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Boosting Food System Sustainability through Intelligent Packaging: Application of Biodegradable Freshness Indicators

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Zhilong Yu,[#] Valeriya Boyarkina,[#] Ziyu Liao, Mengshi Lin, Weicai Zeng, and Xiaonan Lu[*]

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ABSTRACT: World hunger is getting worse, while one-third of foods produced around the globe is wasted and never consumed. It is vital in reducing food waste to promote the sustainability of agri-food systems. Intelligent packaging embedded with freshness indicators can monitor food freshness in a real-time manner and be deployed for cutting food waste produced due to predetermined expiration date and informing consumers of food safety. Biodegradable halochromic films have been increasingly utilized as freshness indicators because of their low environmental impact. In this review, recent advances in biodegradable halochromic indicators for intelligent packaging are reported. The pH-responsive behaviors of natural pigments, the development of biodegradable solid supports for freshness indicators, the colorimetric response of freshness indicators to food products and simulated models, and future challenges in this field are discussed. Particularly, novel technologies coupled with halochromic indictors are highlighted, including sensor arrays, nanocomposites, smartphone-assisted detection, and ink-free printing.

KEYWORDS: *biodegradable halochromic indicator, intelligent food packaging, natural pH-responsive dye, solid support, smart traceability*

1. INTRODUCTION

World hunger has been on the rise since 2014. Although efforts have been made by United Nations toward the "zero hunger" goal that aims to eradicate food insecurity and inadequate nutrition,[1] it is estimated that the global population affected by hunger will hit 840 million by 2030 accounting for 9.8% of the world population.[2] World hunger could get even worse due to compromised functioning of agri-food systems caused by the COVID-19 pandemic, climate change, and violent conflict. Increasing food production serves as a strategy to feed more people, but it requires more land and water resources and would raise greenhouse gas emissions.[3] Given the fact that one-third of all foods produced around the globe is lost or wasted,[4] reducing food loss and waste can be another viable strategy to combat world hunger. It is projected that a reduction of 15% of food loss and waste in the United States alone is sufficient to feed 25 million people annually.[5] Besides increasing food availability, less food loss and waste can also reduce the economic cost of food wastage.[6] From an environmental standpoint, food wastage occupies 30% of agricultural area in the world, not mentioning water and energy used for food production, so that minimizing food loss and waste could largely promote the sustainability of the agri-food systems.

Food packaging is a traditional food preservation technology relying on four basic functions: protection, communication, convenience, and containment.[7] Packaging systems act as a barrier to separate food products from the surrounding environment, therefore limiting extrinsic deterioration factors including humidity, temperature, light, oxygen, and mechanical damage. On the other hand, packaging prevents food waste by informing consumers of product attributes, such as nutrition, shelf life, and handling, to ensure appropriate use. However, traditional food packaging systems remain to be improved in terms of communicating food quality and safety. For example, date labels that indicate food quality, such as "best before", "use by", "sell by", and "expire on", routinely mislead consumers into discarding food products that pass peak quality but are still safe to consume.[8] In addition, traditional food packaging materials are inert and thus cannot inhibit foodborne pathogens or report information on food safety to prevent foodborne illnesses. According to a food safety report by WHO, 600 million people worldwide are affected by contaminated food every year.[9] Once foodborne illness outbreaks occur, millions of dollars of food items will be mandatorily recalled and go to waste.

Smart packaging can be subdivided into active and intelligent packaging and has been developed to ameliorate conventional food packaging systems, with an end goal of prolonging the shelf life of food items, enhancing product traceability, and improving food safety and quality.[10] Active food packaging systems can release or absorb substances into or from the packaged food or the headspace of food packaging,

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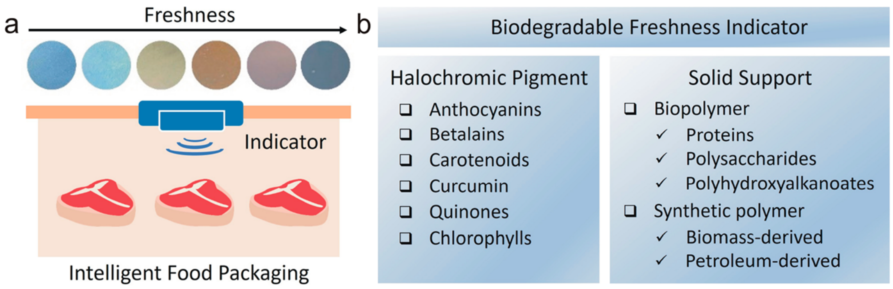

Figure 1. (a) Schematic illustration of intelligent food packaging installed with a freshness indicator. (b) Halochromic pigments and solid supports used for the development of biodegradable freshness indicators.

Table 1. Halochromic Pigments for Use in Biodegradable Freshness Indicators

Halochromic pigments		Typical colorimetric response to pH	References
Type	Major compounds		
Anthocyanins	Cyanidin Delphinidin Pelargonidin Peonidin Malvidin Petunidin	🟪 pH 2 🟪 pH 4 ⬜ pH 5 🟪 pH 7 🟦 pH 9 🟫 pH 10 🟨 pH 12	26
Betalains	Betacyanin Betaxanthin	🟥 pH 2 🟥 pH 4 🟥 pH 5 🟥 pH 7 🟧 pH 9 🟧 pH 10 🟨 pH 12	31
Carotenoids	β-Carotene Lutein Lycopene	🟥 pH <7 🟧 pH 7 🟨 pH >7	38
Curcumin	Curcumin	🟧 pH 2 🟧 pH 4 🟧 pH 5 🟥 pH 7 🟥 pH 9 🟥 pH 10 🟫 pH 12	42
Quinones	Alizarin	🟨 pH 2 🟧 pH 4 🟥 pH 5 🟥 pH 7 🟫 pH 9 🟪 pH 10 🟪 pH 12	48
	Shikonin	🟥 pH 2 🟥 pH 4 🟥 pH 5 🟫 pH 7 🟦 pH 9 🟦 pH 10 🟦 pH 12	49
Chlorophylls	Chlorophyll a, b, c1, c2, and d	🟩 pH <7 🟩 pH 7 🟩 pH >7	22

intended to reduce food safety hazards and retard food spoilage by deterring degradative reactions such as oxidation and microbial growth.[11] Intelligent packaging technologies enable food packaging to monitor conditions of packaged foods or environment surrounding foods through tailored sensing systems installed on the packaging, and to communicate information regarding food safety and quality via an array of signals.[12] For example, freshness indicators that are embedded inside intelligent packaging can report food freshness by detecting changes in pH, temperature, moisture, or levels of certain microbiological metabolites or chemicals linked to food spoilage (e.g., carbon dioxide, organic acids, biogenic amines, volatile nitrogen compounds, and sulfuric compounds).[13] These indicators offer dynamic freshness prediction and inform consumers of discarding spoiled food products by showing visible color changes or signals recognizable by portable digital devices, aiming to improve safety control of food products and help diminish food waste resulted from misinterpretation on product date labels.

One growing concern on food packaging is raised by the massive amount of packaging waste generated in the food systems, which poses a serious threat to the environment and food safety. In Canada, most food packaging waste ends up in landfill, with only 20% of the waste being recovered for recycling or reuse.[14] Particularly, most plastic packaging wastes are nonbiodegradable and can beak down into small plastic particles in the environment, such as microplastics (size, 100 nm-5 mm) and nanoplastics (size, 1−100 nm).[15] These particles are present ubiquitously in marine, freshwater, and agricultural ecosystems, thus bringing a safety challenge to the agri-food system. This problem catalyzes a critical need for biodegradable packaging that features low environmental impact. For example, researchers are increasingly interested in biodegradable plastics that derive from traditional petrochemicals but can degrade completely by microorganisms, including poly(vinyl alcohol) (PVA), poly(butylene adipate-*co*-terephthalate) (PBAT), poly(butylene succinate-*co*-butylene adipate) (PBSA), poly(butylene succinate) (PBS), poly(glycolic acid) (PGA), and polycaprolactone (PCL).[16] Another green solution is to deploy bioplastics that are made of materials deriving from renewable sources (e.g., plant, agricultural, marine, and microbial biomass). Biobased plastics have great potential for commercial applications due to their advantages of being biodegradable, renewable, cost-effective, and readily available.[17]

In this review, we report recent advances in biodegradable freshness indicators that can be leveraged in intelligent packaging (Figure 1a). The pH-responsive behaviors of natural dyes, the development of biodegradable solid supports for freshness indicators, the colorimetric response of freshness indicators to food products and simulated models, and the future challenges in this field are discussed. Particularly, novel technologies coupled with biodegradable freshness indictors are highlighted.

2. NATURAL PIGMENTS AS PH INDICATORS

Microbial growth is a principal factor causing food spoilage and is often associated with pH changes in food products. For example, lactic acid bacteria consume glucose in foods as an energy source to synthesize a variety of organic acids, such as lactic acid and acetic acid, which can reduce the pH of food products.[18] Gaseous carbon dioxide produced by microbes decreases the pH in food environment since it reacts with water to form carbonic acid molecules that can dissociate into protons and bicarbonate ions.[19] Additionally, putrefactive bacteria naturally present on the surface of high-protein foods, including meat and seafood products, can elevate the pH of food samples by releasing nitrogen-containing compounds (e.g., ammonia, trimethylamine, and dimethylamine).[20] Since metabolic products released during food deterioration can largely affect the acidity or alkalinity of food matrices, determining the pH change in food products is considered as a viable approach to monitoring food freshness.

Natural pigments play essential roles in plants, animals, and microbes. Pigment molecules can absorb light in the wavelength range of visible light and thus display an array of colors, such as red, yellow, green, blue, orange, brown, purple, and shades. They also serve as attractants and camouflages, participate in cell metabolisms, and offer protection against oxidation, sun exposure, and radiation. There are various types of pigments in nature, including hemes, carotenoids, chlorophylls, anthocyanins, flavonoids, betalains, melanins, tannins, quinones, and xanthones.[21] Interestingly, some pigments can alter color in response to different pH conditions; they are known as halochromic pigments. Halochromic pigments respond to pH changes by altering their molecular configurations accompanied by shifted light absorption wavelengths.[22] Due to their pH-responsive capability, biodegradability, and nontoxicity, halochromic pigments have been widely used to develop colorimetric food freshness indicators. This section covers different types of natural halochromic dyes with the potential use in freshness indicators by highlighting their main sources and pH-responsive mechanisms (Table 1).

2.1. Anthocyanins.

Anthocyanins are water-soluble pigments imparting blue, red, and purple colors and exist in the flowers, leaves, fruits, stems, and roots of plants (e.g., avocados, blackberries, black carrots, red cabbages, beets, olives, and sweet potatoes).[23] Anthocyanin content in plant varies in the range of 0.1%−1% of dry weight, depending on plant species and growth conditions.[21] Anthocyanins are considered as a member of flavonoids since they are composed of glycosides and acyl glycosides of anthocyanidins, flavylium cations (2-phenylbenzopyrilium ions) with multiple hydroxyl and methyl groups.[24] Types of sugar attached to anthocyanidins contain monosaccharides (e.g., glucose and xylose), disaccharides (e.g., rutinose and suphrose), and trisaccharides (e.g., gentiotriose). Some sugar moieties are acylated with organic acids, such as acetic, malic, ferulic, ascorbic, caffeic, sinapic, gallic, malonic, succinic, citric, and oxalic acids.[23] The most abundant anthocyanins in nature include cyanidine (50%), delphinidin (12%), pelargonidin (12%), peonidin (12%), malvidin (7%), and petunidin (7%).[25] Cyanidine has a magenta color and is identified in berries and red-colored vegetables such as sweet potatoes and red cabbages. Flowers, fruits, and vegetables are prime sources for delphinidin (blue-red and purple), pelargonidin (red and orange), peonidin (magenta), malvidin (purple and blue), and petunidin (dark red and purple).

Anthocyanins respond to pH changes in an environment by showing distinct colors (Table 1).[26] At pH 1−4, anthocyanins are present in the form of flavylium cations and confer a bright red color. When pH is in the range of 4−5, the dehydration and deprotonation of flavylium cations will occur, resulting in color transitions from bright red to pale pink and eventually to colorlessness due to the formation of a carbinol pseudobase. At higher pH levels, flavylium cations are further deprotonated into quinoidal anhydrobase (pH 6−7) and anionic quinoidal base (pH 7−8) exhibiting violet and blue colors, respectively. Above pH 8, chalcone is produced because of the central ring fission of the anhydrobase, showing a light-yellow color. It is noted that the pH-responsive color change of anthocyanins is largely determined by the source of these pigments.[25] Besides pH conditions, the stability of anthocyanins is susceptible to oxidation, hydration, ultraviolet light, temperature, and enzyme degradation. These pigments also react with food components, such as ascorbic acid, sulfur dioxide, and sugars.[27]

The methods for the extraction of anthocyanins comprise solid−liquid extraction (SLE), supercritical fluid extraction (SFE), ultrasound-assisted extraction (UE), microwave-assisted extraction (ME), and pulsed electric field-assisted extraction (PEFE).[28] Selecting an appropriate extraction method is vital as it can affect the yield and purity of anthocyanins. For example, SLE, ME, UE, and PEFE are able to achieve a higher yield of anthocyanins than the traditional SLE. They are also advantageous for adopting water as the extraction solvent instead of hazardous organic solvents. In addition, SFE has been reported as a promising technique to extract anthocyanins in a time-efficient manner, but the crude extract often requires further purification due to the presence of impurities.

2.2. Betalains.

Betalains are a group of water-soluble, nitrogen-containing pigments that can be subdivided into two types: betacyanins and betaxanthins.[29] Betacyanins are red pigments found in prickly pears, red pitaya flesh, red beets, globe amaranth flowers, and red amaranths leaves, while betaxanthins exist as yellow pigments in yellow beets and cactus pears.[29,30] The stability of betalains is affected by environmental factors such as pH, enzymes, oxygen, temperature, and light.[30] This group of pigments possess the highest stability at pH 3−7, but start to degrade at higher pH levels causing a stark color change (Table 1). For instance, betacyanins exhibit an orange color at pH 8−9 and turn to yellow when the pH is increased to 12.[31] This is because betacyanins degrade into colorless cyclo-DOPA 5-O-(malonyl)-*β*-glucosides and yellow betalamic acids at an alkaline condition. The most used extraction technique for betalains is SLE. Traditionally, betalains are extracted by immersing the grounded plant materials in a solvent, either water or 20−50% (*v*/*v*) of methanol or ethanol solutions. However, SLE is time-consuming and has a low yield, thereby driving the need for more efficient extraction methods. For example, PEFE has

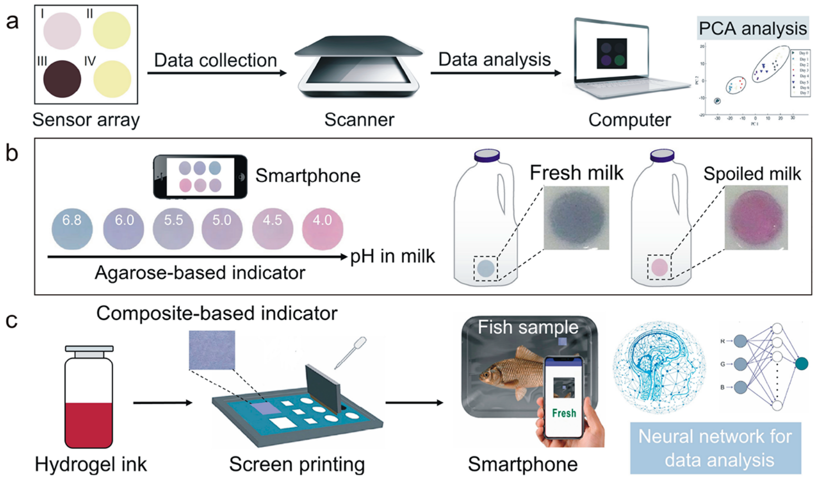

Figure 2. (a) Colorimetric sensor array constructed by printing four natural pigments on a reverse-phase silica gel.[52] Pigments were extracted from red radish (I), spinach (II), black rice (III), and winter jasmine (IV). Color signals were analyzed using principal component analysis (PCA). (b) Red cabbage anthocyanin-incorporated agarose film in conjunction with a smartphone for the detection of milk freshness.[62] (c) Colorimetric composite-based indicator for smartphone-assisted detection of fish freshness.[60] A hydrogel ink containing red cabbage anthocyanins, carboxymethyl chitosan, and oxidized sodium alginate was printed on a cellulose paper to form the indicator.

been deployed to promote the extraction efficiency of betalains by creating high degrees of permeabilization to expedite the mass transfer within the SLE system.[32] Moreover, ME can achieve a doubled efficiency for betalain extraction compared with SLE. The addition of ascorbic acid in ME can further ameliorate the yield of betalains by preventing the final products from degradation.[33]

2.3. Carotenoids. Carotenoids are oil-soluble compounds derived from plants, algae, yeasts, fungi, archaea, and eubacteria.[34] Most carotenoids own a C_{40} isoprenoid skeleton and can produce yellow, orange, or red colors. These pigments are classified into two groups: carotenes and xanthophylls.[35] Carotenes belong to hydrocarbons, including α-carotene, β-carotene, and lycopene. Xanthophylls encompass lutein, neoxanthin, β-cryptoxanthin, violaxanthin, and zeaxanthin, whose molecular structures are characteristic of oxygen-containing functional groups, such as hydroxy, aldehyde, carbonyl, epoxide, and carboxylic groups. The most abundant sources for carotenoids are fruits and vegetables, comprising carrot, apricot, mango, pumpkin, spinach, and broccoli. In addition, microorganism-derived carotenoids have grown popular in recent decades. Astaxanthin, for instance, can be produced by *Haematococcus pluviali*, *Phaffia rhodozyma*, and *Chlorella vulgaris*.[36,37] Carotenoids are prone to oxidation because of unsaturated double bonds in their backbone and disclose the highest stability under neutral conditions. The colorimetric response of carotenoids to pH originates from the instability of pigment molecules in acidic and alkaline conditions caused by ion pairing, protonation, and *cis*−*trans* isomerization.[38] Given the hydrophobic nature of carotenoids, extraction solvents for these pigments include hexane, acetone, and ethanol. Water removal is required to promote the extraction efficiency. For dehydration, lyophilization is more preferred than heat drying since high temperature can induce degradation and isomerization of pigments.[39] Soxhlet extraction is a conventional approach to extract carotenoids, but it is relatively time- and resource-consuming. Other extraction techniques include ME, UE, SFE, PEFE, enzyme-assisted extraction (EE), and accelerated solvent extraction (ASE).

2.4. Curcumin. Curcumin, a diferuloylmethane, is a lipid-soluble yellow pigment ubiquitously present in the rhizome of *Curcuma longa*. Curcumin is a prime curcuminoid and owns a seven-carbon backbone that is linked with an α,β-unsaturated β-diketone moisty and aromatic *o*-methoxy-phenolic group.[40] So far, this pigment has been applied in the food industry as an orange-yellow colorant and a bioactive compound owing to its antimicrobial and antioxidant activities.[41] Moreover, curcumin is able to alter the color in response to different pH levels.[42] Curcumin is most stable at pH 3−7, yet its color will change from yellow to orange due to deprotonation when the pH is increased to 8. With further increase in alkalinity, the pigment will lose more protons and turn into reddish brown. Curcumin possesses two tautomeric forms: the keto form prevalent under acidic and neutral conditions and the enol form dominant in an alkaline condition.[43] Curcumin is sensitive to oxidation and degradation under light and heat, which is often taken into consideration upon the selection of extraction methods. Techniques for curcumin extraction include Soxhlet extraction, ME, UE, EE, SFE, and ionic liquid-based extraction (ILE).[44] ILE has been reported as a promising method for curcumin extraction because ionic liquid, known as a "designer solvent", can be utilized to extract phytochemicals with tunable polarity, viscosity, and hydrophobicity.

2.5. Quinones. Quinones are water-soluble pigments found in algae, fungi, bacteria, flowering plants, and arthropods.[45] According to their molecular structures, quinones can be subdivided into three classes: benzoquinones, naphthoquinones, and anthraquinones.[46] Benzoquinones owning a single benzene ring with two carbonyl groups serve as a basic subunit of a variety of quinones. Particularly, naphthoquinones are benzoquinones attached with an aromatic ring, whereas anthraquinones own a para-benzoquinone structure linked with two aromatic rings at $C_{2,3}$ and $C_{5,6}$ positions, respectively. Quinones can produce different colors depending on their molecular structures, and some of them have been applied as pH sensitive dyes (Table 1). For example, alizarin is a typical anthraquinone extracted from madder plant roots and discloses a yellow color in its neutral state at pH 2−4.[47,48] The alizarin molecule switches to a monoanionic state at pH 5−7 because of resonance effect thereby turning into red, while in high alkalinity conditions (pH > 9), the color transits to purple attributed to the formation of dianionic molecules. Moreover, shikonin, a naturally occurring napthaquinone derived from the roots of *Lithospermum erythrorhizon*, is able to show distinct colors over a wide pH range: bright red at pH 2−5, bluish-red around pH 7, and blue at pH 9−12.[49] The colorimetric response of shikonin extracts to pH varies according to their plant sources and extraction approaches. Extraction methods for quinones include ME, UE, EE, SFE, reflux extraction, Soxhlet extraction, and sublimation-assisted extraction. Reflux extraction has been used as a conventional technique for quinone extraction due to its cost-efficiency and high yield.

2.6. Chlorophylls. Chlorophylls offer a green color in cyanobacteria, algae, and plants. Chlorophylls have a tetrapyrrole structure featuring a magnesium ion in the center of a chlorin and exist in nature in various forms, including chlorophyll a, b, c1, c2, and d, which differ in the pyrrole ring structure or side groups.[50] Major chlorophyll types in plants are a and b, with a methyl group and a formyl group in the C_7 position, respectively. When exposed to light, air, heat, or extreme pH, chlorophylls will display a different color mainly because the magnesium ion in the molecule is replaced by a hydrogen ion or the dissociation of functional groups occurs.[51] For instance, dark green chlorophylls can turn to olive green due to the formation of pheophytins under heat or high acidity, or change to bright green owing to the dissociation of phytol groups induced by enzyme or high alkalinity. However, the color differences are unappreciable to the naked eye. In this scenario, smart devices are deployed to assist in capturing images of pigments and digitalizing color data for further analysis. For example, Huang and colleagues employed chlorophylls extracted from spinach as a pH-responsive dye in a colorimetric sensor array for detecting pork spoilage.[52] Volatile compounds released by pork triggered dynamic color changes of the sensor, which were recorded in a RGB color mode by a scanner and then analyzed based on principal component analysis (Figure 2a). Chlorophylls have been extracted via SLE, EE, and SFE. Despite requiring the use of expensive equipment, SFE gains a higher popularity due to its advantages of high yield, low extraction temperature to mitigate degradation, and low environmental impact because of adopting nontoxic, nonflammable carbon dioxide as a green solvent.[53] Chlorophylls remain to be extracted using other advanced approaches, such as ME, UE, PEFE, and ASE.

3. BIODEGRADABLE FRESHNESS INDICATORS

This review addresses biodegradable freshness indicators that comprise two main components: (1) the halochromic pigment capable of showing a colorimetric response to food freshness and (2) the solid support that is biodegradable and immobilized with the pH-responsive pigment (Figure 1b). The sensitivity, reproducibility, stability, and response time of these freshness indicators are largely governed by the surface and structural properties of support materials. The solid matrix is often designed to provide an abundant surface area suitable for dye immobilization to ensure uniform color distribution. Three-dimensional (3D) structures, particularly porous and nanoscale structures, have been deployed to ease the interactions between the halochromic dye and target molecules. Due to their low environmental impact, biodegradable films have gained considerable attention for the preparation of novel sensing materials. In this section, freshness indicators that are supported with biopolymers, biodegradable synthetic polymers derived from biomass and petroleum, and biodegradable composites are discussed, and their applications in food and simulated models are summarized and listed in Table S1. Biodegradable freshness indicators are prepared based on different methods, including solution casting, thermocompression, extrusion, immersion, electrospinning, inkjet printing, coating, and screen-printing. Among them, the casting method is the most popular technique. This method involves the processes of incorporating the halochromic pigment into a film-making solution, casting the homogeneous mixture into a mold, and eventually evaporating the solvent to obtain an indicator film.[54,55] The thermocompression method is used to produce the indicator film by adding a mixture of the pigment and biodegradable polymers into a mold cavity and then pressing the blended material under a specific heat and pressure condition.[56] For the extrusion approach, the halochromic dye is added in a concentrated film-making solution or compounded with biodegradable polymers into a pellet. Afterward, the mixture is fed in an extruder, heated with gradual temperature rise, and extruded into a film.[57] Moreover, biodegradable freshness indicators can be made by coating or printing a pigment-containing layer on the surface of the solid support, immersing the solid support in a pigment solution followed by drying, or electrospinning fibrous structures incorporated with the halochromic dye.[58−62]

3.1. Polysaccharide-Based Indicators. *3.1.1. Starch.* Starch is a polysaccharide comprising glucose subunits connected through glycosidic bonds, owning a basic chemical formula of $(C_6H_{10}O_5)_n$. Major sources of starch include corn, cassava, potato, and arrowroot. Starches derived from various plants differ in the contents of amylopectin and amylose, thereby showing distinct functional and chemical properties.[63] In nature, starch exists in the form of granules with a diameter in the range of 0.1−200 μm. Starch granules are able to swell and gelatinize in heated water, and result in a solid film after being cast and dried in a flat plate.[64] To prepare starch-based freshness indicators, pH-responsive pigments are often mixed with the starch solution after gelatinization but before drying to allow sufficient interactions among pigment molecules and starch granules. After drying, halochromic dyes (e.g., anthocyanins) can cross-link with starch molecules via strong hydrogen bonds.[65] Plasticizers are incorporated in starch-based indicators to improve flexibility of solid films by promoting the mobility of starch molecules within film matrices. Most used plasticizers in freshness indicator films include glycerol and sorbitol.[56,66] It is worth mentioning that some halochromic pigments can also act as plasticizers. For example, Nogueira and colleagues modified an arrowroot starch-based film with blackberry pulp.[67] The pulp served two roles in the indictor film: a natural dye lending a red color and a plasticizer that significantly ameliorated the elongation at break of the film. The authors also reported that the indicator film was susceptible to intense food processing (e.g., sterilization) due to degradation of the halochromic dye in starch films, which limited its industrial use. Additionally, the hydrophilic nature of starch-based indicator films limits their applications in a humid environment. This challenge could be addressed by applying chemically modified starches or more hydrophobic components into the film matrices. Applications of starch-based freshness indicators have been demonstrated in different protein-rich food models, such as fish, shrimp, chicken, and pork (Table S1).

3.1.2. Cellulose. As the most abundant biopolymer on earth, cellulose is constituted of anhydro-D-glucose units joint by β-1,4-glycosidic bonds, and has a basic chemical formula of $(C_6H_{10}O_5)_n$. Commercial cellulose products primarily originate from wood and cotton, while cellulose produced by bacteria has been catching attention due to its natural nanofibrous structures and superior mechanical properties.[68,69] Cellulose films have been widely applied as solid supports for freshness indicators because of their low cost, highly porous structures to facilitate interactions between indicators and volatile compounds released by foods, and excellent mechanical performance derived from the highly ordered crystalline phase within cellulose fibrous structures and the hydrogen bonds induced by hydroxyl groups of cellulose.[70] However, the hydrophilic nature of cellulose has become a roadblock to the application of cellulose-based indicators in the foods high in moisture content. For example, Filipini and co-workers reported a halochromic film made of methylcellulose and anthocyanins extracted from Jambolão skin, which could degrade in seawater and soil within 2 and 15 d, respectively.[71] The film showed a good strength and flexibility but was highly soluble in water, thereby not suitable to have direct contact with meat and aquatic food products. To tackle this problem, freshness indicators have been prepared using cellulose acetate, which has a higher hydrophobicity than native cellulose and can be utilized to construct films with tailored porous structures by electrospinning. Electronspun films comprising cellulose acetate have been demonstrated to tightly bind with alizarin so that the leaching rate of alizarin from cellulose films can be controlled at a low level even in the foods with a high-water content.[58]

Selecting appropriate halochromic pigments for incorporation in cellulose films is paramount in ensuring notable colorimetric response of indicators. For example, carboxymethyl cellulose (CMC) films embedded with blueberry extract exhibited stronger color signals in response to freshness of raw chicken than CMC films added with red grape skin extract.[72] In addition, Ezati and colleagues developed two indicators by adding alizarin in a carboxymethyl cellulose film and a cellulose nanofiber film, respectively. The latter one reacted to ammonia, a volatile spoilage indicator, with a stronger color signal by providing abundant surface area to allow rapid binding with target molecules.[48] Noticeably, addition of natural pigments is a factor affecting mechanical properties of cellulose-based freshness indicators. For example, Dong and colleagues reported a cellulose film incorporated with naphthoquinones capable of monitoring freshness of raw shrimp and pork based upon colorimetric response.[59] Due to the presence of naphthoquinones, the indicator disclosed a higher tensile strength than a pure cellulose film and commercial plastic materials (polyethylene and polypropylene).

3.1.3. Chitin and Chitosan. Chitin, the second most abundant biopolymer after cellulose, is present prevalently in the exoskeletons of insects and crustaceans as well as cell walls in fungi. This biopolymer is built based on *N*-acetylglucosamine monomers polymerized through β-1,4-linkages. After partial deacetylation in an alkaline environment, chitin can transform into chitosan.[73] Although both chitosan and chitin are inexpensive, biodegradable, and antimicrobial packaging materials, chitosan is more advantageous in terms of mechanical performance and transparency.[74] Since preparation of chitosan films requires an acidic condition, the films are not suitable to incorporate halochromic pigments unstable or insoluble at low pH levels. In addition to enabling colorimetric response to pH, halochromic pigments serve multiple functions in chitin- and chitosan-based freshness indicators. For example, black chokeberry extract has been employed to improve the water-resistant capacity of chitosan films by inducing the formation of hydrogen bonds, electrostatic interactions, and possible ester linkages.[75] Incorporation of sweet potato extract offered chitosan films a higher thermal stability but decreased elongation at break.[76] Likewise, adding curcumin in chitosan films resulted in decreases in both tensile strength and elongation at break.[77] Besides, black eggplant extract and alizarin have been used to enhance the ultraviolet light barrier and antioxidant properties of chitosan films.[78,79] Applications of chitin- and chitosan-based freshness indicators have been demonstrated in a variety of food models, including meat, chicken, seafood, milk, and fresh produce. One future research direction for this group of freshness indicators is the search for novel halochromic pigments used in chitin and chitosan films. For instance, Wang and co-workers reported a novel chitosan-based indicator immobilized with black soybean seed coat extract that could signal distinguished color over the pH range of 3−10.[80]

3.1.4. Gums. Gums, also known as hydrocolloids, are water-soluble carbohydrate polymers that have been widely used in the food industry for the development of food structures. Gum films are characteristic of high tensile strength and thermal stability and serve as popular solid support for halochromic dyes because gums can bind firmly with natural dyes via hydrogen bonds and hydrophobic interactions. A vast range of gums have been used to fabricate biodegradable freshness indicators with great potential for commercialization.

Pectin is an anionic linear polysaccharide primarily constituted of D-galacturonic acid units linked via α-1,4-glycosidic bonds, with a small fraction of rhamnose units in the backbone and xylose, galactose, and arabinose in the side chains.[81] Commercial pectin is mainly extracted from apple pomace and citrus fruit peel and owns different levels of methyl esterification, which are a key factor affecting gelling properties of pectin products. Pectin can form into films with a high strength but poor flexibility. To mitigate the brittleness of pectin films, it is essential to add plasticizers in pectin-based freshness indicators, such as propylene glycol, glycerol, and sucrose,[82] while taking into consideration that plasticizers should not interfere with the interactions between halochromic dyes in pectin films and volatile organic compounds released by foods. Freshness indicators made of pectin have been validated in a wide range of high-protein foods, such as chicken, beef, fish, and shrimp. Their color signals have been well linked with the levels of food spoilage indicators, including total volatile basic nitrogen (TVB-N) and total viable count (TVC).[42,83] However, the indicators remain to be improved as the leakage of pigments from pectin film matrices has been observed.

Carrageenan, a sulfated linear polysaccharide derived from red seaweed, is composed of galactose and anhydrogalactose units connected by alternating α-1,3- and β-1,4-glycosidic bonds. Three types of carrageenans are often deployed to prepare biodegradable films, including iota (τ)-, lambda (λ)-, and kappa (κ)-carrageenans. Among them, κ-carrageenan possesses the highest tensile strength.[84] To increase the flexibility of carrageenan film, the film matrix is often incorporated with plasticizers or supplemented with stronger polymers. Halochromic pigments also play a role in modifying mechanical properties of carrageenan films. For example, Liu and co-workers constructed a halochromic indicator consisting of κ-carrageenan and curcumin to determine pork and shrimp spoilage.[85] Curcumin rendered the film not only a higher tensile strength and thermal stability, but also the ability to display stark color changes in alkaline conditions (pH 8−10). Another study reported a κ-carrageenan film embedded with anthocyanins from *Lycium ruthenicum*, whose presence decreased the strength and stiffness of the gum film but enabled its colorimetric reaction to freshness of milk and aquatic products.[86]

Gellan gum has been reported to act as a suitable solid support for purple sweet potato extract.[87] Anthocyanins in the extract endowed the gum film with a higher hydrophobicity and tensile strength, weaker swelling properties, and the ability to examine the growth of *Escherichia coli* cells according to color signals. When triggered by volatile amines released by the bacteria, the indicator exhibited a color transition pattern from purple to blue to yellow-green, implying its potential to monitor microbial spoilage. Moreover, Taghinia and colleagues fabricated a novel freshness indicator by incorporating curcumin into a film made of *Lallemantia iberica* seed gum.[55] In a plastic package added with shrimp, the indicator showed a growing a^* value (revealing redness) over 5 d, which was elicited by volatile nitrogenous compounds released by shrimp samples. In a previous study, Liang and co-workers demonstrated the use of *Artemisia sphaerocephala* Krasch Gum (ASKG) films as food packaging materials attributed to their good mechanical performance.[88] Afterward, they developed an ASKG-based indicator loaded with anthocyanins from red cabbage.[89] The anthocyanins showed a plasticizing effect in the film matrix, leading to a significant increase in elongation at break when pigment content was over 5% (w/w). This indicator displayed appreciable color changes when placed in different buffer solutions (pH 3−10) and in a humidity-modified container filled with ammonia. Other gums, such as locust bean gum, can also serve as the solid support to construct freshness indicators.

3.2. Protein-Based Indicators. Protein films possess good mechanical properties analogous to polysaccharide films but are more resistant to moisture. Plasticizers are often added in protein films to increase flexibility and decrease brittleness. The formation of protein films involves noncovalent bonds, such as electrostatic interactions, hydrogen bonds, hydrophobic interactions, and van der Waals forces. In some scenarios, cross-linking via covalent bonds is induced in the film matrix by physical or chemical approaches to achieve better mechanical performance. So far, protein films have been prepared by animal proteins (e.g., whey protein, casein, egg white protein, and gelatin) and plant proteins (e.g., corn zein, soy protein, peanut protein, and wheat gluten protein).[90,91] In the past five years, gelatin has been mostly used to fabricate protein-based freshness indicators since the material is inexpensive, water-soluble, and can result in films with desirable mechanical properties and transparency. For example, Musso and colleagues fabricated two types of curcumin-incorporated gelatin films using a casting method.[92] Film-forming solutions containing gelatin and curcumin were prepared in two solvents, either water or water/ethanol mixture. After drying, the latter one resulted in a gelatin film with a stronger color signal because of the higher solubility of curcumin in water/ethanol mixture than water. Similar results were reported by these authors in another study. Two types of gelatin films modified with red cabbage extract were synthesized using water and water/ethanol mixture as solvents, respectively.[93] The latter one displayed a more intense color when dropped with either highly acidic or alkaline solutions. In addition, Liu and co-workers constructed a freshness indicator composed of fish gelatin and haskap berry extract.[94] The extract was well compatible with the film matrix thanks to the formation of intermolecular hydrogen bonds among the hydroxyl groups of anthocyanins and the amino and hydroxyl groups of gelatin molecules. Gelatin-based indicators containing different concentrations of extract (0.5%−3%, w/w) were prepared, and they all showed appreciable colorimetric responses after being immersed in different buffer solutions (pH 3−12). However, in a shrimp model, only the film added with 1% (w/w) extract was able to display an evident color transition from brown to green when the TVB-N level of samples hit the limit of shrimp spoilage.

3.3. Polyhydroxyalkanoate (PHA)-Based Indicators. PHAs, a group of polyesters synthesized by microorganisms, have captured special attention in the packaging industry because they are biodegradable, sustainable, and can be used to develop bioplastics alternative to petroleum-derived plastics.[95] Many PHAs have been reported, including poly(3-hydroxyoctanoate) (PHO), polyhydroxyhexanoate (PHH), poly(3-hydroxybutyrate) (PHB), and polyhydroxyvalerate (PHV). Nevertheless, PHA-based freshness indicators have not yet been extensively studied. This is because preparation of PHA films often requires the use of expensive equipment, such as extruders at laboratory or industrial scales. The extrusion process involves high temperature that can cause degradation of natural pigments. Moreover, mechanical prosperities of PHA films remain to be ameliorated compared with commercial plastics.[96] In a recent study, Latos-Brozio and Masek produced PHB-based indicator films incorporated with curcumin, β-carotene, and chlorophyll, respectively.[57] The indicator films were manufactured by using a laboratory extruder with a chamber temperature of 160 °C, and could signal dynamic color changes over 12 d when exposed to ultraviolet light and high temperature as the key factors causing food spoilage. However, colorimetric response of the indicators to pH was not assessed.

3.4. Synthetic Polymer-Based Indicators. Synthetic polymers used for developing biodegradable indicators are grouped into two types: biodegradable biomass-derived and petroleum-derived polymers. The former ones are synthesized based on renewable raw materials. For example, synthesis of polylactic acid (PLA) entails polymerization of lactic acids that are produced through microbial fermentation of the biomass derived from corn, potato, and sugar cane.[97] The latter ones are synthesized based on petrochemicals and include PVA, PBAT, PBSA, PBS, PGA, and PCL. For example, PVA is prepared by hydrolysis of polyvinyl acetate, whose preparation involves polymerization of vinyl acetate that is made from the reaction of ethylene (a petrochemical) with acetic acid and oxygen. In the recent years, studies on synthetic polymer-based freshness indicators have shown an increasing trend, with PVA-based indicators gaining the highest popularity. Preparation of novel indicators by other biodegradable synthetic polymers remains virtually unexplored. Although PVA is advantageous in terms of transparency and mechanical properties compared

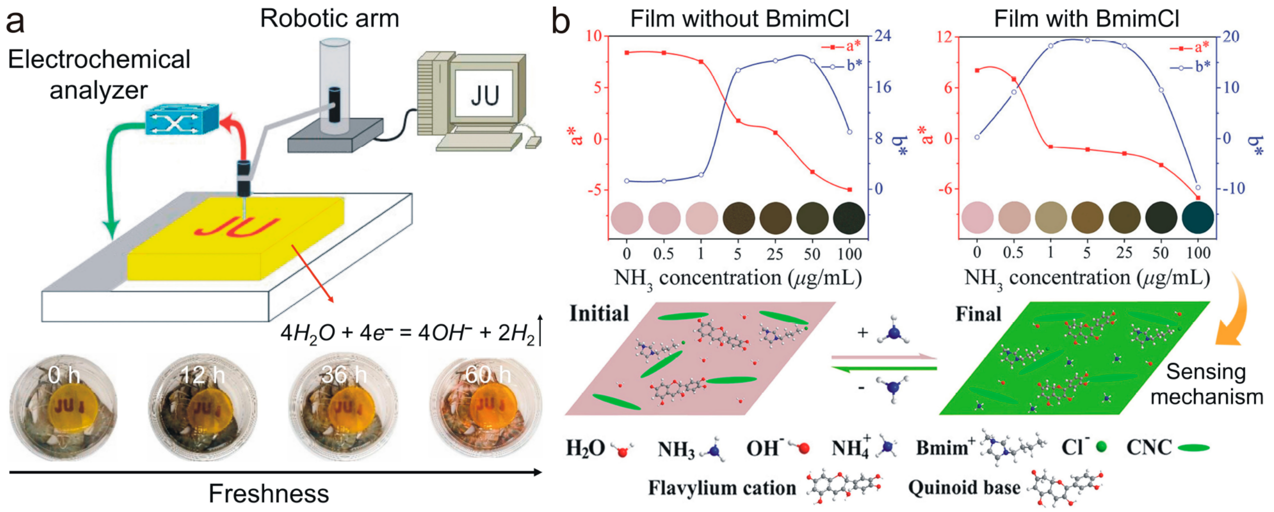

Figure 3. (a) Freshness indicator printed with programmed information through an electrochemical printing device.[113] The indicator is a composite comprising poly(vinyl alcohol), agar, and curcumin. (b) Colorimetric response of composite-based indicators modified with and without ionic liquid to ammonia and the sensing mechanism.[120] 1-Butyl-3-methylimidazolium chloride (BmimCl) was used as the ionic liquid to modify the composite film made of cellulose nanocrystals, hydroxypropyl guar, and anthocyanins.

with biopolymers such as proteins and polysaccharides, this polymer has a higher material cost, lower biodegradability, and limitations for use in moderately acidic conditions.[98] For instance, Weston and colleagues constructed two pH-responsive indicators by incorporating anthocyanins in a PVA film and an agarose film, respectively, followed by determining their colorimetric response to lactic acid in the pH range of 4.0−6.8.[62] The agarose-based indicator displayed stronger color signals than the PVA-based indicator and therefore was selected to detect milk freshness in conjunction with a smart device for data collection and analysis (Figure 2b). The PVA-based indicator showed poorer sensitivity because amorphous moieties of PVA hydrated in aqueous solution leading to partial ionization of hydroxyl and acetate groups, which caused a localized pH transition in the film to the range of 5−6. The upgraded pH was close to the pH created by lactic acid and thus interfered with the colorimetric response of indicator films. It is noteworthy that the high water solubility of PVA allows blending PVA with biopolymers in aqueous film-forming solutions to produce strong and transparent composite films for halochromic dye immobilization. Examples of PVA-based composite freshness indicators are described in the following subsection 3.5. In addition, PLA as a generally recognized as safe (GRAS) material approved by FDA has great potential for use as a solid support to load halochromic dye. For example, PLA films incorporated with curcumin, β-carotene, and chlorophyll, respectively, were developed as indicators to determine exposure time of packages to ultraviolet light and high temperature. Nevertheless, their applications for the detection of food freshness have not been reported yet.[57] In another study, Ghorbani and colleagues constructed an anthocyanins-incorporated PLA film whose application as a freshness indicator was validated in four food models, including fish roe, raw shrimp, ground beef, and raw chicken.[99] Two additives were used in this film matrix to enhance sensing performance: polyethylene glycol as an opening agent to offer the PLA film a porous surface structure for promoting the diffusion of amine gases with the film; calcium bentonite that contributed to the uniform distribution of anthocyanins in the film matrix. This indicator had a remarkable water-resistant capability and did not show significant leakage of pigments when immersed in water for up to 24 h, indicating its potential use in high-moisture food products.

3.5. Biodegradable Composite Films as Indicators.

Desirable solid supports for freshness indicators are expected to own good mechanical properties, water-resistant capability, compatibility with halochromic dye, and low production cost. To meet these needs, two or more film-forming constituents are often incorporated into one film matrix to generate a composite film that possesses superior physicochemical properties and/or extra functions compared with films made of one single polymer alone. Composite films for the application in freshness indicators can be prepared with different biopolymers, synthetic polymers, or combination of at least one biopolymer and synthetic polymer.

Composite films made of proteins and polysaccharides have been applied as solid supports in a variety of freshness indicators. A study reported by Hu and colleagues introduced a quaternary ammonium chitosan/fish gelatin film incorporated with amaranth extract for the determination of shrimp freshness.[100] Quaternary ammonium chitosan offered hydroxyl groups and positively charged trimethylammonium groups that allowed the formation of hydrogen bonds and electrostatic interactions with gelatin, therefore resulting in a strong composite film. The extract rich in betalains acted as a plasticizer in the film resulting in a significant increase in elongation at break. Roy and Rhim reported κ-carrageenan/gelatin-based films showing multiple functions for the use in intelligent food packaging.[101] Main constituents in the films played different roles: κ-carrageenan and gelatin rendering smooth surface and compact structures as solid supports, shikonin incorporated as a pH-responsive dye, and propolis allowing extra antimicrobial and antioxidant effects. The resulting films were harnessed to detect milk spoilage, exhibiting visual color change in response to the decrease in pH as milk spoiled. Interestingly, Chayavanich and co-workers developed a smartphone-coupled freshness indicator for shrimp and chicken.[102] The starch/gelatin composite modified with red radish extract showed dynamic color changes during food storage, with a smartphone that worked in tandem with the indicators by capturing film color, digitalizing data with an image processing software, and linking color signals to different freshness levels. In another study, an anthocyanin-loaded composite comprised of carboxymethyl chitosan and oxidized sodium alginate was developed to detect freshness of fish products (Figure 2c).[60] Natural pigments and film-forming components were dispersed in silica sol to generate a hydrogel ink, which was then printed on a cellulose paper to obtain the indicator film. After the film was installed in the inner compartment of a plastic container filled with raw fish fillets, nitrogen-containing compounds released from fish started to accumulate in the container and gradually triggered different color patterns of the indicator, which were imaged by a smartphone. The color signals displayed by the film were then analyzed using a supervised machine learning algorithm via back-propagation neural network and then linked to three levels of fish freshness: fresh, less fresh, and spoiled.

Biopolymers have been blended with synthetic polymers to generate strong, biodegradable composites for halochromic dye immobilization. For example, PVA has been added in starch films and chitosan films to develop different composites for use as halochromic indicators.[31,103−108] Incorporation of PVA endows composite films with a stronger tensile strength than films made of starch or chitosan alone. Compared with PVA/starch composite, PVA/chitosan composite is stronger but less suitable for the fabrication of freshness indicators because the presence of acetic acid in the film matrix mitigates color response of halochromic dye to volatile compounds released by protein-rich foods. In addition, halochromic indicators have been developed based upon novel composite film matrices that mix PVA with gelatin, tara gum, glucomannan, okra mucilage, and agar, respectively.[109−113] For example, the addition of okra mucilage and rose anthocyanins is able to lend PVA films a lower crystallinity but higher tensile strength and Young's modulus due to new hydrogen bonds formed among film components.[111] Application of the indicator in a shrimp model was demonstrated, with the film showing distinguished color change over 32 h along with the rise in TVB-N content in shrimp samples. Moreover, it is noteworthy that an ink-free printing technology has been applied to print information on a PVA/agar composite added with curcumin (Figure 3a).[113] An electrochemical printing device is equipped with a robotic arm holding a cathode that can generate hydroxide ions on the surface of the indicator film through physical contact. The printed area with a change in pH discloses a distinct color on the film. Both the indicator film and electrochemically printed information can change color over time in a seafood model but display significantly different color signals.

Nanomaterials are materials with at least one dimension at nanoscale (1−100 nm) and have been added in composites to generate nanocomposites.[114] Biodegradable nanocomposites are used in freshness indicators aiming to offer strong solid supports, stabilize natural pigments, enhance color signals, promote halochromic dye distribution, and expedite the response of indicators to food freshness through designed structures. Nanomaterials incorporated in freshness indicators include nanochitin, nanochitosan, nanocellulose, and metal and metal oxide nanoparticles. Functions of nanomaterials vary in different film matrices. For example, chitosan nanofibers (diameter, 20−50 nm) have been used in an anthocyanin-incorporated methyl cellulose film to enhance mechanical resistance and improve colorimetric response in high-moisture foods.[115] Titanium dioxide nanoparticles (average diameter, 10 nm) have been employed in a chitosan-based film immobilized with apple pomace extract to shorten colorimetric response time and enhance color signals for the detection of fish freshness; also, they can function as antimicrobial agents and ethylene scavengers in smart packaging systems.[116,117] Oxidized chitin nanocrystals (diameter, 10−15 nm) could be filled in an anthocyanin-added chitosan film to ameliorate tensile strength and modify optical properties in the wavelength range of visible light.[118,119] Moreover, cellulose nanocrystals have been added into a hydroxypropyl guar-based film containing anthocyanins to impart a stronger mechanical strength.[120] Interestingly, 1-butyl-3-methylimidazolium chloride (BmimCl), an ionic liquid, is also added in the nanocomposite showing a plasticizing effect and allowing the indicator to disclose more distinct colors in response to ammonia released from raw shrimp during storage (Figure 3b). The mechanism underlying the color variation is explained by the red shift of wavelength of the indicator film, which is caused by the aromatic ring structure with p−π conjugation in BmimCl and the linkage of anthocyanins to chloride ions. It is worth of mentioning that fluorescent nanomaterials, such as carbon dots (CDs), have been harnessed to develop fluorescent freshness indicators. For example, a freshness indicator was prepared by modifying the surface of a paper strip with a mixture of two fluorescent colorants, including blue CDs derived from o-phthalaldehyde and a red fluorescent dye (1-aminoanthraquinone).[121] The fluorescent indicator was able to respond to different concentrations of histamine (a freshness indictor of fish) with distinct colors based upon the interactions between aldehyde groups on CDs and the amino group on histamine. A portable sensing platform constructed by combining the indicator with a smartphone was used to determine the freshness levels of fish products under ultraviolet light. In another study, phthalic acid and triethylenediamine were used to prepare CDs that can be added in milk to detect freshness relying on the change in fluorescence intensity.[122] The freshness of milk decreased with an increase in acidity, which could reduce the fluorescence intensity of CDs due to the protonation of carboxylic groups. Although fluorescent nanomaterials have been used to develop novel freshness indicators, their applications in the food industry are limited due to their uncertain toxicity. The toxicity of most fluorescent nanomaterials is unknown and remains to be explored. It is possible that toxic fluorescent nanomaterials incorporated in intelligent packaging may leach into food products. Therefore, it is highly recommended that the toxicity of fluorescent nanomaterials should be taken into consideration upon the development of freshness indicators. Besides, a nanocomplex constructed by chitosan hydrochloride and carboxymethyl chitosan was used to encapsulate anthocyanins to raise their color stability in freshness indicator films.[123] It is important to include appropriate film-forming polymers in the composites because they could impact the light barrier properties, mechanical performance, pH-sensitivity, and gas-sensitivity of freshness indicator films.[124]

4. CHALLENGES AND FUTURE PERSPECTIVES

Biodegradable halochromic indicators are embedded in intelligent packaging to monitor food freshness in a real-time manner, with the goals of reducing food waste produced due to a predetermined expiration date, informing consumers of food safety, and boosting the sustainability of current food systems. Halochromic pigments used in the indicators are nontoxic and mainly plant-derived but susceptible to intense food processing because of their poor stability when exposed to oxidation, hydration, ultraviolet light, high temperature, and enzymes in foods. Biodegradable solid supports have a low environmental impact and are vital in ensuring the sensitivity, reproducibility, and stability of freshness indicators. Biodegradable composite films are more advantageous as solid supports for halochromic indicators than films made of one single biopolymer or synthetic polymer alone, because of their superior mechanical performance, high stability in high-moisture foods, strong interactions with natural pigments for immobilization, modulatory effect on color signal, and affordable production cost. However, developing biodegradable halochromic indicators for commercial use still faces significant challenges. First, although biodegradable freshness indicators have been validated in a vast array of food models, they may experience dye leakage via direct contact with foods, which could mitigate their sensing performance. If the leakage occurs, the halochromic dyes that migrate from indicators into food products will be considered as indirect food additives whose presence in foods is strictly regulated by government agencies for safety concerns. Second, most reported indicators have been prepared at the laboratory scale using the casting method due to convenience and low production cost of this method. It is essential to develop novel freshness indicators by extrusion and thermocompression methods, which are more suitable for larger scale production. Third, consumer attitudes to the use of colorimetric freshness indicators in intelligent food packaging remain largely obscure. Benefits of these products have not been well promoted. Fourth, current research only focuses on investigating colorimetric response of freshness indicators under simulated storage conditions, but their performance along the food supply chain has not been reported yet. Fifth, the stability of halochromic dyes in indicator films remains to be improved since most natural dyes can react with food components and are susceptible to oxidation, hydration, ultraviolet light, temperature, and enzyme degradation.

Future studies on biodegradable freshness indicators are suggested to focus on four perspectives. First, robust freshness indicators with remarkable sensing performance should be developed by adopting nanotechnology. Particularly, biodegradable nanocomposites will be applied as solid supports for freshness indicators to offer tailored structures easing the interactions of halochromic dyes with volatile compounds generated from food products. CDs owning stable fluorescence and resistance to intense food processing will be utilized as halochromic fluorescent dyes for fabrication of freshness indicators. Second, halochromic indicators should be coupled with smart devices such as smartphones for data collection and analysis, thereby preventing consumers from misestimating the signal from colorimetric indicators by the naked eye. Third, sensor arrays based on multiple freshness indicators should be applied in intelligent packaging to provide more accurate information on food freshness, but their color signals need to be analyzed based upon machine learning algorithms that can link the color response of indicators to different food freshness levels. Fourth, more advanced technologies, such as electrospinning and 3D-printing, should be leveraged to manufacture the freshness indicator with a desirable size and shape that allow the material to be well embedded in food packaging. For example, the halochromic dye can be incorporated in a polymer solution and electrospun into a film with a highly fibrous structure, or the dye can be added in a polymeric ink and 3D-printed into a sensor with a tailored size and shape. Finally, freshness indicators installed in intelligent packaging can be integrated with the Internet of Things and cloud computing technologies. Images of indicators will be read by a smart device that can send the data to a cloud server for further data analysis and management so that the industry will be able to track food freshness along the supply chain and promote food system sustainability in the long term.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsfoodscitech.2c00372.

> Applications and colorimetric responses of biodegradable freshness indicators in Table S1 (PDF)

AUTHOR INFORMATION

Corresponding Author

Xiaonan Lu − *Department of Food Science and Agricultural Chemistry, Faculty of Agricultural and Environmental Sciences, McGill University, Sainte-Anne-de-Bellevue, Quebec H9X 3 V9, Canada;* orcid.org/0000-0003-0254-0345; Email: xiaonan.lu@mcgill.ca

Authors

Zhilong Yu − *Department of Food Science and Agricultural Chemistry, Faculty of Agricultural and Environmental Sciences, McGill University, Sainte-Anne-de-Bellevue, Quebec H9X 3 V9, Canada*

Valeriya Boyarkina − *Department of Food Science and Agricultural Chemistry, Faculty of Agricultural and Environmental Sciences, McGill University, Sainte-Anne-de-Bellevue, Quebec H9X 3 V9, Canada*

Ziyu Liao − *Department of Food Science and Agricultural Chemistry, Faculty of Agricultural and Environmental Sciences, McGill University, Sainte-Anne-de-Bellevue, Quebec H9X 3 V9, Canada*

Mengshi Lin − *Food Science Program, Division of Food, Nutrition & Exercise Sciences, University of Missouri, Columbia, Missouri 65211, United States;* orcid.org/0000-0002-6967-2257

Weicai Zeng − *Antioxidant Polyphenols Team, Department of Food Engineering, Sichuan University, Chengdu, Sichuan 610065, People's Republic of China;* orcid.org/0000-0002-5819-4333

Complete contact information is available at: https://pubs.acs.org/10.1021/acsfoodscitech.2c00372

Author Contributions

[#]Z.Y. and V.B. contributed equally to writing the article. Z.L. summarized the references and made Table S1. X.L., M.L., and W.Z. conducted critical revision of the article.

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REFERENCES

(1) World Food Programme (WFP). Causes and Solutions, Hunger. https://www.wfp.org/zero-hunger (accessed 2022−06−05).

(2) FAO, IFAD, UNICEF, WFP and WHO. The State of Food Security and Nutrition in the World 2020. Transforming Food Systems for Affordable Healthy Diets; FAO, 2020.

(3) UNEP. Food Loss and Waste Must Be Reduced for Greater Food Security and Environmental Sustainability. https://www.unep.org/news-and-stories/press-release/food-loss-and-waste-must-be-reduced-greater-food-security-and (accessed 2020−09−29).

(4) FAO. Food Wastage Footprint. Impacts on Natural Resources; FAO, 2013.

(5) USDA. USDA and EPA Join With Private Sector, Charitable Organizations to Set Nation's First Food Waste Reduction Goals. https://www.usda.gov/media/press-releases/2015/09/16/usda-and-epa-join-private-sector-charitable-organizations-set (accessed 2015−09−16).

(6) FAO. Food Loss and Waste Database. https://www.fao.org/platform-food-loss-waste/flw-data/en/ (accessed 2022−06−05).

(7) Han, J. H. *Innovations in Food Packaging*; Elsevier, 2005.

(8) Gunders, D. *Wasted: How America Is Losing up to 40% of Its Food From Farm to Fork to Landfill*; Natural Resources Defense Council, 2017.

(9) WHO. WHO Estimates of the Global Burden of Foodborne Diseases; World Health Organization, 2015.

(10) Kerry, J.; Butler, P. *Smart Packaging Technologies for Fast Moving Consumer Goods*; John Wiley & Sons, 2008.

(11) Brody, A. L.; Strupinsky, E. P.; Kline, L. R. *Active Packaging for Food Applications*; CRC Press, 2001.

(12) Yam, K. L.; Lee, D. S. *Emerging Food Packaging Technologies: Principles and Practice*; Woodhead Publishing, 2012.

(13) Yousefi, H.; Su, H. M.; Imani, S. M.; Alkhaldi, K.; Filipe, C. D. M.; Didar, T. F. Intelligent food packaging: A review of smart sensing technologies for monitoring food quality. *ACS Sens.* **2019**, *4*, 808−821.

(14) Environment and Climate Change Canada (ECCC). Plastic Challenge: Food Packaging. https://www.ic.gc.ca/eic/site/101.nsf/eng/00036.html (accessed 2020−02−25).

(15) Kumar, M.; Chen, H.; Sarsaiya, S.; Qin, S.; Liu, H.; Awasthi, M. K.; Kumar, S.; Singh, L.; Zhang, Z.; Bolan, N. S.; Pandey, A.; Varjani, S.; Taherzadeh, M. J. Current research trends on micro- and nano-plastics as an emerging threat to global environment: a review. *J. Hazard. Mater.* **2021**, *409*, 124967.

(16) Salgado, P. R.; Di Giorgio, L.; Musso, Y. S.; Mauri, A. N. Recent developments in smart food packaging focused on biobased and biodegradable polymers. *Front. Sustain. Food Syst.* **2021**, *5*, 630393.

(17) Iwata, T. Biodegradable and bio-based polymers: future prospects of eco-friendly plastics. *Angew. Chem., Int. Ed.* **2015**, *54*, 3210−3215.

(18) Gänzle, M. G. Lactic metabolism revisited: metabolism of lactic acid bacteria in food fermentations and food spoilage. *Curr. Opin. Food Sci.* **2015**, *2*, 106−117.

(19) Rukchon, C.; Nopwinyuwong, A.; Trevanich, S.; Jinkarn, T.; Suppakul, P. Development of a food spoilage indicator for monitoring freshness of skinless chicken breast. *Talanta* **2014**, *130*, 547−554.

(20) Matindoust, S.; Farzi, A.; Baghaei Nejad, M.; Shahrokh Abadi, M. H.; Zou, Z.; Zheng, L.-R. Ammonia gas sensor based on flexible polyaniline films for rapid detection of spoilage in protein-rich foods. *J. Mater. Sci. Mater.* **2017**, *28*, 7760−7768.

(21) Simpson, B. K.; Benjakul, S.; Klomklao, S. Natural Food Pigments. In *Food Biochemistry and Food Processing*; John Wiley & Sons, 2012; pp 704−722.

(22) Alizadeh-Sani, M.; Mohammadian, E.; Rhim, J. W.; Jafari, S. M. pH-sensitive (halochromic) smart packaging films based on natural food colorants for the monitoring of food quality and safety. *Trends Food Sci. Technol.* **2020**, *105*, 93−144.

(23) Khoo, H. E.; Azlan, A.; Tang, S. T.; Lim, S. M. Anthocyanidins and anthocyanins: colored pigments as food, pharmaceutical ingredients, and the potential health benefits. *Food Nutr. Res.* **2017**, *61*, 1361779.

(24) Cortez, R.; Luna-Vital, D. A.; Margulis, D.; Gonzalez de Mejia, E. Natural pigments: stabilization methods of anthocyanins for food applications. *Compr. Rev. Food Sci. Food Saf.* **2017**, *16*, 180−198.

(25) Gould, K.; Davies, K.; Winefield, C. *Anthocyanins: Biosynthesis Functions, and Applications*; Springer Science & Business Media, 2008.

(26) Habtemariam, S. *Medicinal Foods as Potential Therapies for Type-2 Diabetes and Associated Diseases: The Chemical and Pharmacological Basis of Their Action*; Academic Press, 2019.

(27) Kammerer, D. R. Anthocyanins. In *Handbook on Natural Pigments in Food and Beverages: Industrial Applications for Improving Food Color*; Woodhead Publishing, 2016; pp 61−80.

(28) Silva, S.; Costa, E. M.; Calhau, C.; Morais, R. M.; Pintado, M. E. Anthocyanin extraction from plant tissues: a review. *Crit. Rev. Food Sci. Nutr.* **2017**, *57*, 3072−3083.

(29) Hussain, E. A.; Sadiq, Z.; Zia-Ul-Haq, M. *Betalains: Biomolecular Aspects*; Springer International Publishing, 2018.

(30) Khan, M. I. Stabilization of betalains: a review. *Food Chem.* **2016**, *197*, 1280−1285.

(31) Qin, Y.; Liu, Y.; Zhang, X.; Liu, J. Development of active and intelligent packaging by incorporating betalains from red pitaya (*Hylocereus polyrhizus*) peel into starch/polyvinyl alcohol films. *Food Hydrocoll.* **2020**, *100*, 105410.

(32) Chalermchat, Y.; Fincan, M.; Dejmek, P. Pulsed electric field treatment for solid-liquid extraction of red beetroot pigment: mathematical modelling of mass transfer. *J. Food Eng.* **2004**, *64*, 229−236.

(33) Cardoso-Ugarte, G. A.; Sosa-Morales, M. E.; Ballard, T.; Liceaga, A.; San Martín-González, M. F. Microwave-assisted extraction of betalains from red beet (Beta vulgaris). *LWT-Food Sci. Technol.* **2014**, *59*, 276−282, DOI: 10.1016/j.lwt.2014.05.025.

(34) Britton, G.; Liaaen-Jensen, S.; Pfander, H. *Carotenoids: Handbook*; Springer Science & Business Media, 2004.

(35) Rao, A. V.; Rao, L. G. Carotenoids and human health. *Pharmacol. Res.* **2007**, *55*, 207−216.

(36) Kim, D. Y.; Vijayan, D.; Praveenkumar, R.; Han, J. I.; Lee, K.; Park, J. Y.; Chang, W. S.; Lee, J. S.; Oh, Y. K. Cell-wall disruption and lipid/astaxanthin extraction from microalgae: *Chlorella* and *Haematococcus*. *Bioresour. Technol.* **2016**, *199*, 300−310.

(37) Yin, C.; Yang, S.; Liu, X.; Yan, H. Efficient extraction of astaxanthin from *Phaffia rhodozyma* with polar and non-polar solvents after acid washing. *Chin. J. Chem. Eng.* **2013**, *21*, 776−780.

(38) Maoka, T. Carotenoids as natural functional pigments. *J. Nat. Med.* **2020**, *74*, 1−16.

(39) Saini, R. K.; Keum, Y. S. Carotenoid extraction methods: a review of recent developments. *Food Chem.* **2018**, *240*, 90−103.

(40) Farooqui, T.; Farooqui, A. A. Curcumin: historical background, chemistry, pharmacological action, and potential therapeutic value. In *Curcumin for Neurological and Psychiatric Disorders: Neurochemical and Pharmacological Properties*; Academic Press, 2019; pp 23−44.

(41) Rafiee, Z.; Nejatian, M.; Daeihamed, M.; Jafari, S. M. Application of curcumin-loaded nanocarriers for food, drug and cosmetic purposes. *Trends Food Sci. Technol.* **2019**, *88*, 445−458.

(42) Ezati, P.; Rhim, J. W. pH-responsive pectin-based multifunctional films incorporated with curcumin and sulfur nanoparticles. *Carbohydr. Polym.* **2020**, *230*, 115638.

(43) Sahne, F.; Mohammadi, M.; Najafpour, G. D.; Moghadamnia, A. A. Enzyme-assisted ionic liquid extraction of bioactive compound from turmeric (*Curcuma longa* L.): isolation, purification and analysis of curcumin. *Ind. Crops Prod.* **2017**, *95*, 686−694.

(44) Jiang, T.; Ghosh, R.; Charcosset, C. Extraction, purification and applications of curcumin from plant materials-a comprehensive review. *Trends Food Sci. Technol.* **2021**, *112*, 419−430.

(45) Land, E. J.; Ramsden, C. A.; Riley, P. A. Quinone chemistry and melanogenesis. *Meth. Enzymol.* **2004**, *378*, 88−109.

(46) Demir, Y. Naphthoquinones, benzoquinones, and anthraquinones: molecular docking, ADME and inhibition studies on human

serum paraoxonase-1 associated with cardiovascular diseases. *Drug Dev. Res.* **2020**, *81*, 628−636.

(47) Nawrocka, A.; Krawczyk, S. Electronic excited state of alizarin dye adsorbed on TiO_2 nanoparticles: a study by electroabsorption (stark effect) spectroscopy. *J. Phys. Chem. C* **2008**, *112*, 10233−10241.

(48) Ezati, P.; Rhim, J. W.; Moradi, M.; Tajik, H.; Molaei, R. CMC and CNF-based alizarin incorporated reversible pH-responsive color indicator films. *Carbohydr. Polym.* **2020**, *246*, 116614.

(49) Ezati, P.; Bang, Y. J.; Rhim, J. W. Preparation of a shikonin-based pH-sensitive color indicator for monitoring the freshness of fish and pork. *Food Chem.* **2021**, *337*, 127995.

(50) Allakhverdiev, S. I.; Kreslavski, V. D.; Zharmukhamedov, S. K.; Voloshin, R. A.; Korol'Kova, D. V.; Tomo, T.; Shen, J. R. Chlorophylls *d* and *f* and their role in primary photosynthetic processes of cyanobacteria. *Biochem.* **2016**, *81*, 201−212.

(51) Queiroz Zepka, L.; Jacob-Lopes, E.; Roca, M. Catabolism and bioactive properties of chlorophylls. *Curr. Opin. Food Sci.* **2019**, *26*, 94−100.

(52) Huang, X. W.; Zou, X. B.; Shi, J. Y.; Guo, Y.; Zhao, J. W.; Zhang, J.; Hao, L. Determination of pork spoilage by colorimetric gas sensor array based on natural pigments. *Food Chem.* **2014**, *145*, 549−554.

(53) Kwartiningsih, E.; Ramadhani, A. N.; Putri, N. G. A.; Damara, V. C. J. Chlorophyll extraction methods review and chlorophyll stability of katuk leaves (*Sauropus androgynous*). *J. Phys. Conf.* **2021**, *1858*, 012015.

(54) Huang, S.; Xiong, Y.; Zou, Y.; Dong, Q.; Ding, F.; Liu, X.; Li, H. A novel colorimetric indicator based on agar incorporated with *Arnebia euchroma* root extracts for monitoring fish freshness. *Food Hydrocoll.* **2019**, *90*, 198−205.

(55) Taghinia, P.; Abdolshahi, A.; Sedaghati, S.; Shokrollahi, B. Smart edible films based on mucilage of *lallemantia Iberica* seed incorporated with curcumin for freshness monitoring. *Food Sci. Nutr.* **2021**, *9*, 1222−1231.

(56) Andretta, R.; Luchese, C. L.; Tessaro, I. C.; Spada, J. C. Development and characterization of pH-indicator films based on cassava starch and blueberry residue by thermocompression. *Food Hydrocoll.* **2019**, *93*, 317−324.

(57) Latos-Brozio, M.; Masek, A. The application of natural food colorants as indicator substances in intelligent biodegradable packaging materials. *Food Chem. Toxicol.* **2020**, *135*, 110975.

(58) Aghaei, Z.; Emadzadeh, B.; Ghorani, B.; Kadkhodaee, R. Cellulose acetate nanofibres containing alizarin as a halochromic sensor for the qualitative assessment of rainbow trout fish spoilage. *Food Bioprocess Technol.* **2018**, *11*, 1087−1095.

(59) Dong, H.; Ling, Z.; Zhang, X.; Zhang, X.; Ramaswamy, S.; Xu, F. Smart colorimetric sensing films with high mechanical strength and hydrophobic properties for visual monitoring of shrimp and pork freshness. *Sens. Actuators B: Chem.* **2020**, *309*, 127752.

(60) Fang, S.; Guan, Z.; Su, C.; Zhang, W.; Zhu, J.; Zheng, Y.; Li, H.; Zhao, P.; Liu, X. Accurate fish-freshness prediction label based on red cabbage anthocyanins. *Food Control* **2022**, *138*, 109018.

(61) Saliu, F.; Della Pergola, R. Carbon dioxide colorimetric indicators for food packaging application: applicability of anthocyanin and poly-lysine mixtures. *Sens. Actuators B Chem.* **2018**, *258*, 1117−1124.

(62) Weston, M.; Phan, M. A. T.; Arcot, J.; Chandrawati, R. Anthocyanin-based sensors derived from food waste as an active use-by date indicator for milk. *Food Chem.* **2020**, *326*, 127017.

(63) Nakamura, Y. *Starch: Metabolism and Structure*; Springer, 2015.

(64) Cheng, H.; Chen, L.; McClements, D. J.; Yang, T.; Zhang, Z.; Ren, F.; Miao, M.; Tian, Y.; Jin, Z. Starch-based biodegradable packaging materials: a review of their preparation, characterization and diverse applications in the food industry. *Trends Food Sci. Technol.* **2021**, *114*, 70−82.

(65) Choi, I.; Lee, J. Y.; Lacroix, M.; Han, J. Intelligent pH indicator film composed of agar/potato starch and anthocyanin extracts from purple sweet potato. *Food Chem.* **2017**, *218*, 122−128.

(66) Luchese, C. L.; Sperotto, N.; Spada, J. C.; Tessaro, I. C. Effect of blueberry agro-industrial waste addition to cornstarch-based films for the production of a pH-indicator film. *Int. J. Biol. Macromol.* **2017**, *104*, 11−18.

(67) Nogueira, G. F.; Soares, C. T.; Cavasini, R.; Fakhouri, F. M.; de Oliveira, R. A. Bioactive films of arrowroot starch and blackberry pulp: physical, mechanical and barrier properties and stability to pH and sterilization. *Food Chem.* **2019**, *275*, 417−425.

(68) Cazón, P.; Vázquez, M. Bacterial cellulose as a biodegradable food packaging material: a review. *Food Hydrocoll.* **2021**, *113*, 106530.

(69) Pourjavaher, S.; Almasi, H.; Meshkini, S.; Pirsa, S.; Parandi, E. Development of a colorimetric pH indicator based on bacterial cellulose nanofibers and red cabbage (*Brassica oleraceae*) extract. *Carbohydr. Polym.* **2017**, *156*, 193−201.

(70) Liu, Y.; Ahmed, S.; Sameen, D. E.; Wang, Y.; Lu, R.; Dai, J.; Li, S.; Qin, W. A review of cellulose and its derivatives in biopolymer-based for food packaging application. *Trends Food Sci. Technol.* **2021**, *112*, 532−546.

(71) da Silva Filipini, G.; Romani, V. P.; Guimaraes Martins, V. Biodegradable and active-intelligent films based on methylcellulose and jambolão (*Syzygium cumini*) skins extract for food packaging. *Food Hydrocoll.* **2020**, *109*, 106139.

(72) Kurek, M.; Hlupić, L.; Ščetar, M.; Bosiljkov, T.; Galić, K. Comparison of two pH responsive color changing bio-based films containing wasted fruit pomace as a source of colorants. *J. Food Sci.* **2019**, *84*, 2490−2498.

(73) Priyadarshi, R.; Rhim, J. W. Chitosan-based biodegradable functional films for food packaging applications. *Innov. Food Sci. Emerg. Technol.* **2020**, *62*, 102346.

(74) Sani, M. A.; Azizi-Lalabadi, M.; Tavassoli, M.; Mohammadi, K.; McClements, D. J. Recent advances in the development of smart and active biodegradable packaging materials. *Nanomaterials* **2021**, *11*, 1331.

(75) Halász, K.; Csóka, L. Black chokeberry (*Aronia melanocarpa*) pomace extract immobilized in chitosan for colorimetric pH indicator film application. *Food Packag. Shelf Life* **2018**, *16*, 185−193.

(76) Yong, H.; Wang, X.; Bai, R.; Miao, Z.; Zhang, X.; Liu, J. Development of antioxidant and intelligent pH-sensing packaging films by incorporating purple-fleshed sweet potato extract into chitosan matrix. *Food Hydrocoll.* **2019**, *90*, 216−224.

(77) Suzihaque, M. U. H.; Jamian, A. S. Development of intelligent food packaging from turmeric (*Curcuma longa*). *Int. J. Eng. Adv. Technol.* **2019**, *9*, 5624−5630.

(78) Ezati, P.; Rhim, J. W. pH-responsive chitosan-based film incorporated with alizarin for intelligent packaging applications. *Food Hydrocoll.* **2020**, *102*, 105629.

(79) Yong, H.; Wang, X.; Zhang, X.; Liu, Y.; Qin, Y.; Liu, J. Effects of anthocyanin-rich purple and black eggplant extracts on the physical, antioxidant and pH-sensitive properties of chitosan film. *Food Hydrocoll.* **2019**, *94*, 93−104.

(80) Wang, X.; Yong, H.; Gao, L.; Li, L.; Jin, M.; Liu, J. Preparation and characterization of antioxidant and pH-sensitive films based on chitosan and black soybean seed coat extract. *Food Hydrocoll.* **2019**, *89*, 56−66.

(81) Chen, J.; Liu, W.; Liu, C. M.; Li, T.; Liang, R. H.; Luo, S. J. Pectin modifications: a review. *Crit. Rev. Food Sci. Nutr.* **2015**, *55*, 1684−1698.

(82) Valdés, A.; Burgos, N.; Jiménez, A.; Garrigós, M. C. Natural pectin polysaccharides as edible coatings. *Coatings* **2015**, *5*, 865−886.

(83) Dudnyk, I.; Janeček, E. R.; Vaucher-Joset, J.; Stellacci, F. Edible sensors for meat and seafood freshness. *Sens. Actuators B Chem.* **2018**, *259*, 1108−1112.

(84) Sedayu, B. B.; Cran, M. J.; Bigger, S. W. A review of property enhancement techniques for carrageenan-based films and coatings. *Carbohydr. Polym.* **2019**, *216*, 287−302.

(85) Liu, J.; Wang, H.; Wang, P.; Guo, M.; Jiang, S.; Li, X.; Jiang, S. Films based on κ-carrageenan incorporated with curcumin for freshness monitoring. *Food Hydrocoll.* **2018**, *83*, 134−142.

(86) Liu, J.; Wang, H.; Guo, M.; Li, L.; Chen, M.; Jiang, S.; Li, X.; Jiang, S. Extract from *Lycium ruthenicum* Murr. incorporating κ-carrageenan colorimetric film with a wide pH-sensing range for food freshness monitoring. *Food Hydrocoll.* **2019**, *94*, 1−10.

(87) Wei, Y. C.; Cheng, C. H.; Ho, Y. C.; Tsai, M. L.; Mi, F. L. Active gellan gum/purple sweet potato composite films capable of monitoring pH variations. *Food Hydrocoll.* **2017**, *69*, 491−502.

(88) Liang, T.; Wang, L. Preparation and characterization of a novel edible film based on *Artemisia sphaerocephala* Krasch. gum: effects of type and concentration of plasticizers. *Food Hydrocoll.* **2018**, *77*, 502−508.

(89) Liang, T.; Sun, G.; Cao, L.; Li, J.; Wang, L. A pH and NH_3 sensing intelligent film based on *Artemisia sphaerocephala* Krasch. gum and red cabbage anthocyanins anchored by carboxymethyl cellulose sodium added as a host complex. *Food Hydrocoll.* **2019**, *87*, 858−868.

(90) Reddy, N.; Yang, Y. Thermoplastic films from plant proteins. *J. Appl. Polym. Sci.* **2013**, *130*, 729−738.

(91) Gennadios, A. *Protein-Based Films and Coatings*; CRC Press, 2002.

(92) Musso, Y. S.; Salgado, P. R.; Mauri, A. N. Smart edible films based on gelatin and curcumin. *Food Hydrocoll.* **2017**, *66*, 8−15.

(93) Musso, Y. S.; Salgado, P. R.; Mauri, A. N. Smart gelatin films prepared using red cabbage (*Brassica oleracea* L.) extracts as solvent. *Food Hydrocoll.* **2019**, *89*, 674−681.

(94) Liu, J.; Yong, H.; Liu, Y.; Qin, Y.; Kan, J.; Liu, J. Preparation and characterization of active and intelligent films based on fish gelatin and haskap berries (*Lonicera caerulea* L.) extract. *Food Packag. Shelf Life* **2019**, *22*, 100417.

(95) Volova, T. *Polyhydroxyalkanoates-Plastic Materials of the 21st Century: Production Properties, Applications*; Nova Publishers, 2004.

(96) Roy, I.; Visakh, P. M. *Polyhydroxyalkanoate (PHA) Based Blends, Composites and Nanocomposites*; Royal Society of Chemistry, 2014.

(97) Auras, R. A.; Lim, L. T.; Selke, S. E.; Tsuji, H. *Poly (lactic acid): Synthesis, Structures, Properties, Processing, and Applications*; John Wiley & Sons, 2011.

(98) Abdullah, Z. W.; Dong, Y.; Davies, I. J.; Barbhuiya, S. PVA, PVA blends, and their nanocomposites for biodegradable packaging application. *Polym. Plast. Technol. Eng.* **2017**, *56*, 1307−1344.

(99) Ghorbani, M.; Divsalar, E.; Molaei, R.; Ezati, P.; Moradi, M.; Tajik, H.; Abbaszadeh, M. A halochromic indicator based on polylactic acid and anthocyanins for visual freshness monitoring of minced meat, chicken fillet, shrimp, and fish roe. *Innov. Food Sci. Emerg. Technol.* **2021**, *74*, 102864.

(100) Hu, H.; Yao, X.; Qin, Y.; Yong, H.; Liu, J. Development of multifunctional food packaging by incorporating betalains from vegetable amaranth (*Amaranthus tricolor* L.) into quaternary ammonium chitosan/fish gelatin blend films. *Int. J. Biol. Macromol.* **2020**, *159*, 675−684.

(101) Roy, S.; Rhim, J. W. Preparation of gelatin/carrageenan-based color-indicator film integrated with shikonin and propolis for smart food packaging applications. *ACS Appl. Bio Mater.* **2021**, *4*, 770−779.

(102) Chayavanich, K.; Thiraphibundet, P.; Imyim, A. Biocompatible film sensors containing red radish extract for meat spoilage observation. *Spectrochim. Acta A Mol.* **2020**, *226*, 117601.

(103) Chen, H. Z.; Zhang, M.; Bhandari, B.; Yang, C. H. Novel pH-sensitive films containing curcumin and anthocyanins to monitor fish freshness. *Food Hydrocoll.* **2020**, *100*, 105438.

(104) Ma, Q.; Liang, T.; Cao, L.; Wang, L. Intelligent poly(vinyl alcohol)-chitosan nanoparticles-mulberry extracts films capable of monitoring pH variations. *Int. J. Biol. Macromol.* **2018**, *108*, 576−584.

(105) Yao, X.; Hu, H.; Qin, Y.; Liu, J. Development of antioxidant, antimicrobial and ammonia-sensitive films based on quaternary ammonium chitosan, polyvinyl alcohol and betalains-rich cactus pears (*Opuntia ficus-indica*) extract. *Food Hydrocoll.* **2020**, *106*, 105896.

(106) Zhai, X.; Shi, J.; Zou, X.; Wang, S.; Jiang, C.; Zhang, J.; Huang, X.; Zhang, W.; Holmes, M. Novel colorimetric films based on starch/polyvinyl alcohol incorporated with roselle anthocyanins for fish freshness monitoring. *Food Hydrocoll.* **2017**, *69*, 308−317.

(107) Zhang, J.; Zou, X.; Zhai, X.; Huang, X.; Jiang, C.; Holmes, M. Preparation of an intelligent pH film based on biodegradable polymers and roselle anthocyanins for monitoring pork freshness. *Food Chem.* **2019**, *272*, 306−312.

(108) Zia, J.; Mancini, G.; Bustreo, M.; Zych, A.; Donno, R.; Athanassiou, A.; Fragouli, D. Porous pH natural indicators for acidic and basic vapor sensing. *Chem. Eng. J.* **2021**, *403*, 126373.

(109) Ardiyansyah; Apriliyanti, M. W.; Wahyono, A.; Fatoni, M.; Poerwanto, B.; Suryaningsih, W. The potency of betacyanins extract from a peel of dragon fruits as a source of colourimetric indicator to develop intelligent packaging for fish freshness monitoring. *1st Int. Conf. Food Agri.* **2018**, *207*, 1−7.

(110) Kanatt, S. R. Development of active/intelligent food packaging film containing *Amaranthus* leaf extract for shelf life extension of chicken/fish during chilled storage. *Food Packag. Shelf Life* **2020**, *24*, 100506.

(111) Kang, S.; Wang, H.; Xia, L.; Chen, M.; Li, L.; Cheng, J.; Li, X.; Jiang, S. Colorimetric film based on polyvinyl alcohol/okra mucilage polysaccharide incorporated with rose anthocyanins for shrimp freshness monitoring. *Carbohydr. Polym.* **2020**, *229*, 115402.

(112) Ma, Q.; Du, L.; Wang, L. Tara gum/polyvinyl alcohol-based colorimetric NH_3 indicator films incorporating curcumin for intelligent packaging. *Sens. Actuators B Chem.* **2017**, *244*, 759−766.

(113) Zhang, J.; Huang, X.; Zou, X.; Shi, J.; Zhai, X.; Liu, L.; Li, Z.; Holmes, M.; Gong, Y.; Povey, M.; Xiao, J. A visual indicator based on curcumin with high stability for monitoring the freshness of freshwater shrimp, *Macrobrachium rosenbergii*. *J. Food Eng.* **2021**, *292*, 110290.

(114) Visakh, P. M.; Morlanes, M. J. M. *Nanomaterials and Nanocomposites: Zero- to Three-Dimensional Materials and Their Composites*; John Wiley & Sons, 2016.

(115) Alizadeh-Sani, M.; Tavassoli, M.; McClements, D. J.; Hamishehkar, H. Multifunctional halochromic packaging materials: Saffron petal anthocyanin loaded-chitosan nanofiber/methyl cellulose matrices. *Food Hydrocoll.* **2021**, *111*, 106237.

(116) Lan, W.; Wang, S.; Zhang, Z.; Liang, X.; Liu, X.; Zhang, J. Development of red apple pomace extract/chitosan-based films reinforced by TiO_2 nanoparticles as a multifunctional packaging material. *Int. J. Biol. Macromol.* **2021**, *168*, 105−115.

(117) Zhang, X.; Liu, Y.; Yong, H.; Qin, Y.; Liu, J.; Liu, J. Development of multifunctional food packaging films based on chitosan, TiO_2 nanoparticles and anthocyanin-rich black plum peel extract. *Food Hydrocoll.* **2019**, *94*, 80−92.

(118) Wu, C.; Sun, J.; Chen, M.; Ge, Y.; Ma, J.; Hu, Y.; Pang, J.; Yan, Z. Effect of oxidized chitin nanocrystals and curcumin into chitosan films for seafood freshness monitoring. *Food Hydrocoll.* **2019**, *95*, 308−317.

(119) Wu, C.; Sun, J.; Zheng, P.; Kang, X.; Chen, M.; Li, Y.; Ge, Y.; Hu, Y.; Pang, J. Preparation of an intelligent film based on chitosan/oxidized chitin nanocrystals incorporating black rice bran anthocyanins for seafood spoilage monitoring. *Carbohydr. Polym.* **2019**, *222*, 115006.

(120) Meng, Y.; Luo, H.; Dong, C.; Zhang, C.; He, Z.; Long, Z.; Cha, R. Hydroxypropyl guar/cellulose nanocrystal film with ionic liquid and anthocyanin for real-time and visual detection of NH_3. *ACS Sustain. Chem. Eng.* **2020**, *8*, 9731−9741.

(121) Qin, Y.; Huang, P.; Wu, F. Y. Histamine-responsive dye-incorporated carbon dots for visual monitoring of food spoilage. *Sens. Actuators B Chem.* **2022**, *365*, 131911.

(122) Choudhary, S.; Joshi, B.; Joshi, A. Translation of carbon dot biosensors into an embedded optical setup for spoilage and adulteration detection. *ACS Food Sci. Technol.* **2021**, *1* (6), 1068−1076.

(123) Qin, Y.; Yun, D.; Xu, F.; Chen, D.; Kan, J.; Liu, J. Smart packaging films based on starch/polyvinyl alcohol and *Lycium ruthenicum* anthocyanins-loaded nano-complexes: Functionality, stability and application. *Food Hydrocoll.* **2021**, *119*, 106850.

(124) Yao, X.; Liu, J.; Hu, H.; Yun, D.; Liu, J. Development and comparison of different polysaccharide/PVA-based active/intelligent packaging films containing red pitaya betacyanins. *Food Hydrocoll.* **2022**, *124*, 107305.