of alternating cationic Kraft lignin and anionic lignosulfonate formed via a layer by layer deposition. d) SEM images of *Trichoderma* spores before coating and after 50 layers of coating. Reproduced with permission.[197] Copyright 2020, Elsevier.

They found that negatively charged carriers remained macroscopically stable while some aggregation occurred for cationic nanocarriers. Xylan-based nanocarriers loaded with fungicides were reported to be active in vitro against several pathogenic fungi associated with plant diseases.[199] Interestingly, empty xylan-based nanocarriers stimulated the growth of fungal mycelium, indicating the degradation of xylan in the presence of the fungi. This analogy to lignin makes it a candidate for infection-responsive fungicide. Cellulose-based and pectin-based nanocarriers loaded with fungicides were also reported to target cellulase-segregating and pectinase-segregating fungi.[200,201] However, these carriers respond to enzymes instead of specific pathogens, thus their selectivity is generally limited.

To sum, the triggered release of cargo molecules offers unprecedented opportunities to enhance the precise administration of agrochemicals in response to biotic and abiotic stressors, but current technologies still need to show applicability in real-life conditions. The technological bottleneck lies in the sensitivity to and selectivity of the molecules that plants use as a signal for stress events. For example, small signaling molecules and hormones have been investigated extensively, but they are usually involved in multiple metabolic responses. Recent studies have revealed that peptides and RNA also function as signaling molecules. It is possible that these signaling molecules provide more specificity for stressor-specific signaling and can trigger payload release at physiological concentrations. Innovation at the interface between plant and biomaterials will result in new release triggering mechanisms that enhance precise plant care in stress management. Moreover, monitoring internal stimuli mandates exposure to stimuli-responsive cargos in plant tissues that are often remote and difficult to interrogate. Deployment of stimuli-responsive carriers using previously mentioned spatial precision delivery tools such as microneedles may be a good solution.

2.3. Summary and Outlook

While seed enhancement technologies are instrumental to boosting germination, enhancing root development, and stimulating initial crop growth especially under stressed conditions, the amount of bioactive ingredients (particularly agrochemicals such as nutrients and pesticides) that can be incorporated during seed priming and within seed coatings without causing phytotoxicity is far from sufficient to support crop growth till harvest. Therefore, another important sector of modern agriculture deals with precision agrochemical delivery to plants throughout their growth cycle, where both spatial and temporal precision delivery were discussed at length in Section 2.2. Here, the material formats, cargo types, targeted plant tissues/organelles/vasculatures, as well as advantages and limitations of each precision delivery strategy are summarized in **Table 1**, for the readers to have a clearer evaluation and an easier comparison.

Moving forward, we envision that biofertilizers (i.e., PGPR) will play an increasingly important role particularly in seed enhancement technologies, as they represent one of the most effective approaches to significantly reduce the amount of chemical fertilizers and pesticides applied, to enhance soil fertility and biodiversity, and to make crop production more sustainable.[19] Challenges in facilitating PGPR utilization in agriculture across the globe mainly include ensuring PGPR survival during desiccation and resuscitation, protecting PGPR in their competition against the often better-adapted native microflora, and development of low-cost and easy-to-implement microbe delivery technologies that can be integrated into the whole seed processing and treatment workflow to allow for their application at scale. We also want to note that PGPR are plant- and soil-specific, making it challenging to have a universal deployment strategy of PGPR. However, as we understand more about soil health, effects of soil composition on PGPR growth and metabolism, and microbe–plant interactions under various abiotic/biotic stressors, the efficacy of microbe-based biofertilizers will be greatly improved by more precise microbe selection and deployment. Moreover, there is a pressing need for technologies that address desiccation tolerance of PGPR, as studies have estimated that 95% of PGPR die in the ≈4 h time window between seed inoculation and planting, and that 83% of the surviving microbes die in the soil within 22 h after sowing.[202] By learning anhydrobiosis from organisms such as tardigrades which produce trehalose and intrinsically disordered proteins to promote water substitution and vitrification,[203] new strategies and seed enhancement formulations are being developed to better preserve PGPR vigor during seed handling and their deployment in the field.

In the precision payload delivery domain, we suggest more future work on unveiling the mechanisms of action. For example, the interaction between microneedles and plants and the mechanism of CPP traveling through cell wall are yet to be fully understood. On the materials side, technical challenges in biopolymer design to allow for controlled and programmable release of payloads still remain. Being able to solve these challenges would take us one step further toward applying these technologies in the field and having tangible impacts in the real world. With more knowledge and findings provided by plant biologists on plant responses to different stresses and molecules that plants use as signals to mitigate stresses, material scientists will be able to design triggers that have higher sensitivity to and selectivity of such signaling molecules, thereby achieving real "on-demand" release of cargoes. All these efforts will collectively contribute to our ultimate goal of combining spatial and temporal precision in delivering cargo molecules to plants, which will have significant impacts on maximizing resource use efficiency and minimizing environmental footprints of agriculture practices.

3. Edible Coatings for Food Preservation

Addressing the issue of food loss and food waste is of high importance to combat hunger, raise income and enhance food security, especially in the world's poorest communities. Globally, food is lost or wasted throughout the supply chain, from initial crop production to final household consumption.[7] In high-income areas like North America and Europe, a significant amount of food is wasted at the consumer end, where consumers behaviors like unmindful planning of purchase and obsession with discarding

Table 1. Precision delivery strategies.

Precision delivery strategies		Formats	Cargos	In vivo target	Advantages	Limitations	Refs.
Spatial precision delivery	Breaking barriers	Microneedles	Small molecules, macromolecules, bacteria, nanomaterials	Various tissues (leaf, vasculature, shoot)	■ Targeting various tissues ■ Wide size range of cargos ■ Both local and systematical delivery	■ Expertise and instrument needed when used at microscale ■ Limited loading capability	[102,103]
	Traveling through intact barriers	Nanomaterials with desirable physiochemical properties	Small molecules, DNA, RNA, siRNA, quantum dots	Leaf cells and their organelles	■ Precisely tunable physiochemical properties (e.g., size, shape, and charge)	■ Biocompatibility and safety of inorganic nanomaterials ■ Limited loading capability	[117,118,124,128]
		Nanomaterials decorated with physiologically functional molecules		Leaf cells and their organelles	■ Taking advantage of physiological pathways ■ Intrinsic biocompatibility and safety	■ Mechanism unclear	[135–148]
Temporal precision delivery	Constructing barriers for controlled release	Coating	Macronutrients	External	■ Limited demand of coating materials ■ Higher fertilizer use efficiency and less environmental side effects	■ Regulatory restriction on synthetic polymers with outstanding performances ■ Challenges in controlling release rate using biopolymers	[162,163,166–172,175–180]
		Micro-/nanomatrix	Micronutrients, phytohormones, and pesticides	External	■ Higher cargos use efficiency and less environmental side effects and toxicity	■ Potential safety concerns associated with micro-/nanomatrix and release kinetics ■ Potential regulatory restrictions on some materials	[183–189]
	Designing triggers for stimuli-responsive release	Nanomaterials responsive to pathogens	Micronutrients, phytohormones, pesticides, and biofungicides	External or vasculature	■ Straightforward design mechanisms ■ High sensitivity	■ Limited selectivity ■ Release kinetics in vivo have not been well studied	[196–201]
		Macro-/micro-/nanomaterials responsive to multistimuli		External or vasculature	■ Straightforward design mechanisms ■ High sensitivity ■ High responsiveness	■ Potential over response ■ Limited selectivity	[192–194]

food right after its labeled "best before" date are major contributors to food being wasted while they are still suitable and safe for human consumption. In low-income regions like Africa and South Asia, food waste at the consumer level becomes less of an issue while food loss during the early and middle stages of the supply chain is considerable, due to financial and technical limitations in harvesting techniques, storage, and cooling facilities, transportation, and packaging systems.

One significant portion of food waste comes from the premature deterioration of perishable commodities. As many fruits and vegetables possess high metabolic activity and suffer from severe microbial/fungal contamination, they have very short shelf-life post-harvest. To extend the shelf life of perishable food, traditional treatments including cryopreservation, exposure to chemical fungicides, the addition of synthetic preservatives, modified atmosphere packaging and osmotic treatments, etc. have proved to be useful.[204] Meanwhile, the application of edible coatings on food has also emerged as a simple and effective strategy to preserve food against fast exchange of gases with the environment and microbial growth.[205]

Food coatings should be mechanically robust and flexible matrices with decent amounts of hydrophobic groups to allow for low water vapor permeability, to reduce dehydration and retain firmness. They should also possess low and ideally selective oxygen and carbon dioxide permeability, to lower food respiration rate and metabolic activity while avoiding anaerobic conditions. Other compelling properties for a food coating material include biodegradability, edibility, transparency, being tasteless and odorless, and good film-forming capability. To meet all these criteria, polysaccharides, proteins, lipids and their combinations are the commonly used options for food coating formulations.[206] In general, polysaccharides and proteins are known to form conformable films with good mechanical properties but poor gas permeability due to their high hydrophilicity, while lipids show improved gas barrier properties but usually form brittle films that easily fall apart. In this section, we will break down the commonly used components for food coatings, discuss their advantages and disadvantages, and introduce their applications in various food systems.

3.1. Polysaccharides

Polysaccharides are linear or branched polymeric carbohydrates that constitute the largest portion of biopolymers. Food coatings made of polysaccharides usually have low oxygen permeability due to the abundance of hydrogen bonds in their structures, but they are not good water vapor barriers because most of the polysaccharides used in the food industry are hydrophilic.[207] The most widely used polysaccharides for food coating/packaging include cellulose, chitosan, starch, pectin, and alginate,[208] which have been applied to prolong the shelf life of fruits, vegetables, seafood, cheese, and meat products etc. by reducing respiration rates, metabolic activities, microbial growth, and oxidative rancidity.

3.1.1. Cellulose

Cellulose is a linear chain of several hundred to many thousands of $\beta(1\rightarrow4)$ linked D-glucose units found in many plant cell walls as a structural component.[209] It can be isolated from wood, cotton, hemp, and other plant-based materials as well as secreted by microorganisms. Cellulose is tasteless, odorless, biodegradable, and hydrophilic, but it is insoluble in water and most organic solvents,[210] which to some extent limited its direct use as food coatings due to the difficulty in dissolving it into film-forming suspensions. To increase water solubility, various cellulose derivatives including methylcellulose (MC), carboxymethylcellulose (CMC), hydroxypropyl cellulose (HPC), and hydroxypropyl methylcellulose (HPMC) are created through cellulose reaction with methyl chloride, chloroacetic acid, and propylene oxide.[211] The films obtained from these cellulose derivatives are generally transparent, water-soluble, flexible, resistant to lipids, with good barrier properties against oxygen but relatively high water vapor permeability.[212,213] Aqueous solution of CMC at 1–2 wt% was found to be effective in extending the shelf life of strawberries,[214] citrus fruit,[215] and carrots.[216] Antioxidants such as ascorbic acid could also be added in the dip-coating CMC solution to be applied on fresh-cut produce against tissue softening and surface browning.[217] MC and HPMC also have the capability to undergo reversible thermally induced sol-gel transition, which in combination with their resistance to fat and oil make them good coating materials for deep fried food.[218] For example, mashed potato balls coated with film-forming solutions of MC and HPMC at 225 wt% in 50% ethanol showed a reduction of 83.6% and 61.4% fat uptake respectively during frying, when compared to the uncoated control.[219]

3.1.2. Chitosan

Chitosan is a linear polysaccharide composed of randomly distributed β-(1→4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is obtained by alkaline deacetylation of chitin which is abundant in the shells of shrimp and many crustaceans.[220] Chitosan is insoluble in pure water and in common organic solvents, but can be easily dissolved in acid solutions below pH 6.3, with its solubility mostly depending on the degree of deacetylation and molecular weight.[221,222] Besides the common properties of other polysaccharides, chitosan also possesses antimicrobial activities against many bacteria, fungi, and yeast,[223] which makes it a particularly compelling material for food coatings. So far, chitosan coatings have been tested on a wide range of food models including fresh produce, fresh-cut fruit, cheese, meat, and seafood. Strawberries coated with chitosan were found to have reduced weight loss, delayed discoloration and flesh browning, and increased activity of antioxidant enzymes.[224] Chitosan coatings also prolonged the shelf-life of fresh-cut mango slices and cucumbers by reducing dehydration (from 15.24% to 6.98% weight loss of sliced mango after 5 d of storage at 6 °C) and inhibiting microbial growth (from 5.87 to 3.75 log CFU g^{-1} of fresh-cut cucumber stored at 5 °C for 12 d).[225,226] Edible coatings made from chitosan powders were also successfully applied on shredded carrot/radish, which showed better color retention and sensory acceptability, decreased respiration rate, and lower microbial load compared to uncoated controls, thereby extending the shelf-life from 5 to 10 d of storage at 10 °C.[227,228] The cheese industry also benefited from chitosan coatings which helped the preservation of a variety of cheeses such as ricotta,[229] cheddar,[230] goat's milk cheese,[231] and Emmental.[232] Altieri et al. demonstrated that chitosan applied on mozzarella cheese was able to selectively inhibit the growth of some spoilage microorganisms (e.g., coliforms) but not others, and slightly stimulate the growth of useful microbes such as lactic acid bacteria.[233] Chitosan coatings were also proved to be effective against microbial spoilage, lipid oxidation, and rancidity when applied on roasted meat,[234] chicken breast fillets,[235] and salmon.[236] It is noted that although chitin and chitosan are not known to be allergenic, incomplete deproteinization of chitin during its commercial manufacture from the shells of crustaceans may lead to the presence of allergenic proteins such as tropomyosin in the final material.[237] The chitin and chitosan used in the food industry thus need to be of high purity to avoid any allergic reactions.

3.1.3. Starch

Starch is a naturally existing carbohydrate polymer produced by most green plants from excess glucose as a reserve of energy. Commercially starches are extracted and refined from the seeds of corn and wheat, roots of cassava, and tubers of potatoes. Most starches comprise amylose (a linear chain polymer) and amylopectin (a branched chain polymer). Amylose, which accounts for about 10–30% of most starches, is responsible for their film-forming capabilities.[238] Starch is not soluble in cold water due to its semicrystalline nature and hydrogen-bonded structure. Heating at temperatures between 65 and 90 °C and an excess of water (>90% w/w) are often required to break the amylopectin matrix and release the amylose, and to obtain a homogeneous film-forming suspension of starch.[211] Starch films occur in transparent or translucent forms depending on their crystallinity, with higher crystallinity also corresponding to better gas barrier properties. Pure starch films are very brittle which can hardly be used as food coatings and incorporation of plasticizers such as glycerol and sorbitol are generally

needed.[239] Starch-based edible coatings were found to be effective in extending the shelf life of minimally processed fruit such as strawberries[240] and pomelos,[241] by lowering their respiration rate (up to 33%), weight loss (up to 67%) and delaying surface discoloration. However, similar starch coatings worked not as well on fresh-cut fruit because they were not able to reduce microbial proliferation,[242,243] which is a major determinant of fresh-cut fruit's shelf life. Interestingly, starch-based coatings can also be used to preserve nutrients in food dried at high temperature. For example, application of a corn starch coating minimized carotenoid degradation during pumpkin drying in hot air and resulted in dehydrated pumpkin slices with better color and higher retention of trans-α-carotene and trans-β-carotene than uncoated slices.[243] Similar effects were also found in dried carrots.[244]

3.1.4. Pectin

Pectin is a structural heteropolysaccharide contained in the primary cell walls and middle lamella of terrestrial plants. Its major component is galacturonic acid which can be either free or methyl-esterified to modulate the gelling properties.[245] Pectin is mainly produced from citrus peels and apple pomace and is widely used in the food industry, mainly as gelling agents for jams and jellies, as bakery fillings, and as stabilizers in fruit juices and milk drinks.[246] It has a "generally considered as safe" (GRAS) status issued by the US food and drug administration (FDA). Like other polysaccharide films, pectin-based films have decent gas barrier properties and can be used to retard moisture loss and lipid migration.[247] However, it is not very popular as a food coating material because pectin does not have antimicrobial properties. Some studies even suggested that pectin films promoted microbial growth because pectin is used as a carbon source by bacteria and fungi.[211] Nevertheless, application of pectin on several produce including lime,[248] melon,[249] and cucumbers[250] were found to be effective in reducing respiration rate and dehydration, and maintaining fruit color and firmness. For example, pectin coatings suppressed the respiration rate of limes to 1.06 mL CO_2 (kg h)$^{-1}$, compared to 7 mL CO_2 (kg h)$^{-1}$ of uncoated controls stored under the same conditions.[248] Similar to starch, pectin-coatings applied on papaya slices before air-drying had a protective effect against discoloration and oxidation of bioactive compounds in papaya compared to uncoated slices, without affecting drying efficiency.[251]

3.1.5. Alginate

Alginates are linear copolymers of β-$_D$-mannuronate (M) and α-$_L$-guluronate (G) residues in (1→4)-linkage, arranged in a block-wise pattern along the linear chain.[252] The overall composition of the two acids and their distribution along the polymer chain vary depending on the natural source and influence the properties of alginates.[208] Alginates are mainly refined from brown seaweeds *Phaeophyceae*. In view of their abundance and edibility, alginate has been widely used in the food industry as a thickening and gelling agent. Most of their applications are related to alginates' gel-forming ability in the presence of polyvalent cations of alkaline earth metals (Ca^{2+} being the most used). Gelation results from strong complexation between Ca^{2+} and the G residues, leading to chain-chain associations and formation of a stable 3D network pictured as the "egg-box" model.[253] Alginate forms films after solvent evaporation and alginate crosslinking promoted by Ca^{2+} can be used to improve the mechanical and gas barrier properties of the final films/gels.[254] Although alginate coatings exhibit relatively high water vapor permeability, their hygroscopicity can help slow food dehydration. Generally, edible coatings made from alginate possess similar characteristics to those made from pectin.[211] Plums dip-coated in 1–3 wt% alginate solution showed less ethylene production, dehydration, softening, and discoloration during storage at 2 °C, compared to uncoated controls.[255] Therefore, the alginate coating helped extend the storage period of plums by 2–3 weeks. Similar preservation and shelf-life extension effects of alginate coatings were also found on cherries,[256] peaches,[257] fresh-cut apples[258] and pineapples,[259] and mozzarella cheese.[260]

3.2. Proteins

Proteins are polymer chains of amino acids linked together by peptide bonds. They are good film formers possessing excellent oxygen, carbon dioxide, and lipid barrier properties, particularly at low relative humidity.[252] However, proteins are also humidity sensitive and exhibit high water vapor permeability due to their predominantly hydrophilic nature. In terms of mechanical properties, protein films generally possess satisfactory flexibility and strength, although in some cases, plasticizers are needed to overcome the brittleness of films made from protein alone. Edible film-forming proteins can be obtained from animals (casein, whey proteins, and egg white proteins), plants (zein, soy protein, and wheat gluten) and insects (silk fibroin), which have all been found to have beneficial effects in food preservation and shelf-life extension.[261] However, it is important to note that as many proteins are common allergens,[262,263] their use as food contact materials should be pursued with caution and be explicitly noted in the food labels.

3.2.1. Casein and Whey Proteins

Casein is a family of related phosphoproteins found in mammalian milk. Four principal components, α_{s1}-, α_{s2}-, β-, and κ-caseins, have been identified, which differ in amino acid compositions.[264] The most common forms of casein are sodium and calcium caseinates.[265] Casein and caseinate films have been used as edible food coatings since they possess low oxygen permeability and good mechanical strength, although they are poor water vapor barriers and have limited mechanical flexibility.[266] For example, calcium caseinate applied on celery[267] and zucchini[268] contributed to up to 75% reduction in dehydration of the vegetables; calcium caseinate coatings applied on apple and potato slices[269] effectively delayed surface browning by acting as oxygen barriers and reactive oxidative species scavengers, showing a 66% inhibition in the formation of colored compounds in the flesh, compared to uncoated controls.

Whey protein is a collection of water-soluble globular proteins isolated from whey, which consists of β-lactoglobulin (≈48–58%), α-lactalbumin (≈13–19%), bovine serum albumin (≈6%), immunoglobulins (≈13%) and proteose peptones (≈4%).[266] Industrial processes such as ultrafiltration, diafiltration, and reverse osmosis are commonly used to recover whey proteins and produce whey protein concentrate (WPC, 25–80% protein) or whey protein isolate (WPI, >90% protein).[261] Whey protein coatings are generally transparent, flexible, colorless, odorless, and are good oxygen, aroma, and oil barriers at low-to-intermediate humidity. Fresh-cut apple slices coated with an emulsion of WPI showed less enzymatic browning and weight loss compared to uncoated slices.[270] Similar effects were seen on whey-coated asparagus with retarded dehydration, discoloration, and tissue hardening in the basal part.[271] WPI coatings were also able to reduce hardness loss and color change of cheese during storage, and inhibit pathogenic microorganism growth without affecting the regular growth of lactic acid bacteria.[272] Furthermore, whey-coatings, acting as moisture and oxygen barriers, were found to be effective against lipid oxidation of frozen fish.[273,274] Both caseins and whey proteins are well-known food allergens, so their allergenic properties should be evaluated before being used as edible food coating materials. Common approaches to reduce the allergenicity of milk proteins include denaturation through heat processing (e.g., sterilization) and non-enzymatic glycation which can either destroy the proteins' epitopes or render them inaccessible.[262]

3.2.2. Egg White Proteins

Egg white is an alkaline solution composed of ≈90% water and ≈10% proteins. Ovalbumin constitutes more than half of egg white proteins and contains four free thiol (SH) groups, while the other major protein components in egg white such as ovotransferrin, ovomucoid, and lysozyme contain many disulfide bonds (S–S).[275] These inter- and intramolecular S−S bonds and SH groups play an important role in film formation from egg white. Moreover, most egg white proteins are predominantly in random coils conformation, which also contributes to the good film-forming ability of egg white.[276] Preparation of egg white films generally involve denaturation of egg white proteins by adjusting solution to pH 10.5 to 12, followed by heating at 40 °C for 30 min.[277] At alkaline pH, the S−S bonds are reduced to SH groups which are then converted to inter- and intramolecular S−S covalent crosslinks during heat treatment,[278] conferring more stretchability to the final films obtained after solvent evaporation.[279] Examples of using egg white proteins for food preservation include reduced moisture loss from egg albumen-coated raisins when stored with bran flakes,[280] less dehydration and enhanced shell strength of eggs coated with egg albumen solution,[281] and increased shelf-life of cheese coated with essential oil-incorporated egg white protein powder films.[282] Egg white-coated potato slices showed a 12% reduction in oil uptake, 30–50% decrease in peroxide amount, and better water retention after being deep-fried, compared to uncoated potato slices.[283] Egg white proteins in their original forms are also allergenic but their allergenicity can be diminished to a harmless level through extensive heating.[262]

3.2.3. Zein

Zein is a class of prolamine protein found in corn.[284] Being rich in nonpolar amino acids, zein is water-insoluble and zein films show improved barrier properties against water vapor.[285] Film-forming solutions can be easily prepared by dissolving zein in aqueous alcohol, and plasticizers like glycerol can be added for better film flexibility. Other treatments such as γ-irradiation of zein solution and addition of phosphorus oxychloride ($POCl_3$) to induce zein phosphorylation can also be used to further improve the water barrier properties and stretchability of zein films.[286,287] Due to its abundance, low cost, and ease of processing, zein is one of the most widely used proteins in making edible food coatings. Zein coatings were effective in extending the shelf-life of a variety of produce including tomatoes (a 6 d delay in ripening without adverse effects),[288] apricots (inhibiting microbial growth by around 2 log CFU g^{-1}),[289] apples (decreasing moisture loss from 4.4% to 1.7% which effectively avoided shriveling of the peel for 14 days of storage at 20 °C)[290] and mangoes (reducing decay percentage from 96% to 15% at the 18th day of the storage period),[291] by lowering respiration rate, suppressing ripening, retarding weight and firmness loss, inhibiting bacterial growth and better retaining ascorbic acid and phenolic contents in the fruits.

3.2.4. Soy Protein

Soy protein films are mostly made from soy protein isolate (SPI) which contains more than 90% protein. SPI has two major components, β-conglycinin, and glycinin, also known as 7S and 11S globulin, respectively.[207] SPI films can be formed at both alkaline and acidic pH. However, it was found that SPI films prepared from alkaline solutions (pH 6 to 11) show much higher tensile strength and extensibility, and slightly lower water vapor permeability than SPI films made from acidic solutions (pH 1 to 3).[292] A pH near the isoelectric point of SPI (i.e., pH 4.5) should be avoided when preparing the film-forming solutions. The addition of plasticizers like glycerol and sorbitol is generally needed to improve the texture and flexibility of the final films.[293] Moreover, the dried SPI films can be post-treated with heat curing and γ-irradiation to further improve the mechanical properties.[294] Generally speaking, soy protein films are good oxygen barriers but have high water vapor permeability and moderate mechanical properties, due to the inherent hydrophilicity of soy proteins and the substantial amounts of hydrophilic plasticizers needed to impart film flexibility.[295] Guerrero et al. found that SPI-based edible coatings were effective in delaying lipid oxidation and quality deterioration of beef patty and the textural parameters of SPI-coated beef patties were maintained up to 14 days during cold storage.[296] Compared to uncoated controls, fresh-cut eggplants dip-coated in SPI solutions amended with 1% cysteine showed much less enzymatic browning and can be stored up to 8–9 d at 5 °C without the need for modified atmospheric conditions.[297] Soy protein based 1-methylcyclopropene-releasing pads were also pursued to extend the shelf life of tomatoes by inhibiting ethylene production and delaying tomato ripening.[298] Soy proteins can cause severe allergic reactions.[263]

Heat processing and hydrolysis with trypsin, pepsin, and chymotrypsin are commonly used to prepare hypoallergenic soy protein formulations.[262]

3.2.5. Wheat Gluten

Wheat gluten is a hydrophobic protein of wheat flour. It is mainly composed of two proteins–gliadin and glutenin. Gliadins are prolamines of low molecular weights (28–55 kDa), while glutenins are large protein complexes linked by interchain disulfide bonds and are insoluble in aqueous alcohols.[299] Like other plant proteins, plasticizers like glycerol and ethylene glycol are needed to ensure good flexibility of gluten-based films.[300] Other modifications including covalent crosslinking of gliadin chains by dialdehydes and thermal treatment can be used to further improve the water vapor barrier property and mechanical strength of wheat gluten films.[301] Strawberries coated with wheat gluten had an extended shelf life up to 12 d at 7–10 °C and delayed senescence was characterized by better firmness retention and less discoloration, compared to uncoated controls which only lasted 6 days.[302] Similar effects of wheat gluten coatings were also found on cherry tomatoes and Sharon fruits.[303] Wheat gluten is also a food allergen to certain population. Unlike other allergenic proteins, heating at high temperature not only does not denature gluten, but also induces formation of protein aggregates with higher allergenicity. Certain enzymes such as cellulase and actinase have been found to be effective in decomposing and hydrolyzing wheat allergens, making the final materials hypoallergenic.[262]

3.2.6. Silk Fibroin

Unlike other biopolymers introduced so far which all have a long history in their use as food coating/packaging materials, silk fibroin was only recently pursued as a coating material for perishable food preservation.[304,305] As a structural protein that has been designated as a GRAS food item by the US FDA and evaluated to possess no toxicological and allergenic effects at doses less than 500 mg kg^{-1} bodyweight per day,[306] silk fibroin represents a compelling candidate for use as edible food coatings. Through an all-water-based processing, silk fibroin can easily form conformable thin films wrapping around practically any surfaces after water evaporation. Silk fibroin films are transparent, tasteless and odorless, mechanically robust and flexible, as well as biodegradable. More importantly, gas permeabilities of silk fibroin films can be tuned by controlling silk polymorphs.[307] Marelli et al. demonstrated that silk fibroin coatings can effectively preserve the freshness and firmness of both nonclimacteric (strawberries) and climacteric fruits (bananas) for longer periods of time by suppressing fruit respiration and restricting dehydration.[304] Silk fibroin coatings on fruits were applied through a two-phase process (**Figure 7**a): Fruits were first dip-coated in 1 wt% silk fibroin suspension repeatedly up to four times, followed by incubation of the silk-coated fruits in a vacuum chamber of high humidity (>90%) for different periods of time to modulate the β-sheet contents in silk fibroin. Films of silk fibroin with increasing β-sheet contents showed significantly improved gas barrier properties (over 2 and 1 order of magnitude decrease in water vapor and oxygen permeability, respectively), thereby further slowed down fruit respiration (Figure 7b). As a result, silk fibroin-coated strawberries and bananas exhibited statistically significant improvement in freshness and firmness retention over the studied storage time (Figure 7c,d).

3.3. Lipids

Lipids are naturally occurring small and hydrophobic or amphiphilic molecules, including fatty acids, waxes, sterols, glycerides, and phospholipids. Due to their apolar nature, lipids are widely employed in edible food coatings as a strong barrier against water vapor transfer.[308] However, it is important to note that lipids alone do not have the capability to form cohesive and integral films, and they need to be coupled with film-forming agents (namely the various polysaccharides and proteins introduced earlier in this section) when applied on food.[207]

Waxes (including beeswax, candelilla wax, carnauba wax, and others) have been commercially applied as protective coatings for fresh produce since the 1930s with the purpose of blocking moisture transport, reducing surface abrasion during produce handling, and imparting gloss and shine to produce appearance.[309,310] Waxes possess minimal polar groups, so they can barely form any interactions with water and are completely insoluble in water.[311] That is why waxes are arguably the most effective barrier against water vapors in edible coatings. Waxing produce can also inhibit their respiration and ripening, sometimes to the extent that a significant increase in alcoholic contents might occur due to anaerobic respiration,[312,313] which can be either desirable or undesirable depending on the produce type. The use of waxes in edible food coatings has been so extensive and mature covering most of the fruit and vegetables known so far,[309,311,314] that we won't go into any details in this review. Another lipid that has gained increasing interest as edible coating materials is shellac.[315,316] Shellac is resin secreted by the insect *Laccifer lacca* and is easily soluble in alcohols and alkaline solutions.[208] Incorporation of shellac in food coatings was initially pursued to provide extra shining to food appearance.[317] Other than that, shellac coatings are also very good moisture barriers and possess low permeability to O_2, CO_2, and ethylene. It is noted that some climacteric fruits do not tolerate shellac coatings well due to the overly suppressed ripening resulted from the modified atmosphere (low O_2 and high CO_2) created by shellac coatings.[207,310] For this reason and others, shellac is rarely used as a major component of edible food coatings, but rather as a complementary ingredient. Lastly, lipids that have increased polar groups (e.g., monoglycerides) are sometimes used as emulsifiers in edible food coatings to enhance adhesion and interaction between two parts having distinct hydrophobicity, e.g., between the coating and the food, or between waxes and proteins/polysaccharides in a composite film.[318,319]

3.4. Composites

Composite food coatings are heterogeneous in nature and consist of a combination of different types of materials. They

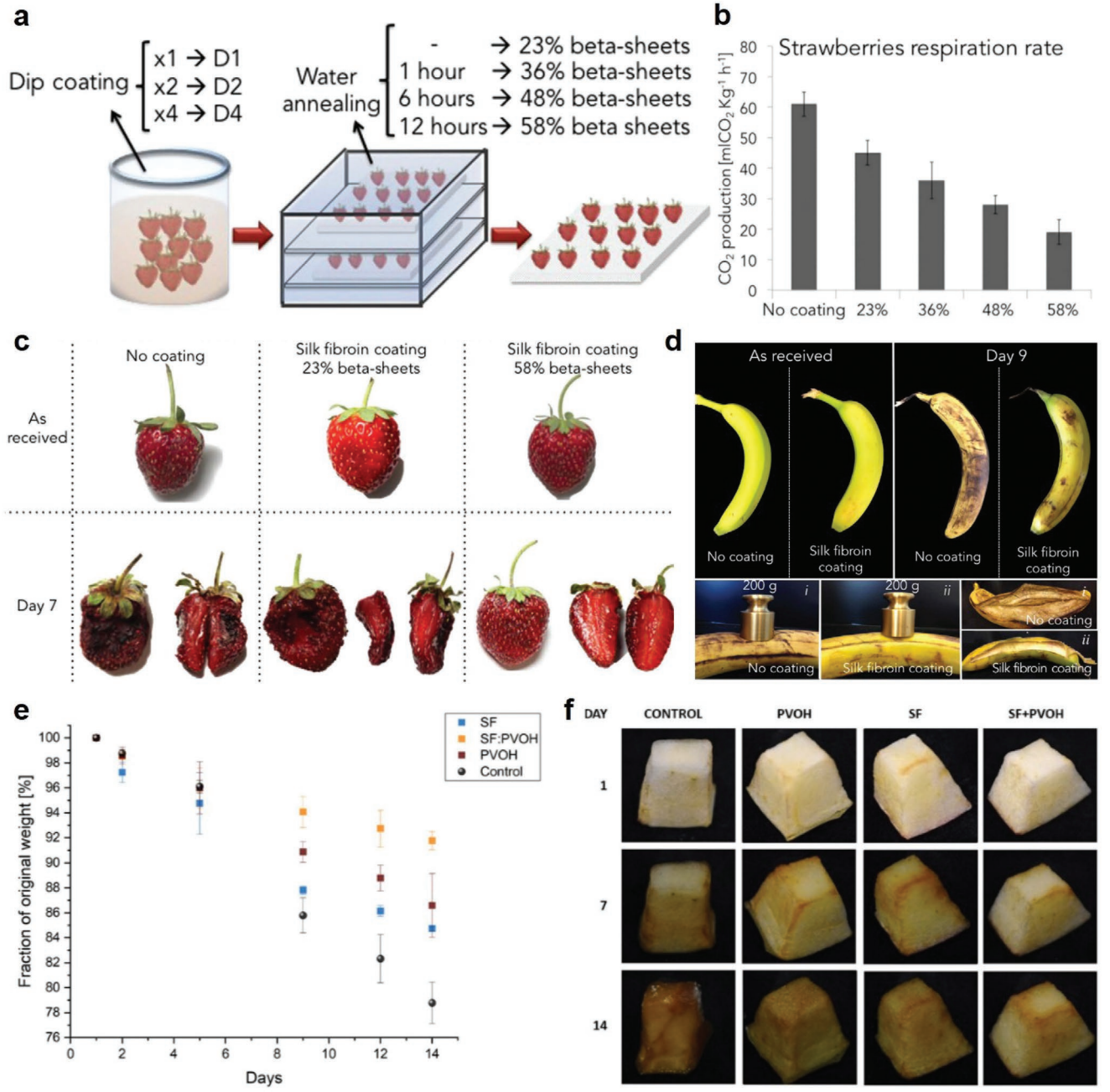

Figure 7. Silk fibroin-based edible food coatings. a) Schematic of dip-coating strawberries in a silk fibroin suspension followed by drying and water-annealing to induce higher β-sheet contents in the silk coatings. b) Respiration rates of strawberries coated with silk of increasing β-sheet contents. c,d) Time-lapse images of uncoated and coated c) strawberries and d) bananas stored at 22 °C and 38% RH. Reproduced with permission.[304] Copyright 2016, Springer Nature. e,f) Weight loss and time-lapse images of uncoated and coated fresh-cut apple slices. Reproduced with permission.[305] Copyright 2020, American Chemical Society.

are developed to leverage the distinct properties of each component and achieve synergistic effects contributed from all constituents involved, so that the composite film/coating can have multiple and improved functionalities that are not generally possible from a single material. As a matter of fact, due to the wide availability of all sorts of materials and the more and more demanding requirements for food preservation, edible food coatings used nowadays are rarely composed of a single material. As we mentioned earlier, polysaccharides and proteins have good film-forming capabilities but are poor moisture barriers, while lipids form brittle and fragmentary films but possess extremely low water vapor permeability. Composite food coatings can then be made from emulsions of nonmiscible constituents that phase separate into successive layers,[320–322] or a suspension of different components well-blended in a common solvent.[323–325] Both strategies have been extensively

explored to develop new food coating formulations, along with the emerging incorporation of biodegradable nanomaterials and mesoporous particles in edible food coatings as reinforcing and gas-regulating agents.[316,326,327]

To impart further control over the mechanical and gas barrier properties of silk fibroin-based food coatings, Ruggeri et al. blended silk fibroin with poly(vinyl alcohol) (PVOH) at different ratios, from which multilayered coatings were formed.[305] The choice of PVOH was based on its GRAS status, low water vapor and oxygen permeability, immiscibility with silk fibroin, good thermal and chemical stability, and high stretchability. Of all the SF:PVOH ratios studied, SF:PVOH 1:1 resulted to be the most promising material candidate for edible food coatings as demonstrated by efficacy tests on the preservation of fresh-cut apples (Figure 7e,f). Over the course of storage post-cut, apple slices coated with SF:PVOH 1:1 showed statistically significant lower weight loss as compared to uncoated controls and slices coated with pure silk fibroin and PVOH (Figure 7e). SF:PVOH 1:1 films also presented a better preservation of the apple slices from browning/oxidation as compared to pure silk fibroin and PVOH films (Figure 7f). The improved performance of SF:PVOH 1:1 coatings is arguably due to its bi-layered structure that results from a phase separation of silk fibroin and PVOH during simultaneous self-assembly, where silk fibroin forms a layer that is in intimate contact with the apple flesh and PVOH forms an outer protective barrier.

In another example, an edible coating mainly composed of egg-derived polymers and cellulose nanomaterials was developed and applied on fresh produce, to slow down food decay by suppressing respiration, dehydration, and microbial invasion.[327] Preparation of the dip-coating suspension (**Figure 8**a) started with the dissolution of egg white powders in water, followed by addition of glycerol to impart film flexibility and conformability on irregularly shaped produce. A small fraction of egg yolk powders (rich in fatty acids) was then incorporated to increase film resistance to water vapor. Meanwhile, curcumin (an antimicrobial agent) was added to reduce microbial growth. Lastly, cellulose nanocrystals (CNCs) were incorporated to further lower gas permeability and reinforce the mechanical strength of the coating. Effectiveness of the composite coating in preserving fruit freshness was tested on three climacteric fruits (banana, avocado, and papaya) and one nonclimacteric fruit (strawberry). After being stored for 8–11 d at room temperature, the coated climacteric fruits still retained a decent exterior appearance and flesh freshness, while the uncoated controls all showed severe enzymatic browning and flesh deterioration (Figure 8b,c). Coated strawberries also exhibited better exterior appearance, minimal mold growth (Figure 8d), and significantly reduced weight loss, compared to uncoated strawberries which were already almost dead at day 5 due to mold contamination and substantial dehydration.

Inspired by the structure and function of plant leaf stomata, Zhou et al. designed a biomimetic hybrid membrane with controllable gas permeation and CO_2/O_2 selectivity.[316] The hybrid membrane was generated from a shellac solution containing mesoporous chitosan or poly-$_L$-lactic acid (PLLA) microspheres, which can either be applied directly on fruit surface through dip-coating or used as a food packaging material (**Figure 9**a). The chitosan porous microspheres (CSPMs) used in this study had an average diameter of 38 μm and nanoscale through-pores of pore diameter ≈6 nm (Figure 9b), and they can be uniformly embedded in the shellac matrix, with their porous structures well-preserved (Figure 9c). After incorporating CSPMs, the hybrid membrane's CO_2/O_2 selectivity (defined as CO_2 permeability divided by O_2 permeability) increased with CSPMs' volume fraction (Figure 9d). Mangoes dip-coated by the hybrid membranes presented good exterior appearance and much higher edible rates after 10 days of storage at room temperature, while the uncoated mangoes all showed enzymatic browning and freshness decay on the exterior (Figure 9e). Moreover, sweet cherries stored in polypropylene boxes and sealed with the hybrid membranes retained vivid exterior quality and had the highest edible rates (≈96%) after 72 h of storage at room temperature (Figure 9f), while most of the cherries stored in both ambient and polyethylene-packaged conditions were rotted due to microbial growth.

3.5. Materials Selection and Application

Selection of the optimal materials for edible coatings largely depends on the characteristics of the food product itself. As a general rule, food with high water content requires more hydrophobic coatings to reduce dehydration as much as possible. This can be achieved by incorporating lipids in the coating formulation or by increasing the coating components' crystallinity (e.g., β-sheet contents in proteins). Food with high fat content such as meat and cheese, on the other hand, need superior oxygen barriers to fight against oxidation and rancidity, in which case a primary use of hydrocolloids (i.e., polysaccharides and proteins) as coating materials is commonplace. In the case of fruit, it is important to consider whether the fruit is climacteric or non-climacteric. Especially for climacteric fruits, coatings that possess a medium level of O_2 and CO_2 permeability are sometimes needed to avoid anaerobic conditions. It is known that high contents of waxes and shellac in the coating formulation tend to overly restrict the gas exchange between atmosphere and fruit, to the extent that the internal O_2 level becomes too low to support aerobic respiration, leading to high levels of ethanol and acetaldehyde production and accumulation of off-flavors in the fruit.[310,316] So, there is always a trade-off among all the desired properties for a food coating, and the sweet spot often hinges on the food to which the coatings are applied.

Besides, as edible coatings are usually consumed with the coated food, their organoleptic properties and consumer acceptance should be given enough consideration. In this aspect, hydrocolloids usually generate transparent coatings, while lipid-based coatings often present a greasy and translucent appearance that could make food unappealing. Coating thickness is also an important factor, where we want the coating to be as thin as possible without impairing its gas barrier properties so that it does not affect food texture. Moreover, addition of functional ingredients such as antimicrobials and antioxidants in food coatings could affect the food's sensory qualities by introducing unpleasant odor and flavor. This is particularly true with many of the essential oils. Emerging technologies like nanoencapsulation of the functional ingredients might be a solution to

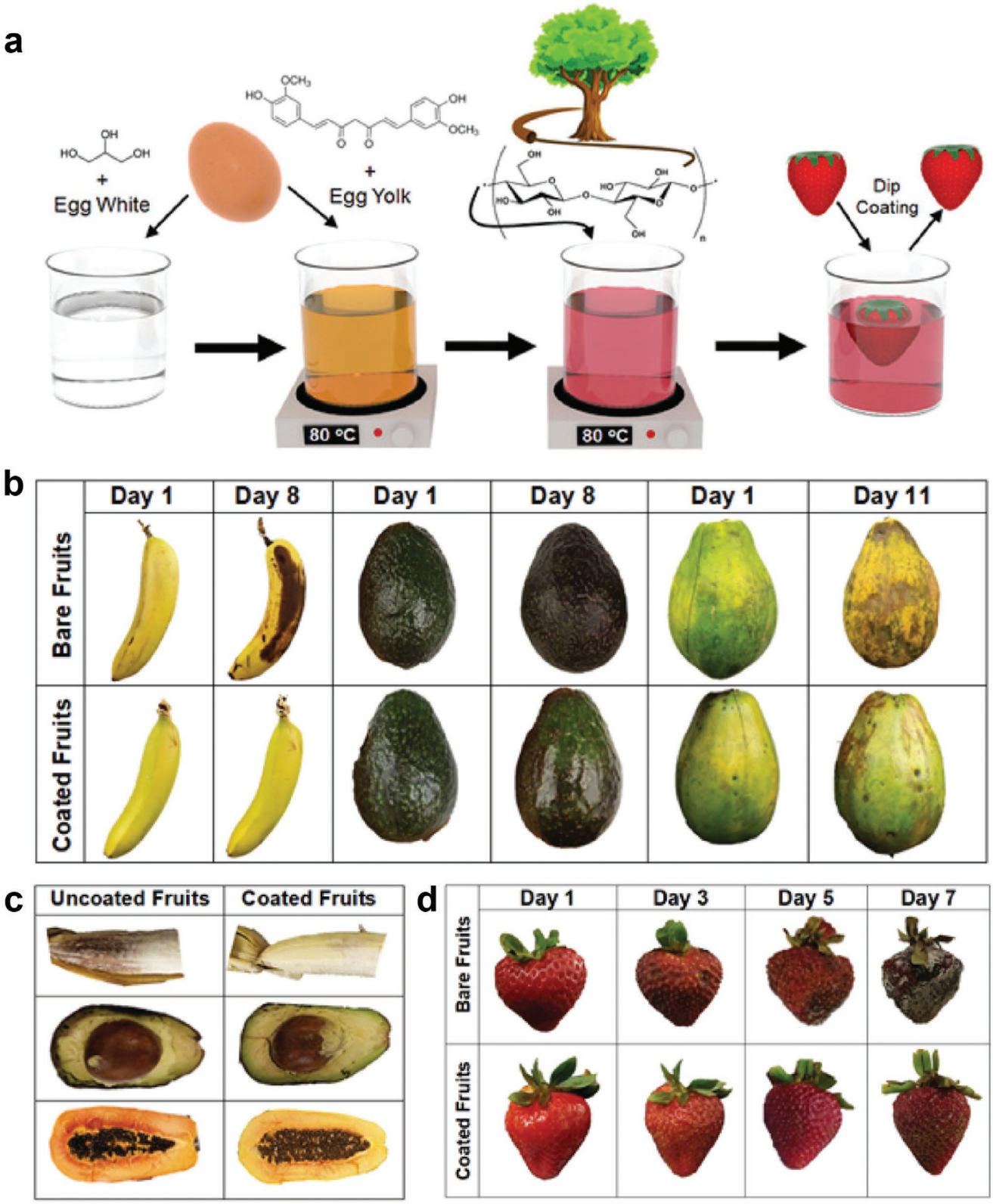

Figure 8. Cellulose nanocrystal reinforced poly(albumen) nanocomposite coating. a) Schematic illustration of the nanocomposite synthesis and dip-coating process on fruits. b,c) Time-lapse photographs of the exterior and interior of uncoated and coated climacteric fruits. d) Time-lapse photographs of uncoated and coated strawberries (non-climacteric fruit). Reproduced with permission.[327] Copyright 2020, Wiley-VCH.

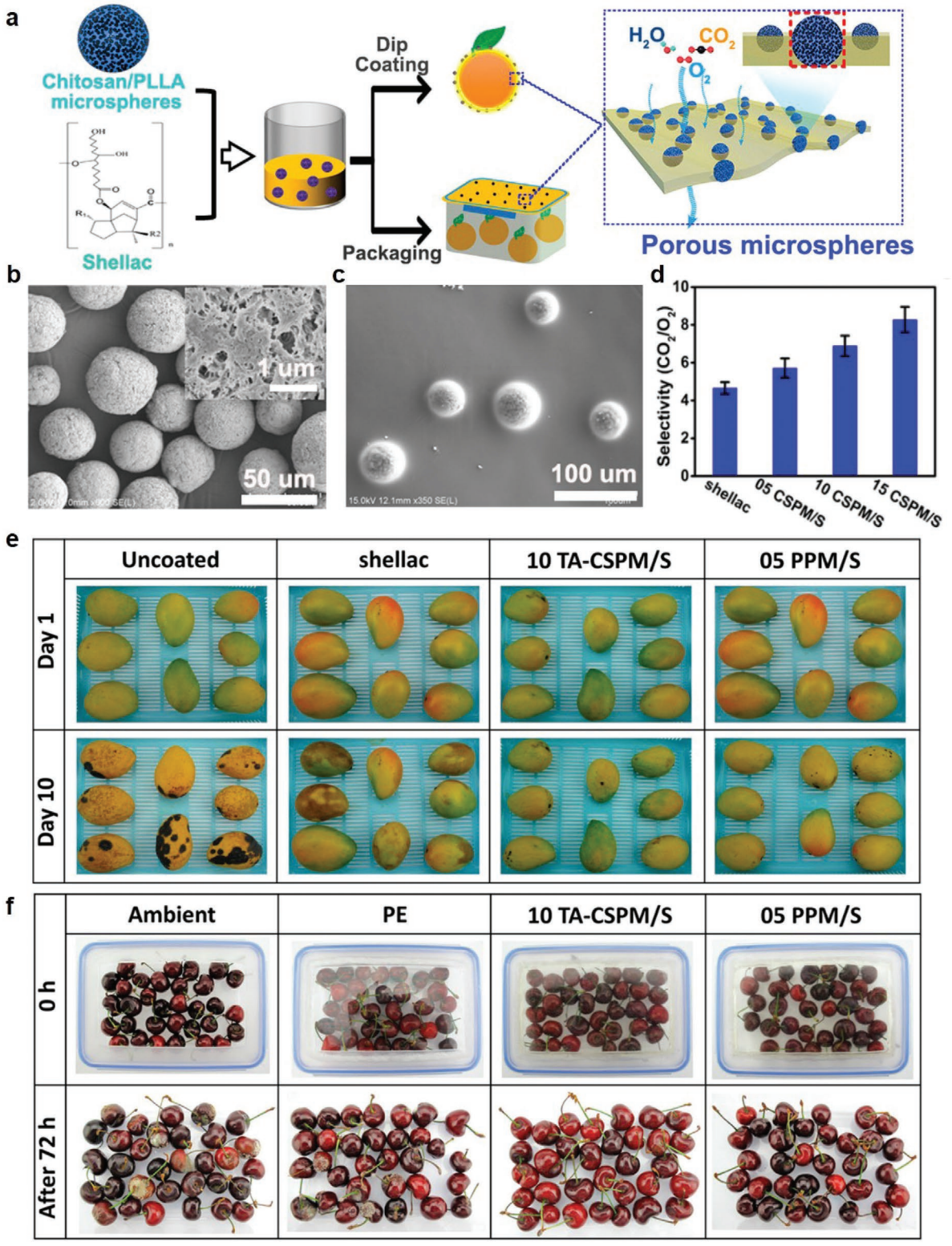

Figure 9. Bioinspired hybrid membranes with regulated gas permeability. a) Schematic illustration of the hybrid membrane preparation and their application on fruits through dip-coating and packaging. b) SEM images of CSPMs and their surface. c) SEM image of a CSPM/shellac membrane. d) The CO_2/O_2 selectivity of CSPM/shellac membranes with different amounts of CSPMs added. e) Time-lapse photographs of uncoated and coated mangoes stored at room temperature. f) Time-lapse photographs of unpackaged and packaged cherries stored at room temperature. Reproduced with permission.[316] Copyright 2021, American Chemical Society.

this problem,[328–330] which can effectively reduce the amount of active compounds needed without compromising their efficacy.

Food coating application methods including dipping, spraying, and brushing are usually selected based on the size and surface characteristics of the food.[331] Almost every food can be dip-coated and dip-coating is particularly useful for irregularly shaped food with rough surfaces. Spraying is a more time-saving option when huge amounts of food need to be coated, but coatings generated by spraying are usually not as homogenous as those applied through dip-coating. Brushing is sometimes used in small industries since it does not require big and complex machinery. Edible coatings can also be premade as freestanding films by solution casting or melt extrusion and then wrapped around the food.[332]

4. Detection of Food Spoilage and Pathogen

As one of the major threats to public health and the well-being of society, Foodborne contamination kills 420 000 people annually worldwide.[333] Difficulties in tracking the source of contamination and identifying pathogen information of individual food items often result in precautious broad food recall and disposals in foodborne outbreak events regardless of actual contamination. Predetermined expiration labels are currently prevalent to provide food quality information in the supply chain. However, more than 80% of American consumers misinterpret the labels and throw fresh produce away prematurely due to safety concerns.[334] Developing food sensors that rapidly detect pathogens and inform real-time food quality is one straightforward solution to build a sustainable global food system by preventing foodborne diseases and reducing food waste.[335,336] Smart food labeling and packaging systems have been developed for the real-time monitoring of ubiquitous food quality indicators (e.g., CO_2 concentration,[337] pH,[338] humidity,[339] and storage temperature[340]) and specific chemical compounds (e.g., fungicides, nematicides, insecticides, and herbicides).[341] However, such systems have limitations in addressing food complexity and natural variations, identifying the cause of spoilage, and stabilizing sensing components upon contact with food surfaces.[336] Detecting foodborne pathogens, such as *Escherichia coli* (*E. coli*) O157:H7 and *Salmonella Typhimurium,* is even more challenging because many of them are lethal with a tiny infection dose (e.g., ≈50 CFU for *E. coli* O157:H7).[342] Polymerase chain reaction and standard cell culture techniques are commonly used in the screening protocols for quality control in the current food supply chain.[343] These microbial analyses involve sophisticated laboratory equipment and professional operations and are disruptive, time-consuming, and expensive.[344,345] Enzyme-linked immunosorbent assay (ELISA) using specific antibody-antigen reactions is also widely investigated. Typical ELISA-based food sensors mainly consist of a recognition element, signal transducer, and signal processor.[336] These approaches often require relatively large sampling volumes, and preparing proper antibody pairs with high selectivity and sensitivity is difficult.[346] Researchers have developed new immunoassay techniques to enhance resolution, precision, and accuracy by coupling with chemiluminescence,[347] impedance spectroscopy,[348] microfluidic devices,[344] and surface-enhanced Raman spectroscopy (SERS).[349] The development of affordable attachments for portable devices, such as smartphones, for these technologies improves the practicability of intelligent food packaging systems.[335,347,350,351]

Despite all the advances, researchers are still struggling to develop low-cost food sensors that provide real-time food quality and pathogen information to non-expert customers. The materials used for the new food sensing platforms should be safe upon contact with food (i.e., approved as food contact materials) and sustainable in their life cycles (e.g., biodegradable or upcyclable). They also need to meet the law, policy, and public perception restrictions, which are becoming stricter worldwide. Many researchers seek innovative solutions using polymeric materials produced by living organisms, such as structural/extracellular proteins and polysaccharides. Biomaterials developed for diagnostic or therapeutic purposes can be successfully adapted to develop new food sensing materials or sensing platforms. This section introduces recent studies on biomolecules and bioinspired materials/approaches to develop sensors (i.e., recognizing elements), devices, and platforms for detecting food spoilage and pathogen.

4.1. Sensing Components

4.1.1. Aptamers and DNAzyme

Due to their specific binding preference with high affinity to desired targets molecules, single-stranded oligonucleotides known as aptamers have emerged as promising biorecognition elements for food sensors.[346] Different aptamers, such as DNAs, RNAs, and synthetic nucleic acids (XNAs), have been used for clinical diagnostics, therapeutic agents, and environmental monitoring.[352] Their high selectivity toward certain food bacteria, such as *E. coli*, *salmonella*, and Norovirus, attracted researchers to develop aptamer-based point-of-need food sensors by coupling with optical devices, fluorescent tags, and electrochemical techniques.[353] Ledlod et al. used aptamer (Ap6)-modified gold nanoparticles to enable rapid colorimetric detection of *Salmonella spp.*, *Listeria monocytogenes*, and *E. coli*.[354] They achieved >96% accuracy, specificity, and sensitivity of the assay by investigating 50 meat samples collected from a local grocery without pre-culture, DNA extraction, and amplification. In another study, Li et al. developed a cost-effective and chemically stable tuberculosis infection screening system using an aptamer that selectively recognizes glycolipids on the surface of *Mycobacterium tuberculosis* (*M. tb*). Through dot-blot assays utilizing streptavidin-labeled horseradish peroxidase, biotin-labeled aptamer, and 3,3',5,5'-tetramethylbenzidine chromogen, they enabled colorimetric analysis using images captured by a smartphone camera and an Android platform application (**Figure 10**a,b).[351] Aptamers were also used to functionalize interdigitated electrodes (IDE) in a portable impedance-based sensing system for improved biorecognition. Abdelrasoul and co-workers presented a DNA aptamer-based non-faradaic impedance biosensor for detecting *E. coli* using a surface modified IDE with an *E. coli* outer membrane protein Ag1, which had a sensitivity of ≈1.8 Ohm CFU^{-1} and a detection limit of 9 CFU mL^{-1}.[355] The current impedance-based platforms with

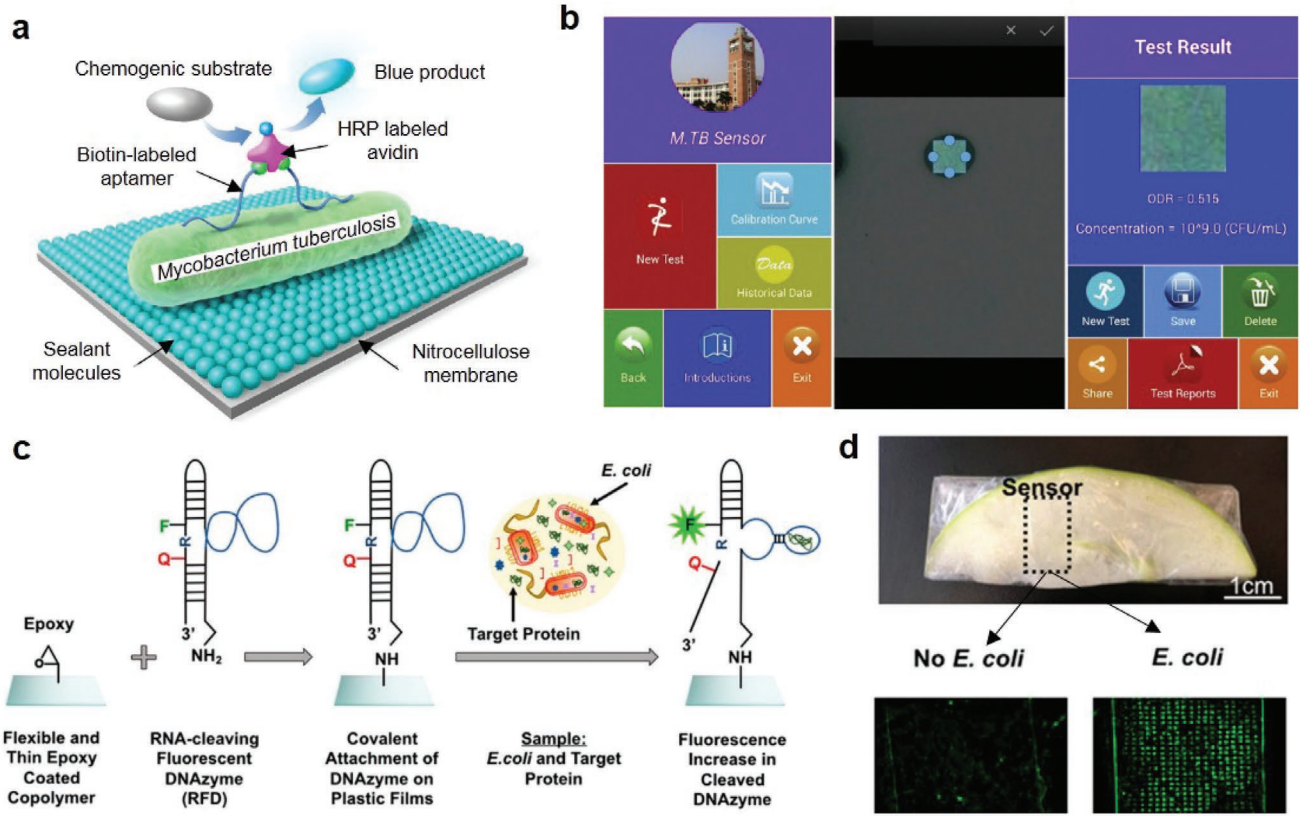

Figure 10. DNA aptamers and DNAzymes as food sensors. a) Schematic illustration of a direct dot-blot assay showing immobilization of *M. tb* bacteria by an aptamer on nitrocellulose membrane for colorimetric read-out. b) Example smartphone application interfaces for sensing *M.tb* bacteria. Reproduced with permission.[351] Copyright 2017, Elsevier. c) Schematic illustration of DNAzyme cleaving by live *E. coli*: Amine-terminated DNAzyme probe is covalently attached to epoxy films. In the presence of the target proteins produced by live *E. coli* cells, the ribonucleotide connecting the fluorogenic and quencher substrates of the DNAzyme is cleaved. d) An apple slice wrapped in a food film embedding DNAzyme sensors and representative fluorescence images of sensors demonstrating a successful detection of *E. coli*. The food samples were inoculated with bacteria mixtures with and without *E. coli* at 4 °C. Reproduced with permission.[358] Copyright 2018, American Chemical Society.

high sensitivities are generally destructive, sacrificing edible food portions. In addition, they mainly utilize single-use chips and require separate housing units for sensing. Developing a high-throughput nondestructive diagnosis that uses recyclable chips/electrodes and with miniaturized sensing components would be one future direction of research.

DNAzymes are synthetic, single-stranded DNA molecules that show catalytic abilities for specific reactions.[356,357] In particular, RNA-cleaving fluorescent DNAzymes obtained from specific bacteria are promising for detecting multiple bacterial targets.[358] Yousefi et al. applied an *E. coli*-specific RNA-cleaving fluorogenic DNAzyme probe to a thin, flexible, and transparent cyclo-olefin polymer film for real-time food contamination monitoring (Figure 10c).[358] The sensor detected *E. coli* as low as 10^3 CFU mL^{-1} in meats and apple juices while maintaining its chemical stability at pH 3–9 over two weeks. In addition, they successfully attached the sensors to a food packaging material and detected bacteria in meats and apples (Figure 10d). DNAzymes-based sensors were also reported to detect other food pathogens, such as *Aeromonas hydrophila* from dairy products[359] and *Pseudomonas aeruginosa* from beverages.[360] In addition, Zhou et al. utilized an Mg^{2+}-dependent DNAzyme for the fluorescent-based detection of an abused antibiotic, kanamycin, in milk.[361] They reported that the binding of target kanamycin and the aptamer sequence initiated a polymer exchange reaction to synthesize the DNAzyme autonomously in the presence of Bst-DNA polymerase. Overall, these nucleic acid-based biorecognition molecules are promising for food sensors because they are readily accessible, low toxic, and chemically stable at a wide range of pH and temperature conditions. However, degradation by nucleases and cross-reactivity is challenging for their wide application in the food supply chain.[346]

4.1.2. Imprinted Polymers

Imprinted polymers have attracted attention as synthetic receptors prepared via biomimetic strategies to overcome the limitations of fragile and unstable biological receptors in sensing platforms.[362] Various types of imprinted polymers have been used to detect from small molecules (using molecularly imprinted polymers, MIP)[363] to whole cells (using cell or surface imprinted polymers).[364] The advantages of imprinted polymers, including high selectivity and chemical stability, make them promising solutions in several biomedical

applications, such as immunoassays, drug delivery, bioimaging, and synthetic antibodies.[365] Typical MIP synthesis involves the preparation of a pre-polymerization complex with template and functional monomers, polymerization using crosslinkers, and removal of the template.[366] Ren and Zare introduced a method for preparing cell imprinted polymers using a glass slide covered with bacteria and another glass slide with partially cured PDMS on its surface.[367] A recent study showed that cell-imprinted polymers could effectively detect oocyst of a water-borne parasite, *Cryptosporidium parvum*, with a binding affinity comparable to some standard antibodies.[368]

Relatively easy and low-cost preparation procedures of imprinted polymers, such as a sol-gel method and free radical polymerization,[369] are beneficial for their food applications. By combining with transducing elements, including optical and electrochemical read-out platforms, imprinted polymers have been used for the detection of a wide range of chemicals (e.g., pesticides, drugs, and allergens) and biological substances (e.g., toxins, bacteria, and viruses) that threats food safety.[362] For example, Zhang et al. introduced a fluorescent sensor by coupling nitrogen-doped graphene quantum dots and sol-gel prepared MIPs to detect antibiotics in animal-derived food.[370] In plants, Yang and co-workers utilized a MIP synthesized by bulk polymerization to determine gallic acid, a bioactive food ingredient with antioxidant and antimicrobial effects.[371] In this study, they prepared sensor membranes by combining MIPs and conventional ion-selective electrodes for the potentiometric measurement of gallic acid. Stilman et al. prepared ultrathin surface imprinted polymer layers as receptors for impedance spectroscopy and detected yeast (*Saccharomyces*) strains as low as 30 cells mL^{-1} from yogurt and beer samples.[372] The team anticipated their technology could potentially identify different yeast strains using imprinted polymers and could be transferable to pathogenic microorganisms.

Techniques for imprinted polymers for biosensing have improved their efficacy and stability significantly. For example, nanoscale MIP utilizing nanomaterials, such as gold nanoparticles, quantum dots, and carbon nanotubes, showed remarkable binding properties and significant selectivity.[369] Such an improvement has enabled their use as solid-phase extraction materials that separate and enrich target chemical compounds during sample pretreatments. Gao and co-workers suggested that future MIP fabrication strategies for food applications would need to focus on 1) improvement of the performance in the presence of a polar solvent, such as water, 2) prevention of template leakage, and 3) commercial conversion.[369] The advanced biomaterials, in most cases developed for biomedical applications, can be easily adapted for ex situ analyses of food samples. However, for a comprehensive application of imprinted polymers as next-generation sensing platforms, it is essential to establish a reliable protocol evaluating their safety upon food contact safety and sustainability in the supply chain.

4.1.3. Polydiacetylene

Polydiacetylene (PDA) liposomes have been extensively investigated for detection and diagnostic purposes due to their rapid color change accompanied by fluorescence generation due to environmental stimuli, such as heat, pH, and mechanical pressure.[373,374] PDA liposomes at nano- to micrometer scales can be functionalized with various macromolecules, such as carbohydrates,[375] lipids,[376] peptides,[377] and antibodies,[378] to increase affinities to specific target chemicals or microorganisms in food samples. Oliveira et al. studied behaviors of PDA liposomes, prepared from 10,12-pentacosadienoic acid (PCDA) and 1,2-dimyristoyl-sn-glycero-3-phosphatidylcholine (DMPC), under varying storage temperature and pH, and in the presence of milk components.[379] After conducting parametric analyses, the team later developed a PDA liposome incorporating an antibody to detect *Salmonella* specifically.[380] By modifying physical properties, such as size and surface charges, they enhanced the sensitivity of colorimetric response with an expanded understanding of parameters for PDA liposomes for food applications.

Researchers have innovatively utilized PDA liposomes in the food supply chain. Omenetto and co-workers developed an inkjet-printable bioink using PDA liposomes to detect food contamination during processing.[381] Using silk micelles regenerated from silkworm cocoons, they stabilized the bioink containing PDA liposomes conjugated with *E. coli* targeting antibody into plastic substrates. Their proof-of-principle application on surgical gloves showed the color change of the printed pattern from blue to red after exposure to *E. coli* ($\approx 10^4$ CFU mL^{-1}) to indicate contamination for food processing workers (**Figure 11**a). Marelli and co-workers recently enabled nanoporous flexographic printing of a microscale pattern with the PDA bioink (Figure 11b) using a stamp made of polymer-coated carbon nanotubes (Figure 11c).[382,383] Zhang et al. reported that food sanitizers and surfactants could perturb the colorimetric response of inkjet-printed PDA biosensors.[384] The authors suggested to utilize these properties for detecting chemical residues during food processing. The combination of bioprinting technology and biosensors will miniaturize future food sensing systems that can identify multiple pathogen information simultaneously.

Currently, most PDA-based biosensors are only valid for a particular food type under a certain condition. The real-life applications require the identification of unknown chemical and biological hazards in disparate food types. To overcome this technological barrier, biosensor arrays with engineered types of PDA liposomes can be utilized to enable the detection of multiple pathogens. In a recent study, Zhou et al. optimized the sensitivity and selectivity of PDA biosensors for different bacteria by incorporating phospholipids cholesterol during PDA liposome assemblies.[385] Then, the research team demonstrated the colorimetric finger-print array of different PDA-based sensors for identifying six bacterial species with naked eyes. Recent advances in machine learning could enable colorimetric biosensors arrays to provide a number of different information by interpreting subtle colorimetric changes under different conditions.[378,386] Yang and co-workers prepared a paper chromogenic array with 23 impregnated chromogenic dyes and their combinations.[386] Upon exposure to volatile organic compounds, colorimetric changes of the dyes in the array were digitized and used for multi-layer neural network model training. The trained neural network system simultaneously identified *E. coli* O175:H7 and *Listeria monocytogenes* on fresh-cut lettuce.

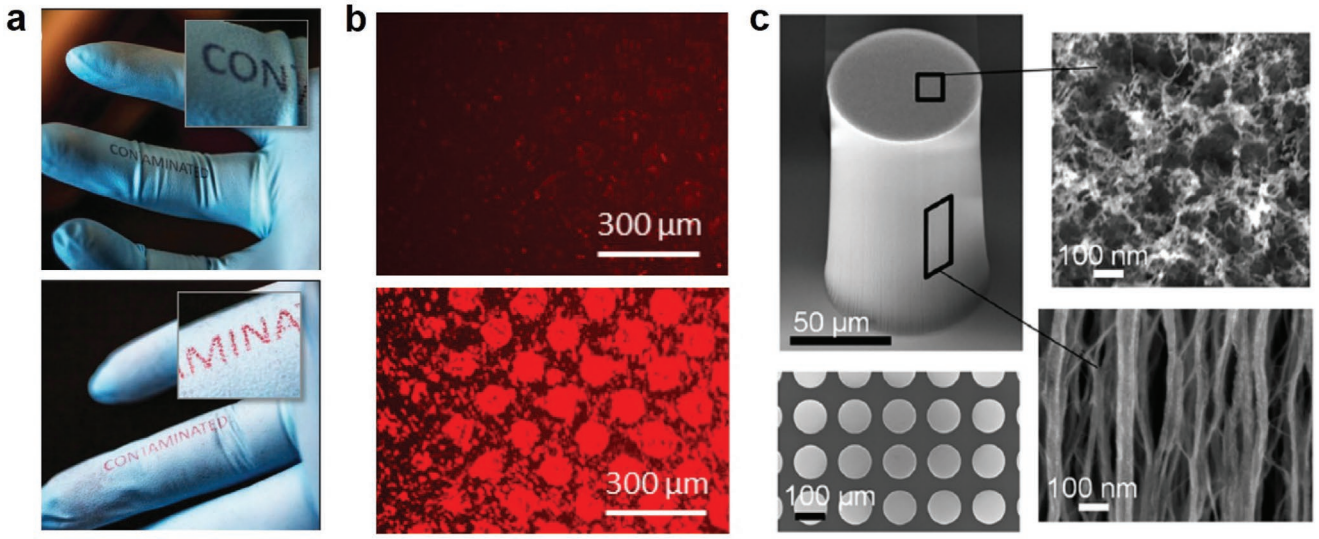

Figure 11. Application of PDA bioinks for detection of food pathogen. a) Inkjet-printing of PDA bioinks conjugated with *E. coli*-targeting antibodies on surgical gloves. The printed letters "CONTAMINATED" showed a colorimetric change from blue (top) to red (bottom) after exposure to *E. coli*. Reproduced with permission.[381] Copyright 2015, Wiley-VCH. b) Fluorescence micrographs of PDA bioinks before (top) and after (bottom) exposure to *E. coli*. Flexographic printing technique with a nanoporous stamp made of polymer-coated carbon nanotubes was used to generate micropatterns of the bioink. Reproduced with permission.[382] Copyright 2020, Wiley-VCH. c) SEM images of a carbon nanotube micropillar (top left, side view) and a pillar array (bottom left, top view) of the nanoporous stamp, as well as zoomed-in images of the top and wall of an individual micropillar (right panel). Reproduced with permission.[383] Copyright 2019, American Chemical Society.

A similar approach was used for PDA biosensors in an earlier study for disease diagnostics by Kolusheva et al.[378] They developed a diagnostic platform comprising lipid/PDA liposomes embedded with a transparent silica-gel matrix array. With a simple machine-learning algorithm, their platform was able to distinguish patients from healthy individuals using their blood plasma samples, highlighting the potential of PDA liposomes for diagnostic and screening applications in biomedical and other fields, including the food industry.

4.1.4. Nanomaterial-Based Biosensors

In addition to the precise delivery carriers and controlled release agents of drugs as discussed in Section 2.2, nanomaterials, showing colorimetric, fluorescence, or electrical responses upon exposure to biological molecules, are widely used for biomedical applications, including bioimaging and biosensors for disease diagnoses.[387] These properties of nanomaterials can be effectively used to develop new food sensors. General descriptions and example applications of nanomaterials for the detection of food spoilage, adulteration, and pathogens are well summarized in recent review articles.[388,389] Due to safety and cost concerns, several nanomaterials widely studied in biomedical fields, such as graphene[389,390] and gold nanoparticles, encounter regulation barriers when entering the food industry. Food-derived nanomaterials are promising candidates for developing cost-effective food contacting devices that circumvent these concerns.[391] Most materials used for edible coating, as introduced in Section 3, including polysaccharides, protein, lipids, and their composites, have also been utilized to develop nanomaterials for biosensing. Generally, food-derived nanoparticles can be synthesized by either top-down (e.g., milling, ultrasonication, and microfluidization) or bottom-up (e.g., antisolvent precipitation, coacervate, microemulsion, and template-guided bio assembly) approaches. They are utilized as supporting media for biosensing or additives to fabricate composite materials with other biopolymer materials.[390,391] For example, bacterial nanocellulose (bottom-up approach) was used as a flexible substrate embedding gold nanorods for SERS analysis to detect *E. coli*.[392] Considering the safety, cost-benefit, and versatile applications with other materials, the demand for food-derived nanomaterials will keep increasing. The advances in the biomedical application of the food-derived would inspire new food sensing systems. For example, Zhang et al. recently introduced a gelatin-based hydrogel as a wearable pressure sensor,[393] which has the potential to be used for monitoring the freshness of meats and fish or changes in the activity of living animals, such as aquaculture fish, due to a specific pathogen.

4.2. Sampling and Reporting Devices

4.2.1. Microneedles

Previously we discussed the use of microneedle devices for the precise delivery focusing on precision delivery of payloads to target tissue locations and control of release properties. In addition, polymeric microneedles have attracted considerable attention as potential diagnostic devices for biomedical applications due to their ability to extract dermal interstitial fluids with minimal invasion.[394] Sampling target fluids from tissues and transporting them to reporting devices are the critical performances required for these microneedles. Therefore, to develop new biomaterials, understanding fluid transport mechanisms,

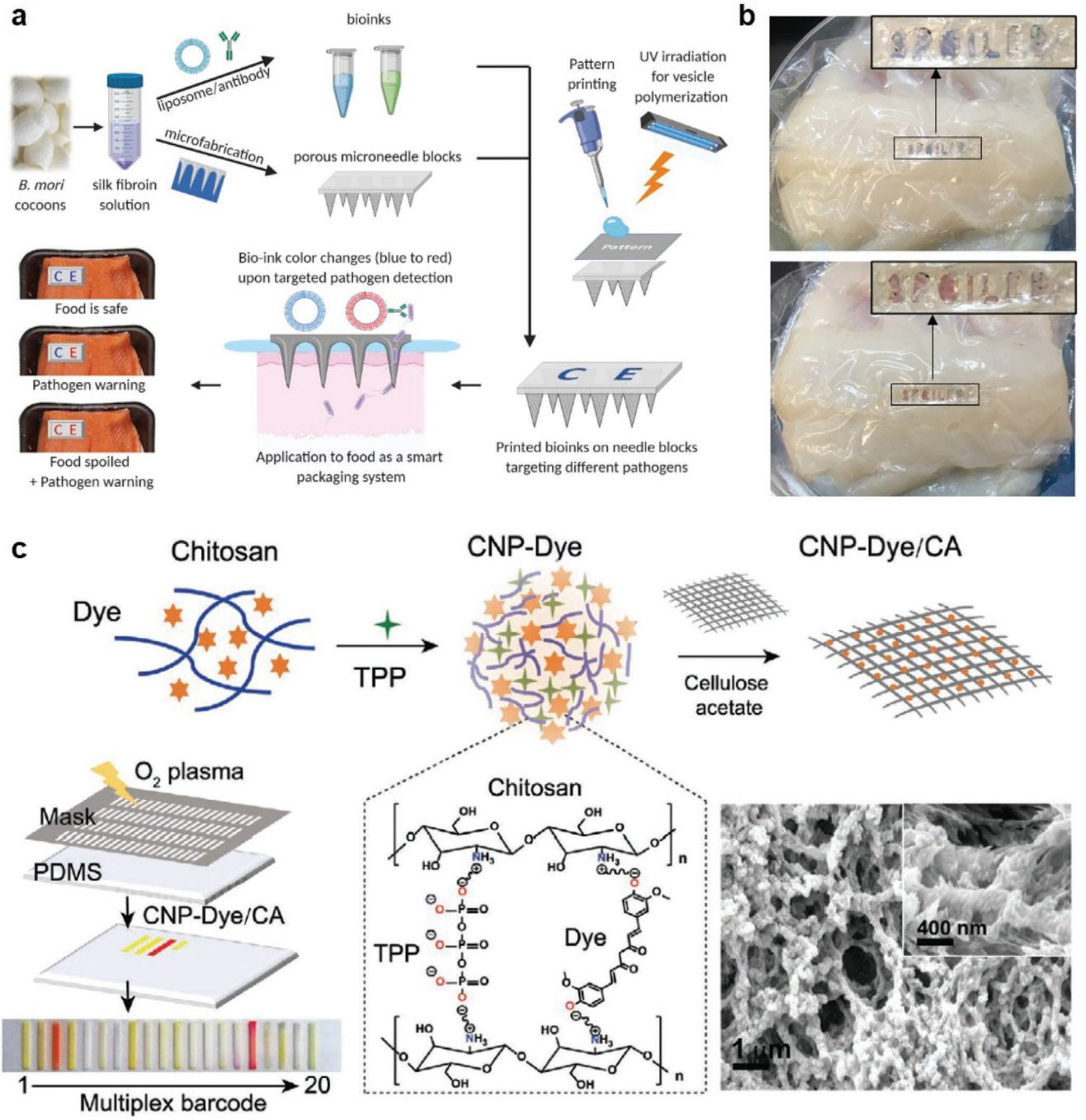

Figure 12. Biopolymer-based platforms for detection of food spoilage and pathogen in the food supply chain. a) Schematic illustration of the proposed food quality monitoring system using a silk-based microneedle device conjugated with PDA bioinks. b) Silk microneedles applied on a haddock fillet at 0h (top) and 4h (bottom). Color change of the printed "SPOILED" at the back of silk microneedles from blue at 0h to red at 4h indicates successful detection of bacteria/pathogens in the haddock fillet. Reproduced with permission.[382] Copyright 2020, Wiley-VCH. c) Fabrication and characterization of colorimetric barcode strips made of chitosan nanoparticles (CNP), dye, and cellulose acetate (CA). Sodium tripolyphosphate (TPP) is used as a crosslinker. Reproduced with permission.[407] Copyright 2020, Wiley-VCH.

such as diffusion, capillary action, osmosis, and pressure-driven convection, and their manipulation in the microneedle devices are required.

In a recent study, Kim et al. demonstrated that a silk-based microneedle device could be a new food sensing platform to detect food pathogen and spoilage (**Figure 12**a).[382] The team developed the microneedle array that samples fluid from the interior of the food by capillary action of porous microneedles and transports the fluid to PDA bioinks on the backside of the array. Through the colorimetric response of bioink patterns, the researchers were able to identify *E. coli* contamination in fish fillets within 16 h of needle injection, which was distinct

from spoilage measured via the sample pH increase. The needles were mechanically robust enough to penetrate commercial food wrap and food tissues (Figure 12b), allowing the sensor to function properly without opening the package. In addition, the use of microneedle would provide several advantages that none of the previous had. Using microneedle as a food-grade device bridging food samples and sensing components may alleviate customers' safety concerns on new engineered materials in the food industry. The microneedles would enhance the detection efficiency for pathogenic microorganisms growing in microscopic cavities of certain food types (e.g., meats and leafy greens),[395] which cannot be thoroughly removed by general household washing.[396] In future research directions, the authors suggested the improvement of PDA bioinks for the universal application to different food types under a wide range of storage conditions. In addition, the microneedle pore structures can be further optimized to enhance the transport of target pathogens or molecules to the bioinks.

Currently, there are few studies about the application of microneedles for food contacting devices. Unlike silk fibroins, many biodegradable polymers or food-derived materials are water-soluble. Thus applications of microneedles made of these materials focus on the controlled delivery of cargos. However, researchers have introduced several microneedles that might be suitable for food contact applications. For example, Zhu et al. reported a gelatin-based microneedle patch to extract interstitial fluid from skins.[397] In their in vitro study, the patch swelled up to 423% and sufficiently extracted interstitial fluid to detect glucose and antibiotic vancomycin. However, the food safety regarding crosslinker methacrylic anhydride remains uncertain, although it can be removed by dialysis after the crosslinking process. In another study, He et al. reported a hydrogel needle patch made of polyvinyl alcohol and chitosan crosslinked through repeated freeze and thawing processes without any chemical crosslinkers.[398] The dried needles were robust enough to penetrate rabbit back skin in vivo, then swelled to extract sufficient interstitial fluid for glucose monitoring with an accuracy comparable to a conventional glucose meter. The authors recovered collected glucose by thermal degradation of the microneedles for the quantification and suggested that an automated platform combining temperature control, microfluidics, and color acquisition would make their device more convenient. For food applications, it will be essential to incorporate the reporting components with the microneedle (e.g., the bioink printing on the backside as shown in Figure 12a,b) in a cost-effective way allowing large-scale production.

4.2.2. Human Sensory Mimicking Systems

Most people empirically judge food quality by smelling, tasting, or visually inspecting foods that they already know. Although subjective and often inconsistent, the human examination, from sensing to classification, is a complicated decision-making process. The human sensory systems and neural networks have inspired researchers to develop various food sensing platforms. The human olfactory system contains thousands of receptors that bind odor molecules, enabling the detection of some odors at parts per trillion levels.[399] The human tongue consists of over 10 000 taste buds with 50–100 taste cells recognizing sweet, sour, bitter, salty, and umami.[400] Over the past decades, significant scientific efforts have been made to mimic the mammalian nose (electronic nose as a gas sensor) and tongue (electronic tongue as a chemical sensor) using individual cross-sensitive sensors and computational interpreters.[401,402] Researchers have applied these techniques to a wide range of food including beverages, fruits, vegetables, cooking oils, meats, and fish.[402] Recent advances in nanoengineering[401] and artificial intelligence (AI)[403] have contributed to improving these human-mimicking sensing systems. Nanoengineered materials have also been extensively used as sensing components due to their high surface area and uniquely tunable optical, electronic, and optoelectronic properties. Semiconducting metal oxides, transition metal dichalcogenides, carbonaceous nanomaterials, and conducting polymers are commonly used materials. Gancarz and co-workers utilized six metal oxide semiconductor sensors in an electronic nose Food Volatile Compound Analyzer to identify volatile organic compounds commonly produced during the spoilage of agricultural or food commodities.[404] Hu et al. used graphene plasmon to identify SO_2, NO_2, N_2O, and NO gases from their rotational-vibrational modes, which have a strong food application potential.[405] In this study, the authors showed that plasmons in a graphene ribbon array were excited using an incident infrared beam. Then, electrostatic doping through a gate voltage tuned the plasmons in situ. The plasmon resonances coupled with molecular excitations served as probes of the rotational-vibrational spectral fingerprints of gas molecules.

Researchers are utilizing several machine learning classifiers to analyze signals obtained by electronic nose and tongue systems. Examples are principal component analysis (PCA), support vector machines (SVM), artificial neural networks (ANN), convolutional neural networks (CNN), and random forests.[403] The general approach to recognizing different sample types by these tools is the aggregation of similar emissions into clusters representing compounds from related food volatiles. In particular, ANN with nonlinear mapping capability is considered a robust machine-learning-based classifier. Thus several types of ANN, such as multi-layer perception, learning vector quantization, and Kohonen network, have been employed for an electronic nose.[406] In a recent study, Guo et al. combined biomaterials and AI to develop a new portable platform to analyze food freshness.[407] They prepared the colorimetric barcode made of 20 different types of porous nanocomposites. Each bar contains different compositions of chitosan, dye, and cellulose acetate to perform as a scent fingerprint classified by a deep convolutional neural networks algorithm (Figure 12c). After supervised training using 3475 labeled barcode images, they achieved an overall accuracy of 98.5% for meat freshness. Moving forward, the application of AI and machine learning in the food safety domain will not be limited to sensory systems. Integrating and processing all data generated throughout the food supply chain in a single stream will allow us to holistically trace the source of pathogens and food quality changes from farm to fork.

4.3. Outlook

Recent advances in biomaterials and nano/microfabrication techniques have significantly improved the selectivity and

sensitivity in detecting biological substances for biomedical applications. These advances are actively being adapted for rapid and precise detection of food pathogens and contaminants. By coupling with machine learning-based signal analyses, food sensors are evolving to provide a large amount of information to nonexpert customers. According to our discussion, current efforts are largely in three fundamental categories: i) novel material design for enhanced selectivity and sensitivity to specific target molecules/organisms (e.g., functional nanomaterials), ii) more effective methods to sample from foods (e.g., porous microneedles), and (iii) efficient and accurate data analysis tools (e.g., AI). Additionally, the development of new food sensing systems should focus on materials safety and also include life cycle and sustainability assessments.

The successful employment of biomaterials in food sensing platforms will expand their application spectrum from disease diagnosis to foodborne disease prevention by providing feedback to stakeholders and consumers before consumption. However, several challenges need to be addressed for a successful integration of food contact biomaterials in the food supply chain. As already required by policymakers, specific studies need to be conducted on maximum daily dose and possible allergies. Establishing standard protocols is required to evaluate non-food grade materials for their transport from sensing platforms to edible portions of foods and their phase transformation during this transport. Regulations and the public's resistance to new materials are considerable challenges to adopting new technology to design food contact devices. Using food-derived materials or generally recognized as safe (GRAS) substances that are already approved by the US Food and Drug Administration (FDA) is a promising solution to overcome these challenges and accelerate their deployment in real-life applications. This approach would require the design of devices made of material already adopted by the food industry without further chemical modification or processes that can be considered harmful to human health.

5. Conclusions and Perspectives

Biomaterials will provide an important tool to underpin disruptive innovation in food and agriculture and to address the thirst for new technologies that will make the AgroFood infrastructure more efficient, resilient, and sustainable. The ability to engineer biomaterials (particularly sustainable and with a circular life cycle such as structural biopolymers) into advanced formats has been shown to benefit a broad range of practices in the agriculture and food industry, including seed enhancement, precision payload delivery in plants, perishable food preservation, and food spoilage detection. Besides crop-based agriculture, biomaterials are also playing increasingly important roles in aquaculture and the emerging cellular agriculture field. For example, carboxymethyl cellulose-based dissolving microneedle patches were used for transcutaneous vaccination of fish against *Aeromonas hydrophila* infection;[408] and plant- and fungus-derived edible biomaterials were pursued to make scaffolds for cultivating meat from stem cells.[409–411] Moreover, biomaterials account for a key component of the novel materials used in urban farming including vertical farming, greenhouse farming, container farming, rooftop farming, and indoor farming, with their ability to serve as novel growing substrates and additives for plant cultivation in place of soil and hydroponics.[412] Applications of advanced biomaterials in agriculture have just started and will continue to advance with the development of both new materials and new fabrication strategies. In this domain, silk fibroin regenerated from *Bombyx mori* cocoons may serve as a good example to illustrate how an ancient material can be reinvented and engineered into various high-tech and multifunctional formats to enhance food safety and security in a sustainable way.[413,414]

Moving forward, utilization of biomaterials in the agriculture and food industry still faces various challenges. Unlike many healthcare applications, which could justify huge investments in the research & development of novel biomaterials-based devices and platforms, agricultural practices generally cannot afford costly raw materials and sophisticated micro-/nanofabrication techniques, which would make the price of food products prohibitive for certain populations, thereby further aggravating food insecurity. The strategy of directly transferring the biomaterials and their design principles used in the medical field to agriculture and food, therefore, will not work properly. Innovations in materials extraction and processing from massively abundant and renewable sources, as well as in micro-/nanofabrication approaches that are cheap and suitable for large-scale production and application in the field are needed to realize biomaterials' potential as an economically viable and practical solution for sustainable agriculture and food security. In this respect, upcycling agri-food waste into functional materials that can be reapplied in various agriculture practices is a compelling strategy to build a food–materials nexus that can positively contribute to the establishment of circular economy in the AgroFood system.[415] The challenge then lies in development of low-impact and cost-effective approaches to upcycle waste into useful materials. As in the case of chitin/chitosan production from seafood waste,[416,417] there is a thirst for innovative solutions that can replace the current chemical extraction processes which are energy-intensive, extremely hazardous to the environment and require large quantities of freshwater consumption, as well as the biological extraction processes which have a high demand of carbon and nitrogen sources during fermentation, cause microbial contamination of the chitin products and leave large amounts of protein residues that require further deproteinization processes.

Additionally, despite the biodegradable and non-toxic nature of most biomaterials, special considerations from a policy-making perspective are needed to foster the use of new biomaterials in food and agriculture. The recent EU's regulations on Single-Use Plastics and Intentionally Added MicroPlastics provide an opportunity to engineer new (bio)materials that already embed a programmable life cycle in their design.[164,165] However, a broader framework needs to be developed to support the design of new biomaterials that positively impact the resiliency and sustainability of the AgroFood infrastructure. Materials applied to seeds, plants and food will inevitably end up in the environment or will be ingested during food consumption. The fact that a material is biodegradable does not guarantee that it has a better environmental performance. Same principles apply to renewable and biological origins. Thus, holistic evaluations

of material performance for AgroFood applications should include not only the established safety and biodegradability assessments, but also life cycle analysis to support the efforts of policymakers, stakeholders, and consumers to build a more sustainable and resilient AgroFood infrastructure. For example, in the case of *Bombyx mori* silk, a life cycle assessment that analyzes the direct and indirect environmental impacts of silk production from mulberry planting and silkworms rearing to cocoons degumming and allocation of co-products are essential to justify large-scale utilization of silk in the AgroFood system, to address any sustainability concerns and to provide guidance for improvements in each silk production step.[418,419]

Finally, engineering biomaterials into fibers and particles of nanoscale dimensions tend to raise ecotoxicity concerns. More research on nanomaterials–plant interactions and mechanisms of action, as well as on environmental and human health risks from engineered nanomaterials, are needed to support the responsible development of novel technologies and their introduction to the market.[420,421] It is paramount that evaluations of the efficacy, potential toxicological effects, environmental footprint, and cost/benefit balance of engineered biomaterials are carried out under more realistic conditions and at larger scales beyond laboratory settings, and the results are transparently communicated with stakeholders to advance their utilization in real-life scenarios.

Acknowledgements

This work was supported by the Office of Naval Research (Awards N000142112402 and N000141912317) and the National Science Foundation (Award CMMI-1752172). B.M. and Y.C. acknowledge funding from Singapore-MIT Alliance for Research & Technology, National Research Foundation, Prime Minister's Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) program. B.M. also acknowledges funds from BASF and OCP S.A. B.M. acknowledges a Paul M. Cook Career Development Professorship and a Singapore Research Professorship.

Conflict of Interest

B.M. is co-founder of a company, Mori Inc., that uses silk fibroin-based materials as edible food coatings to increase the shelf-life of perishable food. The use of silk fibroin as an edible coating, seed coating, and to fabricate microneedles for drug delivery in plants is protected by multiple IP positions where B.M. is listed as a co-inventor.

Keywords

biomaterials, food safety and security, micro-/nanofabrication, structural biopolymers, sustainable agriculture

Received: February 17, 2022
Revised: March 31, 2022
Published online: May 12, 2022

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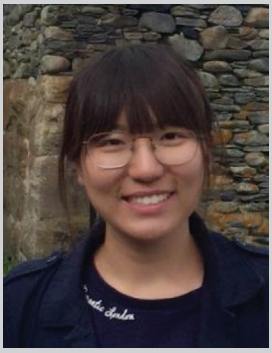

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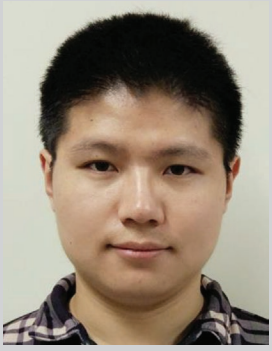

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