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Review

Nanomaterials with Plant or Animal Origin for Greener Biodelivery and Biosensor Applications: A Review

Hazal Turasan [1], Tahrima B. Rouf [2], Tuncay Yilmaz [3], Jozef Kokini [4, *]

1. Weldon School of Biomedical Engineering, Purdue University, West Lafayette, IN, 47907, USA; E-Mail: hturasan@purdue.edu
2. Stephenson School of Biomedical Engineering, University of Oklahoma, Norman, OK 73019, USA; E-Mail: trouf@ou.edu
3. Department of Food Engineering, Manisa Celal Bayar University, Manisa 45140, Turkey; E-Mail: tuncay.yilmaz@cbu.edu.tr
4. Department of Food Science, Purdue University, West Lafayette, IN, 47907, USA; E-Mail: jkokini@purdue.edu

* **Correspondence:** Jozef Kokini; E-Mail: jkokini@purdue.edu

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Abstract

Nanomaterials are now used in almost every field of science; as conductors and electrodes in electronics, as nanodelivery systems in health screenings and drug delivery, as nanofibrils in filtering and textile industry, as nanoparticles in biosensor fabrication for toxin and pathogen detection, and in packaging materials in the food industry. Synthetic materials and plastics accumulate in the environment causing increasing health concerns for their use in food and pharmaceutical products. Therefore, researchers now try to find new greener fabrication methods for nanomaterials. In this review, some of the most recent studies were summarized and discussed where novel green nanomaterials were synthesized from plant or animal-based polymers. The focus has been given on the synthesis of 1) nanodelivery systems for bioactive and drug delivery in the form of nanoparticles, nanotubes and nanofibers, 2) nanophotonic

film or nanofiber-based biosensors for food toxin and pathogen detection, and 3) functional nanocomposite films. The studies summarized here give the reader a clear understanding of the science behind creating green nanomaterial-based systems and how they are used in various applications.

Keywords
Nanomaterials; nanodelivery systems; SDG; biosensors; nanocomposite films; biodegradable polymers

1. Introduction

The use of nanotechnology in electronics, biomedicine, food and environment rapidly increases due to the advancing technology [1-3]. The ability to control the design, shape and the scale of nanomaterials provides exceptional surface, optical, magnetic, electrical and physical properties to the products [4]. Especially in food, medicine and pharmaceutical industries, the size of nanomaterials shows many advantages in detection of analytes, controlled and targeted delivery of bioactives and drugs and in preservation and functionalization of foods [5-7].

Because of their inexpensiveness and mass production abilities, synthetic polymers and plastics are widely used in the fabrication of nanodelivery systems, sensors and food packaging materials. These polymers usually have longer chains compared to natural plant or animal-based polymers, which generally makes them more efficient during applications, such as encapsulation and delivery of a bioactive [8]. However, this mass production and use of these synthetic polymers cause detrimental effects on the environment, animals, plants and human health [9, 10]. In fact, in cases where these polymers are ingested as nanodelivery systems, the accumulation in tissues over a long period of time can cause very serious health issues [11]. These issues make scientists look for new ways to fabricate the nanomaterials that are greener, safer for environment and much less toxic for the human body when ingested [12, 13]. The focus has been on plant and animal-based proteins and polysaccharides, since these polymers have perfect biocompatibility with each other and other materials, and they show excellent mechanical, chemical and surface properties, especially when they are chemically modified or processed with novel processing techniques. Natural polymers are also highly abundant, which makes them highly available.

In this review, three major areas of nanotechnology are summarized where green materials are used instead of synthetic polymers: synthesis of nanodelivery systems for bioactive and drug delivery, fabrication of biodegradable biosensors and synthesis of nanocomposite films. The fabrication techniques and the characterization of these systems are discussed in detail, and applications of these systems in food and pharmaceutical industry are presented.

2. Synthesis of Green Nanodelivery Systems for Bioactive Delivery

2.1 Coacervates

One of the most commonly used techniques to fabricate green nanodelivery systems is the coacervation method. It is considered one of the easiest ways to obtain protein or polysaccharide-

based nanoparticles that are easily adjustable. The principle behind coacervation is a sudden change of ionic forces that drives polymers to join and generate soluble or insoluble particles that precipitate out of solution. While only a single biopolymer can create nanoparticles with simple coacervation, multiple biopolymers can also be used to form complex coacervates through the electrostatic forces between negatively and positively charged biopolymer molecules [14, 15]. Besides electrical affinity, other bonding interactions, such as hydrogen bonding or hydrophobic interactions, could also contribute to coacervation.

The delayed and prolonged release of loaded substances in the gastrointestinal (GI) tract, which avoids the burst release seen with many other types of delivery methods, is one of the key advantages of coacervation [16]. It is key to find the optimum pH value to maximize the attraction between biopolymers. For example, in a recent study, the interaction between amaranth protein and xanthan gum was found to be stronger at pH 4 compared to pH 5.5 [15]. A stronger electrostatic attraction between the polymers prevents dissociation of the nanoparticle complex at low gastric pH, providing a better protection to the encapsulated bioactive. As a result, design criteria such as polymer selection and pH play a critical part in the coacervation technique's success and effectiveness.

In a recent study, isothermal titration calorimetry (ITC) was used to investigate the interaction between two oppositely charged polyelectrolytes, sodium alginate and chitosan, were done to better understand the thermodynamics of nanoparticulation through complex coacervation [17]. First, the zeta potentials (ζ) of the polyelectrolytes were measured at different pH values and pH 4 was found to be the optimal pH for maximum electrical interaction between chitosan and sodium alginate. The authors also investigated the order of polymer addition and the effect of polymer molar charge ratios on the particle size, zeta potential and reaction enthalpy. The overall enthalpy of polyelectrolyte complex formation was -3207 kJ/mol when sodium alginate was added into chitosan, and -1683 kJ/mol when chitosan was added into sodium alginate, indicating that a stronger interaction is possible if the order of polymer addition is as sodium alginate into chitosan. This order of addition also led to smaller nanoparticles (Figure 1). When alginate was added to chitosan, it increased the charge ratio from 0.8 to 1.15, resulting in a greater change in both enthalpy and zeta potential. Overall, the order of polyelectrolyte addition and charge ratios during polyelectrolyte complex formation had a significant impact on the reaction stoichiometry and enthalpy, which influences particle sizes and zeta potentials.

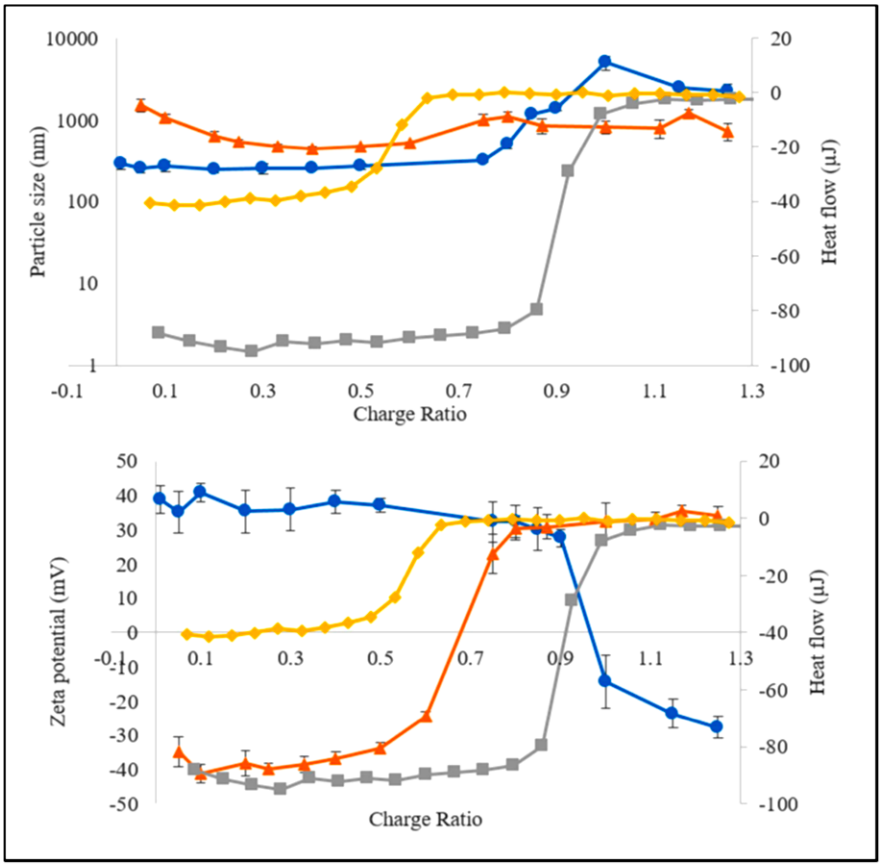

Figure 1 Change of particle size, zeta potential and enthalpy as a function of charge ratio and order of addition. Alg (Sodium Alginate), Chi (Chitosan), D (nm): Particle Size, ζ (mV): Zeta Potential, Q (μJ): Heat of Reaction. Top graph (a), blue: Alg/Chi-D (nm), orange: Chi/Alg-D (nm), grey: Alg/Chi-Q (μJ), yellow: Chi/Alg-Q (μJ). Bottom graph (b), blue: Alg/Chi-ζ (mV), orange: Chi/Alg-ζ (mV), grey: Alg/Chi-Q (μJ), yellow: Chi/Alg-Q (μJ) [17].

In another study, complex coacervates were fabricated from gelatin and gum arabic to encapsulate roasted coffee oil and compared to particles fabricated with spray drying [18]. pH 4 was used for the coacervation since it provided the maximum attraction between the polyelectrolytes. The particles made with coacervation had significantly higher oil retention (42.8%) than those made with spray drying (10.2%). Spray dried particles, on the other hand, had lower surface oil content and higher solubility. Sensory experiments were conducted on the aroma of the dissolved particles, and coacervates were preferred by the assessors.

Encapsulation of curcumin, a polyphenolic compound found in turmeric that has anti-inflammatory properties, was achieved through complex coacervation of bovine serum albumin (BSA) and poly-d-lysine (PDL) [19]. BSA was coupled with both high molecular weight (HMW) and low molecular weight (LMW) PDL. LMW PDL led to smaller particles, smallest of which had an average diameter of 212 nm. Also, LMW PDL/BSA nanoparticles had more regular and spherical shapes than HMW PDL/BSA particles. The highest encapsulation efficiency of curcumin was achieved when the curcumin to BSA ratio was 10 for LMW PDL/BSA particles. Shelf stability test conducted at 25°C and 4°C showed that LMW PDL/BSA nanoparticles were more stable over a 21-day period.

Due to the easiness of their fabrication, coacervate nanoparticles are one of the highest explored

ways to delivery bioactives. Even though only a few studies were summarized in this section, more can be found in the literature for encapsulation and delivery of drugs [20], carotenoproteins [21], flavonoids [22], essential oils [23] or even DNA [24].

2.2 Layer-by-Layer Nanotubes

Another technique to create environmentally friendly bioactive nanodelivery systems is to create protein-based nanotubes using a layer-by-layer (LbL) deposition technique. This technique provides a more controlled fabrication of the carrier system by the use of templates, because the size, volume and length of the nanotubes can be controlled, and the delivery systems can be tuned as desired [25-27]. Also, the properties of the inner and the outer layers of the nanotubes can be changed depending on the properties of the encapsulated bioactives. The formation of LbL nanotubes is achieved through the attraction of oppositely charged polyelectrolytes, which are run through templates sequentially. This way a desired number of layers can be constructed for the nanotubes.

For example, [25] designed human serum albumin (HSA)/polyethylenimine (PEI) nanotubes for DNA loading. They used polycarbonate nanopore templates to form the layers of the tubes. First, they ran positively charged PEI solutions through the templates using a syringe pump, which allows PEI molecules to be electrostatically bind to the negatively charged PC template. After washing the excess PEI, negatively charged HSA solutions were ran through the same pores, leaving a layer of HSA electrostatically bound to the already existing positively charged PEI layers. By repeating the process, 5 bilayers of PEI/HAS was formed inside the pores. To chemically bind the DNA from its positively charged sites, an additional negatively charged PEI layer was assembled on the last layer of HSA. The nanotubes were liberated from the templated by dissolving them in DMF solutions, which only dissolved the PC. DNA loading was done after the nanotubes were liberated and dried. The maximum adsorption capacity of the DNA molecules was 606 mg/g, which was higher than those of nanoparticles in previous studies.

Other green and protein-based nanotubes include α-lactalbumin (LAC)/chitosan (CHI) and bovine serum albumin (BSA)/κ-carrageenan (CAR) LbL nanotubes [28]. These nanotubes were fabricated with the same PC nanopore template technique, where the first layers were positively charged CHI or BSA, followed by the negatively charged second layers of LAC or CAR, respectively. In this study, three different PC templates with 400, 600 and 800 nm pore sizes were tested for nanotube formation. 4 bilayers were formed for the ones with 400 nm, and 5 bilayers were assembled for the 600 nm and 800 nm templates. Figure 2 shows that both LAC/CHI and BSA/CAR nanotubes had very well-defined tubular structures without much deformation. The mechanical strength of the walls was tested using force curve analysis with atomic force microscopy. BSA/CAR nanotubes had higher Young's moduli than LAC/CHI nanotubes, indicating higher robustness. For both types, nanotubes with 400 nm diameter had the highest Young's moduli, which significantly decreased as the diameter increased to 600 and 800 nm. Nanotubes were loaded with curcumin for *in vitro* cytotoxicity studies. While the encapsulation efficiencies of both nanotubes were similar and in the range of 40-45%, BSA/CAR nanotubes had a burst release of curcumin within the first 2 hours in solution and LAC/CHI nanotubes were fairly stable for 2 days. The nanotubes alone did not show any cytotoxicity against HeLa cells at any concentration, however curcumin-loaded nanotubes had significant (up to 65% loss in cell viability) cytotoxicity to HeLa cells, indicating successful loading and release of curcumin.

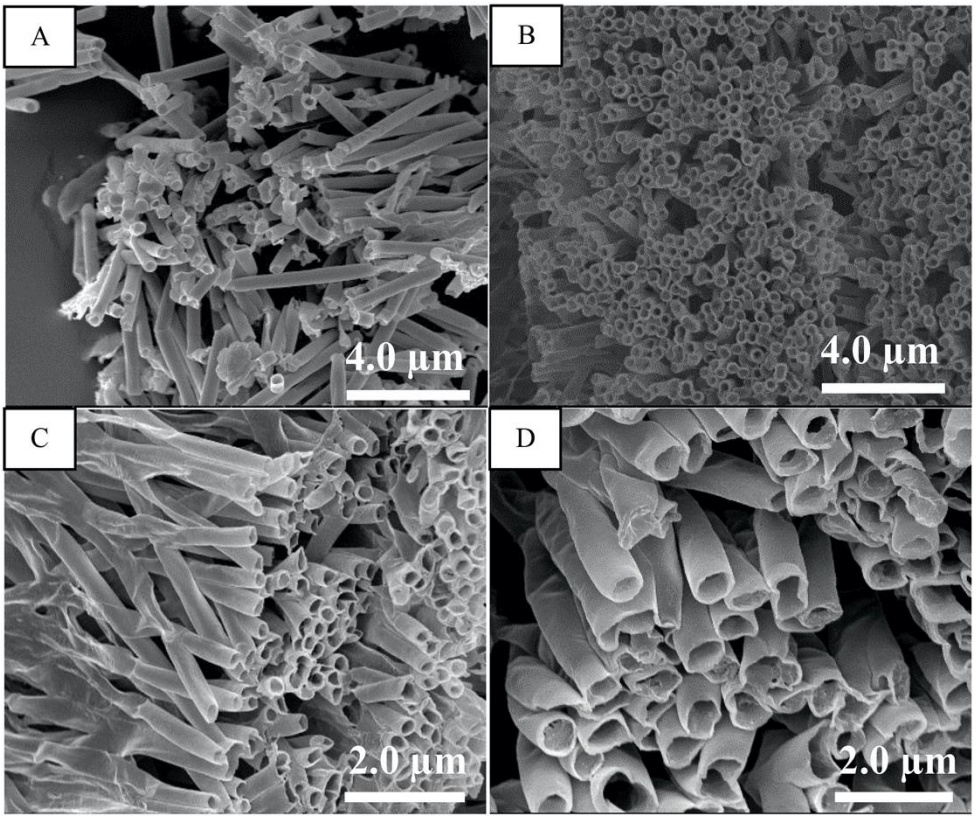

Figure 2 LAC/CHI nanotubes with 400 nm pore size (A) and 800 nm pore size template (B). BSA/CAR nanotubes with 400 nm pore size (C) and 800 nm pore size template (D) [28].

More plant or animal-origin nanotubes fabricated using the LbL technique have been reported in the literature [27, 29, 30], but there are also other ways to produce biodegradable tubular shaped nanocarriers for bioactive delivery, such as self-assembly [31, 32], pulsed electric field [33] or through dynamic microfluidic control [34, 35].

2.3 Hollow Nanoparticles

Fabricating hollow nanoparticles from plant-based proteins is another trending area of green nanodelivery systems. Hollow particles are advantageous over solid nanoparticles, since they are able to carry higher drug loads and the release of the encapsulated materials are more controlled and prolonged compared to solid particles [36]. Hollow nanoparticles were fabricated using zein, which is the most abundant protein found in corn, with the sacrificial template method [36]. First, sodium carbonate was precipitated in 70% ethanol to form crystals that would act as cores that zein molecules can adsorb onto. When sodium carbonate dispersions were mixed with zein solutions in 70% ethanol, zein molecules attach themselves onto sodium carbonate, instead of forming agglomerations on their own. Addition of distilled water into the mixture further precipitated the zein molecules around the sodium carbonate cores and eventually dissolved the sodium carbonate, leaving zein particles hollow inside. While the total diameter of the hollow nanoparticles was around 100 nm, the thickness of the zein layer was only around 10 nm, which left a significant volume inside the particles for drug loading. Metformin, an anti-diabetic drug, was tested for loading the hollow nanoparticles, and was compared to its loading to solid zein nanoparticles. The loading amounts of

hollow nanoparticles were significantly higher than those of solid nanoparticles at any metformin concentration, and the release of metformin was significantly more sustained and controlled.

Another plant-based protein, kafirin, was also tested for fabricating hollow nanoparticles for bioactive delivery [37]. First, hollow and solid kafirin nanoparticles were fabricated with the same sacrificial template method used in the previous paper. Using these particles, layer-by-layer hollow and solid kafirin nanoparticles were also fabricated by first mixing the nanoparticles in dextran sulfate solutions and then further immersing them into chitosan solutions. The electrostatically arranged dextran sulfate and chitosan layers formed a bilayer on top on the kafirin layer, acting a second layer of barrier for the encapsulated material. The last step was also repeated twice to form a double bilayer of dextran sulfate/chitosan on the kafirin particles. LbL technique added approximately 15 nm of thickness to the kafirin nanoparticle per bilayer. Curcumin was loaded into both hollow and solid LbL kafirin nanoparticles, and LbL hollow nanoparticles showed significantly higher encapsulation efficiencies at all curcumin/kafirin mass ratios (Figure 3). Both solid and hollow LbL kafirin nanoparticles showed improved curcumin dissolution profiles in the gastrointestinal tract compared to free curcumin; while the hollow LbL nanoparticles had lower release percentages compared to solid LbL nanoparticles.

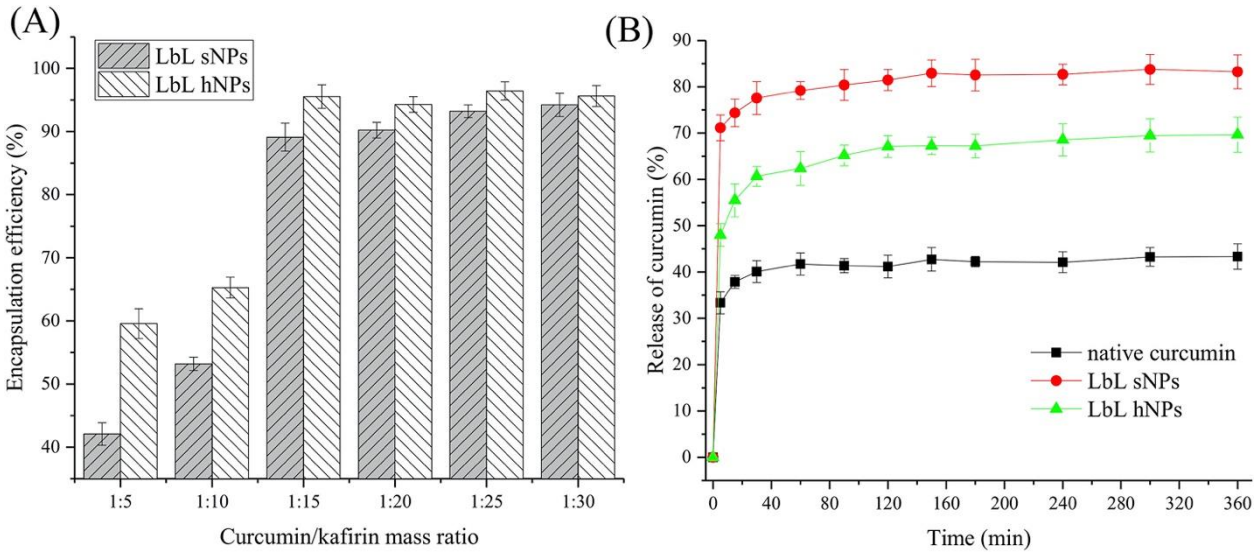

Figure 3 Encapsulation efficiency and release profiles of solid and hollow LbL kafirin nanotubes [37].

A similar sacrificial template method was used in the fabrication of biodegradable chitosan and fucoidan (a polysaccharide found in brown algae) multilayer nanoparticles [38], where the core consisted of polystyrene particles, which later was removed with tetrahydrofuran treatment, leaving the particles hollow. Poyl-L-lysine (PLL), a water soluble bioactive compound was encapsulated in the hollow nanocarriers and in-vitro release kinetics showed that PLL release was pH dependent and the release mechanism did not follow a strict Fick's behavior, but rather was governed by Fick's and Case II transport, possible due to loosening of the nanocapsule structures and polymer relaxation.

Studies on fabrication of hollow nanodelivery systems from plant or animal-based sources are still scarce compared to their non-biodegradable versions, but the results of the few studies show their great potential in delivery of sensitive bioactives into human system. Their edible sources and

non-toxicity also give them an advantage when it comes to delivering nutrients for health applications.

2.4 Nanofibers

Electrospun nanofibers have also been employed in encapsulating bioactive agents and microorganism. [39] were able to fabricate electrospun nanofibers from a sorghum protein, kafirin, for the first time without the use of another synthetic polymer. They achieved that through a double purification step, where the protein became free of impurities that cause blockage during electrospinning. Through careful optimization of the kafirin concentration and the choice of solvent to dissolve kafirin in, round bead-free and distortion-free nanofibers were achieved with a diameter range of 580 to 1300 nm. Kafirin nanofibers were also loaded with two phenolic compounds, thymol and carvacrol, which possess antimicrobial and antifungal properties and are often used against food borne pathogens. Fourier Transform Infrared Spectroscopy confirmed the successful encapsulation of the polyphenolic compounds. The highest encapsulation efficiency of 87% was achieved when 0.1 g/mL carvacrol was encapsulated followed by 77% of thymol encapsulation at 0.1 g/mL concentration. Encapsulation of these bioactives changed some of the secondary structure of the protein: β-turn into β-sheet structures. Additionally, while increasing carvacrol concentration during encapsulation decreased the surface wettability of the nanofiber mats, the opposite was observed in thymol encapsulation.

In a similar study, electrospun gum arabic/pullulan blend fibers were used for the encapsulation of *Lactobacillus*, which is a strain of lactic acid bacteria commonly used in the food industry for fermentation, such as yogurt production [40]. Fourier Transform Infrared Spectroscopy (FTIR) analysis showed that during electrospinning gum arabic and pullulan molecules were miscible and bonding through hydrogen bonding. The viscosity of the solutions significantly decreased as the gum arabic concentration was increased and pullulan was decreased, which reflected as thinning fiber diameter in the electrospun fibers. While 100% pullulan fibers could be fabricated, 100% gum arabic fibers were not possible since the viscosity of the solution was too low and there was not enough polymer entanglement to form a fiber structure. Scanning electron microscopy (SEM) images also showed that when gum arabic was used at high concentrations in the blend, the fibers showed more deformations and bead formations. The optimum GA/Pullulan ratio was chosen as 20:80, since the encapsulated *Lactobacillus* had a better survivability of 85.38-97.83% and retained viability for 28 days at 4°C at this ratio.

Studies summarized in this section show that plant or animal-based polymers provide many advantages in the fabrication of edible and biodegradable bioactive delivery system; their abundance makes them widely available, they are compatible with each other, fabrication of the delivery systems from them can be highly controlled and they provide a very controlled release of the encapsulated bioactive compound. The list of summarized studies as well as other studies focused on green nanodelivery systems can be found in Table 1.

Table 1 Summary of some recent studies on fabrication of green nanodelivery systems.

	Wall materials	Encapsulated bioactive	Reference

Coacervate particles	Gelatin Gum Arabic	Roasted coffee oil	(Böger et al., 2021) [18]
	Bovine Serum Albumin Poly-d-lysine	Curcumin	(Maldonado et al., 2017) [19]
	Whey protein isolate Gum Arabic	Ginger essential oil	(Tavares & Noreña, 2020) [41]
	Soy protein isolate Chitosan	chlorophyll	(Agarry et al., 2022) [42]
	Gelatin Tragacanth gum	Oil leaf extract	(Oliveira et al., 2022) [43]
	Whey protein concentrate Pectin	Vitamin B_{12}	(Akbari et al., 2022) [44]
Layer-by-layer nanotubes	Human serum albumin Polyethylenimine	DNA (polyA_{25})	(Jiao et al., 2015) [25]
	α-lactalbumin Chitosan	Curcumin	(Maldonado et al., 2019) [28]
	Bovine serum albumin κ-carrageenan	Curcumin	(Maldonado et al., 2019) [28]
	Bovine serum albumin Sodium alginate	–	(Maldonado & Kokini, 2018) [45]
	poly-l-arginine Human serum albumin concanavalin A	Dextran	(Shiraishi et al., 2014) [46]
	Collagen poly(styrene sulfonate)	–	(Landoulsi et al., 2009) [29]
	poly-l-arginine Human serum albumin	–	(Qu et al., 2008) [30]
	poly-l-arginine ferritin	–	(Qu et al., 2008) [30]
	poly-l-arginine myoglobin	–	(Qu et al., 2008) [30]
Hollow nanoparticles	Zein	Metformin drug	(Xu et al., 2011) [36]
	Kafirin	Curcumin	(X. Li et al., 2019) [37]
	Chitosan Fucoidan	Poly-L-lysine	(Pinheiro et al., 2015) [38]
	Carrageenan Chitosan	–	(Y. Liu et al., 2012) [47]
	Pectin Chitosan	Doxorubicin hydrochloride	(Ji et al., 2017) [48]
	Chitosan Alginate	Glycomacropeptide 5-aminosalycic acid	(Rivera et al., 2015) [49]

Nanofibers	Kafirin	Thymol Carvacrol	(Higashiyama et al., 2021) [39]
	Gum Arabic Pullulan	*Lactobacillus*	(J. Ma et al., 2021) [40]
	Whey protein concentrate Rye flour	Grape seed extract	(Aslaner et al., 2021) [50]
	Whey protein isolate Pullulan	β-carotene	(Drosou et al., 2022) [51]
	Lycium barbarum polysaccharide Silk fibroin	Eugenol	(Lin et al., 2022) [52]

3. Fabrication of Green Nanosensors

3.1 Film Based Nanosensors

Surface enhanced Raman spectroscopy (SERS) biosensor platforms were fabricated using zein. The platforms were fabricated using the soft lithography technique, where the master mold with inverted nanopyramid structures were initially created with silicon wafers. Polydimethylsiloxane (PDMS) was then cast on the master molds and cured, leaving them with positive pyramid structure. After coating the PDMS molds with gold layer (4 mm), ethanolic zein solutions were cast and dried on the PDMS molds and the initial inverted nanopyramid structures were transformed onto zein films. Since the gold layer on the PDMS favored the surface of the zein films, due to its surface energy, this method resulted in a gold layer coated nanostructured zein films to be used as SERS platforms (Figure 4). The gold layer on top of zein film created dense electron clouds at the bottom of the inverted pyramids, which are referred to as hotspots. When the analyte molecules to be detected fell into these hotspots, their Raman signals intensified, and very low limits of detections were achieved. These zein film-based platforms were successfully used in the detection of acrylamide and the peanut allergen Ara h1 [53, 54].

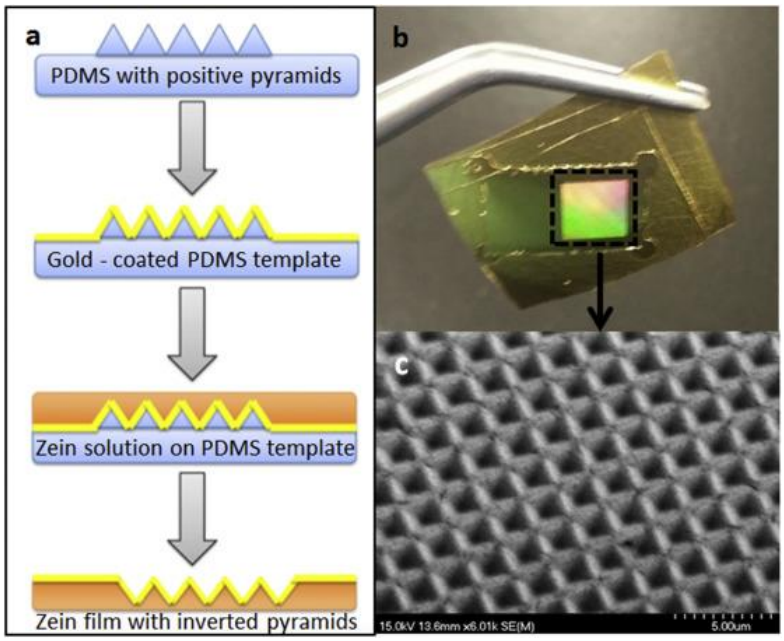

Figure 4 Fabrication of nanostructured zein films with soft lithography [54].

In a follow up study, the zein-film based SERS platforms were further enhanced in sensitivity by decorating their surface with gold nanoparticles [55]. The idea behind adding more gold nanoparticles was to create more hotspots on the surface of the films and reach even lower limits of detection with these sensor platforms. Cysteamine was used to chemically attach gold nanoparticles onto the gold layer coating on top of structured zein films and optimization of its concentration was done between two concentrations: 10 mM and 100 mM. Rhodamine 6G was used to test the Raman signals, and the signals were significantly higher when 100 mM cysteamine was used for the decoration of the gold nanoparticles. The optimized platforms were then used for the detection of pyocyanin, which is the toxin of the bacteria *Pseudomonas aeruginosa.* The limit of detection for pyocyanin was 25 µM.

In another study, different nanoparticles were used for the decoration of nanostructured and gold coated zein-based films, to test if different metals yield different Raman signal enhancement [56]. Gold nanoparticles, silver nanoparticles and silver shelled nanoparticles were decorated on the zein platforms separately and Rhodamine 6G was used to test the enhancement factor (EF) of the platforms. The highest enhancement factor of 3.36×10^5 was reached with silver-shelled-gold nanoparticles, followed by an EF of 2.94×10^5 with silver nanoparticles and an EF of 2.51×10^5 with gold nanoparticles. Silver nanoparticles yield a better SERS enhancement factor than gold nanoparticles due to their higher surface plasmonic strength. In bimetallic nanoparticles, such as silver-shelled-gold nanoparticles, the better plasmonic effect of silver and the better stability of gold are combined and create a synergistic effect, yielding the highest EF of all [57].

Chitosan is another natural polymer that has been widely used in the fabrication of biosensors due to its biodegradability, transducer surface modifying abilities and compatibility with advanced sensor properties [58]. Chitosan films were used for DNA immobilization onto electrodes during biosensor fabrications in different studies. The amine groups of chitosan were activated using chemical reagents, such as glutaraldehyde or EDC/NHS crosslinkers, which later covalently bonded to the eaither 5’ amino groups or 5’ biotin groups of ss-DNA probes, respectively. For example, a glassy carbon electrode was coated with chitosan and multiwalled carbon nanotubes, where the

DNA immobilization was achieved through glutaraldehyde activation of chitosan amine groups [59]. The electrode was then tested with electrochemical impedance spectroscopy (EIS) using $[Fe(CN)_6]^{3-/4-}$ as an indicating probe. The successful immobilization of DNA onto chitosan films led to a wide range of detection concentrations with a limit of detection of 8.5×10^{-14} M.

Especially the redox potential of proteins allows them to facilitate electron exchange, which help them find more use in third generation biosensors [60], such as protein film voltammetry [61, 62]. The list of studies where green plymers were incorporated in biosensor fabrication can be found in Table 2.

Table 2 List of some studies where green biopolymers were incorporated in the fabrication of biosensors and nanocomposite films.

Biopolymer/form	Sensing mechanism	Application	Reference
Zein films	SERS	Peanut allergen detection Acrylamide detection	(Gezer et al., 2016a, 2016b) [53, 54]
Zein films	SERS	Detection of pyocyanin	(Jia et al., 2019) [55]
Zein films	SERS	Rhodamine 6G	(X. Ma et al., 2020) [56]
Chitosan films	EIS	DNA immobilization	(Q. Wang et al., 2011) [59]
Whey protein isolate film	Triboelectric	Pressure sensor	(Lee et al., 2022) [63]
Cellulose fibers (paper)	Colorimetric	COVID-19 biomarker	(Adrover-Jaume et al., 2021) [64]
Zein nanofibers	SERS	Acrylamide detection	(Turasan et al., 2022) [57]
Cellulose acetate fibers	Impedimetric	Blood glucose	(Ahmadi et al., 2021) [65]
BSA fibers	Quartz crystal microbalance	Lysozyme	(Kabay et al., 2017) [66]
Chitosan fibers	Electrochemical	17α-ethinylestradiol (EE2)	(Pavinatto et al., 2018) [67]
Chitosan fibers	Colorimetric	Cholesterol	(Dhawane et al., 2019) [68]
Zein/carbon black nanocomposite film	Differential pulse voltammetry	Hydrogen peroxide	[1] (dos Santos Pereira et al., 2019) [69]
Zein/Laponite Zein/CNT Zein/Graphene oxide nanocomposite films	Cyclic voltammetry, (EIS) Square wave voltammetry	Gliadin	(Rouf et al., 2020) [70]
Zein/carbon nanohorn nanocomposite films	Differential pulse adsorptive cathodic	Fenitrothion	(Itkes et al., 2019) [71]

	stripping voltammetry		
Silk protein/nanowire nanocomposite hydrogels	Electronic skin	External stimuli	(Jo et al., 2018) [72]
Chitosan/CNT/RGO nanocomposite aerogel	Piezoresistive	Human motion	(J. Wu et al., 2020) [73]

3.2 Fiber Based Nanosensors

Nanofiber mats made from green and natural polymers are also started being used for the fabrication of biosensors. The advantages of using nanofiber structure include a very high surface area/volume ratio, which creates an excessive amount of surface to attach analytes, molecules or even biorecognition elements for specific detection. When these sensor platforms are made from green natural materials, the disposal of them becomes environmentally friendly, it quickens the amount of time to degrade in the soil and some of them dissolve once the intended process is concluded, leaving no waste material to be disposed of.

Paper, which is a natural polymer-based platform derived from the cellulose of trees, is in the form of fibers and has been used in many sensors, including the detection of 2019 novel coronavirus (2019-nCoV). In a recent study, paper has been used in the fabrication of a immunosensor to detect IL-6 (Interleukin 6) as a biomarker of the novel coronavirus from patients' blood samples [64]. A reservoir was constructed in the paper where antibody decorated gold nanoparticles were housed. Samples collected from patients were dropped on three capture sites, allowing any existing IL-6 molecules to be absorbed onto the fibers of the paper. Upon drying of the samples, the paper was folded which allowed the interaction between the anti-bodies and IL-6 molecules, and therefore migration of the gold molecules (along with the antibodies) to the IL-6 existing sites. The more IL-6 molecules led to more gold nanoparticle concentration, creating a darker reddish color due to increased gold nanoparticle amount. The degree of color intensity was then measured with a smartphone application, allowing a fast and simple measurement of novel Coronavirus disease marker. The limit of detection reached with this paper-based immunosensor was 10^{-3} pg/mL.

Not all fiber-based biosensor platforms are naturally found in fiber structure nature, like cellulose, but they can also be constructed that way through some processing techniques, such as electrospinning. Electrospinning provides consistent fiber formation from almost any polymer, with nano or micro size diameters, and the fibers find use in many areas, such as tissue engineering, textile industry, membrane system or packaging.

Electrospun nanofibers were fabricated from a plant based polymer, corn protein zein, and were used as a surface enhanced Raman spectroscopy biosensor platform for the first time [74]. The concept of detection with these zein nanofibers were similar to those of zein-film based platforms; decorating the surface of the fibers with metallic nanoparticles to create hotspots to enhance the Raman signal of the analytes. However, fiber formation provides one very significant advantage over the film-based platforms. The surface area created with the fibers were around 1000 times bigger based on the same amount (g) of zein used, providing significantly higher number of hotspots. However, the porosity of the nanofiber structure allowed very fast absorption of the gold nanoparticle colloid droplet during the decoration process, forcing the nanoparticles dissolving into

a large area on the nanofiber mat and separating the nanoparticles further away from each other (Figure 5a). Nanoparticles having larger distances between them could not generate hotspots and the Raman signals were weak. Turasan et al. overcame this problem by chemically crosslinking the zein proteins with the biodegradable glutaraldehyde and turned the surface of the nanofiber mats significantly hydrophobic (Figure 5b) [74]. Upon drying the surface area coverage of nanoparticles were significantly higher than uncrosslinked zein fibers (Figures 5c and d). Testing the uncrosslinked and crosslinked nanofiber mats on the detection of Rhodamine 6G with Raman spectroscopy showed that crosslinking provided about 25 times higher signal of the analyte and about 100 times higher signal compared to the zein film-based sensors (Figure 5e). Additionally, in the fabrication of zein electrospun fiber platforms approximately 800 times amount of gold was used, which increased the sustainability of the sensors.

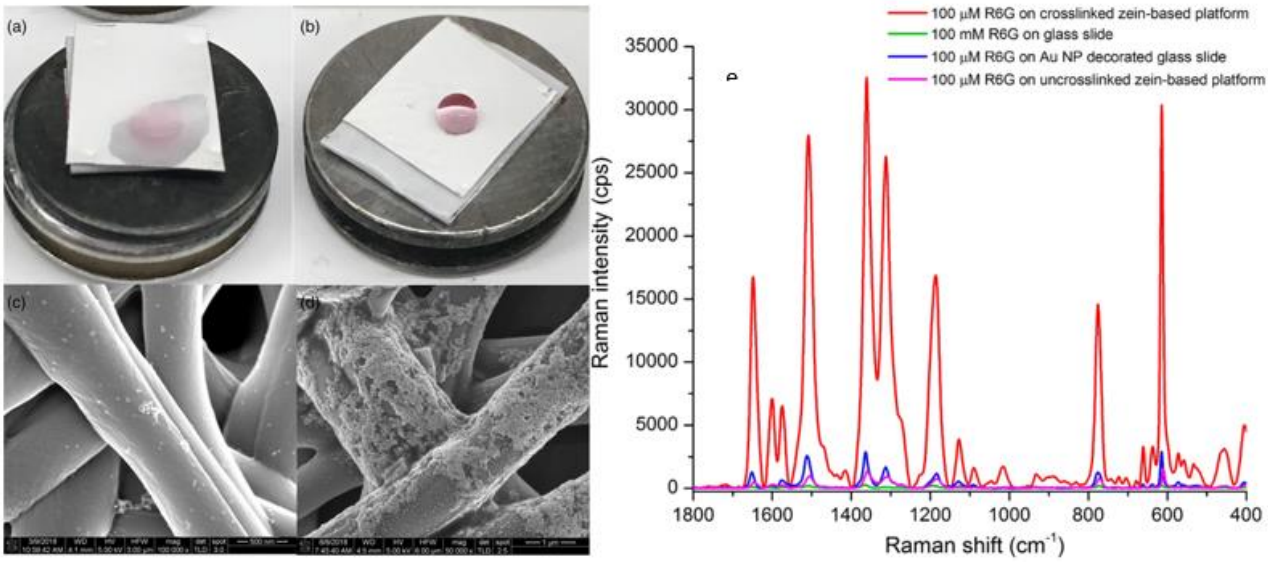

Figure 5 Decoration of zein nanofibers with gold nanoparticles and the effect of chemical crosslinking on the sensitivity of the biosensor [57, 74].

In a follow-up study, the sensitivity of zein electrospun based sensor platforms were further optimized by the testing different metallic nanoparticles for decoration and testing different concentrations of nanoparticle colloids [57]. First, the surface of zein nanofibers were decorated with gold, silver, silver-shelled-gold or a physical mixture of gold and silver nanoparticles, separately, and the SERS enhancement factors were measured using Rhodamine 6G as the Raman marker. Silver-shelled-gold nanoparticles gave the highest signal enhancement of the analyte, consistent with the results of [56]. Further optimization of the shell nanoparticle concentration showed that at 10^{12} particles/mL surface decoration, the sensors produced the highest SERS enhancement factor, and the highest nanoparticle concentration in fact did not create the highest number of hotspots as one would expect, since it covered the surface area of the nanofibers excessively and blocked the majority of the surface created by the 3D structure of nanofibers. This optimized zein nanofiber platform was then tested on the detection of a food carcinogen, acrylamide, which can form in fried or roasted food materials like french fries or coffee. A limit of detection of 2.06 ng/L was achieved for acrylamide, which was lower than the measurements done by chromatographic measurements such as GC-MS or LC-MS/MS, which are considered as the standard methods.

Another example of a natural polymer used in the fabrication of a biosensor in the form of electrospun nanofibers is cellulose acetate [65]. An electrochemical paper-based analytical device (ePAD) was created to measure the glucose levels in whole blood samples. First, cellulose acetate was electrospun, followed by deacetylation in an alkaline solution and trimethyl chitosan (TMC) treatment for smoothness. Screen-printed electrons (working electrode, counter electrode, and reference electrode) were fabricated on the fiber mats by sputtering a thick gold layer on the mats. The surface of the working electrode was further modified with reduced graphene oxide. Finally, glucose oxide was immobilized on the surface of the nanofiber mats in order to catalyze the oxidation of glucose, which is introduced to the system upon sample deposition. Once glucose in the blood oxidizes into gluconic acid, Fe^{+3} was dropped onto the surface of the nanofiber mats, which acted as a mediator to facilitate the electron transfer reactions near the electrodes and increased the sensitivity of the measurement. This ePAD was successfully measured blood glucose in the ranges of 3.3-27.7 mM, with a detection limit of 0.1 mM.

A greener step was taken in the production of mass sensitive biosensors that use Quartz crystal microbalances (QCMs) by decorating the surface of QCMs with amyloid like bovine serum albumin electrospun fibers [66]. This strategy was successfully tested on the detection of lysozyme, which proved that the immobilization of the target analytes on the surface of the transducers can be simplified by this greener approach and eliminate the other synthetic or polymeric methods.

Chitosan is another animal-based polymer repeatedly used in the formation of electrospun fibers, which were employed in the fabrication of biosensors. An electrochemical biosensor was designed with hybrid electrospun nanofibers which consisted of polyvinylpyrrolidone (PVP)/chitosan (Chi)/reduced graphene oxide and was successfully used in the detection of 17α-ethinylestradiol (EE2) (a female synthetic hormone) with a LOD of 0.15 pmol L^{-1} [67]. Electrospun chitosan nanofibers were also used for developing a point-of-care colorimetric cholesterol biosensor, which gave a detection limit as low as 50 mg/dL [68].

Even though there are still a limited number of biosensor studies in the literature, where the food-based polymers form the bigger portion of the biosensor platforms, there are many examples where these polymers are incorporated into some parts of the biosensors in the effort to provide greener detection methods.

4. Synthesis of Nanocomposite Films

4.1 Nanocomposites for Functional Film Applications

Due to their relative availability, ability to form films, biodegradability, and nutritional value, plant and animal proteins have garnered more attention recently and are being employed in the food packaging applications more frequently. Ideally, protein-based films intended for use in food packaging needs to be robust, resilient with minimal permeability. With a focus on the use and fusion of technical breakthroughs, this section of the review seeks to provide an overview of current state-of-the-art protein-based films applied as biodegradable materials relevant to functional film and sensor applications. These developments consist of plasticization, nanotechnology, and composite films. An emerging field of study is nanocomposite films with well-controlled design. Nanocomposite film research offers the chance to create packaging materials and biofilms with the specifically desired functional qualities [75].

Biopolymer nanocomposites are defined as biopolymer matrices supplemented with fillers or

nanoparticle smaller than 100 nm, which enhance their thermal, barrier and mechanical characteristics [76]. In recent years, there has been a lot of research done on the inclusion of, nanoliposomes, nanoemulsions and nanoparticles in protein-based films. The water- and light-barrier properties are enhanced by the inclusion of nanoliposomes. The steric influence of the nanoliposomes and discontinuities into the matrix, however, cause the film's strength and extensibility to decline [77]. Because of the porosity created by the inclusion of nanoemulsions into protein films, which decreases their water vapor permeability while increasing their extensibility and decreasing their solubility [78, 79]. Due to the increased interaction surface between the nanoparticle and the protein matrix, and the resulting formation of hydrogen bonds between them, the addition of NPs, which are positioned in the links between the film-forming polymers, prevents the diffusion of gases and water molecules throughout the film. This increases the films' tensile strength. Nanoparticles that have shown such phenomena are Montmorillonite (MMT) nano-clay [80], Laponite [81, 82], chitosan [83], zein [84], carbon [85], silver [86] etc. On the other hand, plant proteins like wheat proteins, zein, kafirin, peanut protein, soy protein, and other biopolymers like starch, cellulose, chitosan etc. have been suggested as potential possibilities for eco-friendly plastic materials that can be functionalized using different types of nanomaterials [87-90]. On the other hand, plant proteins like wheat proteins, zein, kafirin, peanut protein, and, soy protein, have been suggested as potential possibilities for eco-friendly plastic materials that can be functionalized using different types of nanomaterials.

Zein, a maize prolamin, has high potential for functional film application due to their superior biocompatibility, biodegradability, and non-toxicity. Therefore, it is often studied as a biorenewable material that may be used in place of petroleum-based polymers in a variety of applications. In a study by Rouf et al. the mechanical, thermal, and barrier characteristics of zein films cast from 70% ethanol solutions were dramatically enhanced by nanocomposite creation with the inclusion of silicate nanoparticles (Laponite®). Based on FTIR results, a method for the creation of zein-Laponite® nanocomposite is presented, suggesting Laponite® nanoparticles attach to zein molecules by forming Si-N bonds. Transmission electron microscopy (TEM) images showed that up to 5% addition of Laponite®, uniform exfoliation was visible, but at higher levels of Laponite® (10%) aggregation took place (Figure 6). Water contact angle measurements were used to analyze the changes in the surface energy of the films and revealed an increase in surface hydrophobicity. With increasing nanoparticle concentration, the Young's modulus and tensile strength increased as well. Water vapor permeability decreased as the glass transition temperature increase [81].

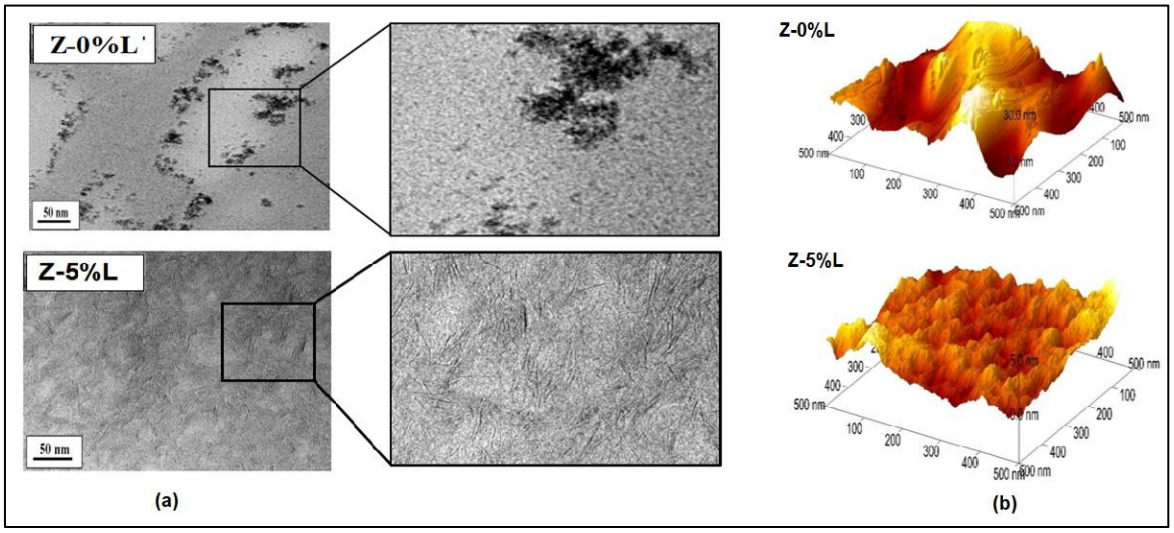

Figure 6 (a)TEM micrographs of plasticized zein film with 0% Laponite® (Z-0%L) and 5% Laponite® (Z-5%L), (b) AFM images of plasticized zein film with 0% Laponite® (Z-0%L) and 5% Laponite® (Z-5%L) [81].

In another study, by the same group, mixing graphene oxide (GO) nanoparticles with zein (Z) during the solvent casting process, it was possible to create zein nanocomposite films with excellent mechanical, barrier, and thermal characteristics. The research provides a mechanistic explanation of how graphene oxide nanofiller affects the physicochemical characteristics of zein. When graphene oxide (Z-GO) nanocomposites were examined under a TEM, the GO sheets were uniformly dispersed up to 1%GO loading. Based on the results of FTIR, Fourier Transform (FT)-Raman, and Differential scanning calorimetry (DSC), mechanisms for the creation of Z-GO nanocomposite through covalent and noncovalent bonding are developed. A nanocomposite film's Young's modulus increased by 300% and its tensile strength by 80% with only 3% loading. According to Atomic force microscopy (AFM) images, improvements in mechanical properties are followed with increases in surface roughness. Even though GO is hydrophilic due to the presence of -OH functional groups, due to their orientation in the films Z-GO nanocomposite films exhibited hydrophobic characteristics. The volume and intensity of GO exfoliation as well as the relative orientation of GO nanoparticles inside the zein film all have a significant impact on the changes in the film's physical properties. Testing for water vapor permeability revealed that the films grew less permeable as GO addition increased. Thermogravimetric analysis (TGA) results indicated that GO enhanced thermal stability [91].

Kafirin, a similar protein to zein, was also studied for nanocomposite functional film formation [82]. The main goal of the study was to assess how adding Laponite® to kafirin films affected their mechanical, surface, and barrier characteristics. Using 70% ethanol, glacial acetic acid and sodium metabisulphite as solvents, kafirin was extracted at 70°C. Use of these solvents gave the extracted kafirin a less hydrophobic nature compared to prior research. Following plasticization with an equal amount of glycerol, lactic acid and polyethylene glycol, kafirin was loaded with various Laponite® concentrations (1, 3, 5, and 10% by weight). TEM, FTIR, water contact angle (WCA), water vapor permeability (WVP), optical microscopy and mechanical characteristics were used to analyze kafirin nanocomposite films (TEM). Collectively, these metrics aided in understanding how Laponite® and kafirin interact. The relative hydrophilicity was associated with the α-helix and β-sheet composition.

When Laponite® was added to kafirin films, the films were more durable and less ductile, but the WVP did not alter much.

Similar to this study, other studies have also found that during nanocomposite formation process empty space between biopolymer chains can be filled with nanofillers, increasing the intermolecular attraction force and making the matrix of the biopolymer more robust with less permeability. Films made of starch, chitosan, konjac glucomannan, alginate, fenugreek seed gum, agar, soy protein, CMC, and whey protein have all shown improved water vapor barrier property and increased tensile strength after the inclusion of nanofillers. The connection between the nanofiller and the biopolymer matrix, where hydrogen and covalent bonds, for example, hydroxyl groups of biopolymers are formed, may also cause the phenomenon of increasing tensile strength. This results in the strengthening of molecular forces between nanoparticles and the biopolymer. The values of tensile strength of gelatin films increased when nanoclay was present in a gelatin matrix. The same pattern was noted in starch-polyvinyl alcohol films containing cellulose nanocrystals (CNC). The stiffness of the CNC and the creation of hydrogen bonds between the CNC and the polymer matrix were found to increase the mechanical properties of these films [87].

The findings show that protein-based films' functional characteristics are still incomparable to those of synthetic films, but promising prospective approaches may help protein-based films' mechanical and barrier qualities even further. Although nanocomposite technology is still in its infancy, it has already shown promise for enhancing the barrier and mechanical capabilities of the pristine polymer. In order to promote the use of biopolymers in food packaging, current research are concentrating on the construction and expansion of more suitable nanocomposite systems [75].

4.2 Nanocomposites for Sensor Applications

The use of biomolecule immobilization in a variety of applications, including immunosensors, electrochemical sensors, wastewater treatment, biofuels, and other areas, has caught the interest of several disciplines, including fine chemistry and biomedicine. The substrate and immobilization technique used determine how well immobilized biomolecules perform. In sensor applications, zein is anticipated to provide a favorable environment for biomolecules immobilization due to its extraction from natural sources, a multitude of functional groups and stability in aqueous solutions. Zein also offers promise for wearable biocompatible sensors and biosensors for applications in health monitoring, sports and cosmetics [6, 92].

Electrochemical biosensors that include hemoglobin are effective at detecting hydrogen peroxide by oxidizing the iron ion, however hemoglobin immobilization technique is crucial for attaining high efficiency in these types of sensors. Due to its high promise in biomolecule immobilization, zein in conjugation with carbon black is used to immobilize hemoglobin and create an electroactive film that could detect hydrogen peroxide using differential pulse voltammetry (DPV). Additionally, the biosensor was able to identify H_2O_2 in commercial samples of milk, oxygenated water and synthetic serum (both glycoside and physiological). According to SEM and TEM images, the porous film with hemoglobin anchored on zein microspheres and carbon black exhibited outstanding performance due to its wide surface area and conductive nature. This is a significant study as it shows that protein from sustainable sources (zein) and carbon black, which is a cheap form of carbon can work together to create a matrix for anchoring biomolecules and fabricate a highly efficient sensor detection range between 4.9×10^{-6} to 3.9×10^{-4} mol L^{-1}, and

detection limit of 4.0×10^{-6} mol L^{-1} [69].

Zein protein's biomolecule immobilization capabilities have been utilized in another sensor research [70], where zein is combined with three types of nanoparticles Laponite®, carbon nanotubes (CNT) and graphene oxide (GO) with the objective of fabricating electrochemical sensor that could identify the protein "gliadin," which causes a dangerous autoimmune illness called celiac disease. In the manufacturing process, zein is combined with the nanoparticles, to substitute harmful synthetic compounds that are used to attach the capture antibody in the working electrode. Biodegradable coatings made from zein nanocomposites, including zein-multiwalled carbon nanotubes (Z-MWCNT), zein-graphene oxide (Z-GO) and zein-Laponite® (Z-LAP) were tested using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and square wave voltammetry (SWV). When the electrochemical signals from pristine zein and the three nanocomposites were compared, Z-MWCNT produced the strongest and highest signals. Due to zein's multiple functional groups capable of attaching the capture antibody and target, and the high electrical conductivity of MWCNT, Z-MWCNT acts as a high-performance natural linker molecule in a sensor. Layer-by-layer deposition was used to functionalize the electrochemical sensor's active tip with a sequence of Z-MWCNT nanocomposite, and other linker molecules. Both SWV and CV curves have been used to show the gradual attachment of gliadin antibody onto the electrode with Z-MWCNT. The biosensor effectively provided CV signals for gliadin allergens at levels as low as 8×10^{-7} mol L^{-1}. When tested against other dietary toxins including acrylamide and formamide, the sensor showed high selectivity for gliadin, and the Z-MWCNT nanocomposite remained stable over a 30-day period [70].

For the detection of fenitrothion (FT), zein and single-walled carbon nanohorns (SWCNH) modified glassy carbon electrode (GCE) has been studied using the differential pulse adsorptive cathodic stripping voltammetry (DPACSV) technique [71]. SEM, CV, and EIS were used to characterize the suggested film. Using the CV and EIS curves, the functionalized electrode (SWCNH-ZE/GCE) showed a 3-fold greater electroactive surface area and a quicker electron transfer kinetic than bare GCE in terms of electrochemical characterization. DPACSV technique were used to analyze the analytical curve, which showed a linear response with a limit of detection (LOD) of 1.2×10^{-8} mol L^{-1}. The suggested sensor was effectively used to determine the presence of FT in samples of orange juice and natural water. Additionally, due to the superior film stability, the sensor demonstrated strong reproducibility and repeatability, indicating that the suggested design has several potential uses in sensing and biosensing.

Another study using zein (Z) as the support material and deep eutectic solvents (DM) as crosslinker, developed a magnetic molecularly imprinted polymer (ZDM-MIPs) that could adsorb and detect aspartame (ASP) [93]. A portable electrochemical detection station, that measures the electrochemical response of the ZDM-MIPs modified magnetic glassy carbon electrode (ZDM-MIPs-MGCE) using DPV and CV was applied to measure the presence of ASP in sample. A linear correlation between ASP concentrations in the range of 0.1-50 $mgmL^{-1}$ was suggested by the ZDM-MIPs-MGCE electrochemical response. With recovery percentages ranging from 84% to 107%, the sensor systems showed outstanding precision and accuracy. These results indicated that the ZDM-MIPs produced had a high capacity for ASP adsorption for soft drinks, and this technique may be applied to measure ASP in actual food samples.

Rattanopas et al. studied the fabrication and evaluation of efficient amperometric sensors for the cathodic sensing of hydrogen peroxide (H_2O_2) [94]. The suggested electrodes combine a carbon

nanotube (CNT)/Prussian Blue (PB) layer for H_2O_2-signaling with a coating of zein/gelatin biopolymers for preventing PB leakage. The screen-printed carbon electrode (SPCE) platform's carbon disk was coated sequentially with CNT suspensions in a PB solution, zein in ethanol, and gelatin in water to create the sandwich-type sensor. The sensor response was linear up to 700 M ($R^2 > 0.998$) in calibration trials, with a sensitivity of 0.425 μA μM^{-1} cm^{-2} and a LOD of 1 μ mol L^{-1}. Gelatin-zein-PB/CNTSPCEs quantification of H_2O_2 in model and actual samples demonstrated a recovery of about 100% of the genuine value. Gelatin-zein-PB/CNT-SPCEs proved to be an efficient tool for electrochemical H_2O_2 studies in health care goods, human body fluids and bleach and germicide companies, because their simple and inexpensive, and precise target evaluations. The study recommended that their H_2O_2 probes will be particularly useful for employees with little background in sensor manufacture and limited resources.

Zein has proven to be an excellent green alternative to synthetic immobilizing compounds used in sensors. Proteins similar to zein, like silk, is also being investigated for sensor fabrication. Jo et al. reported on extremely stretchy and conformal electronic skin (e-skins) that incorporate metallic nanowire networks and silk protein hydrogel. Under hydration, the e-skins have good extensibility and stability [72]. These characteristics enable the e-skins to simultaneously monitor strain-sensing, electrochemical and electrophysiological signals. Dual functional e-skins for monitoring temperature and pressure sensing data were created by Wang et al. and built using carbon fiber membranes generated from silk nanofibers (Silk CFM) [95]. By using Chitosan (CB) as a binder, Luo et al. have proposed a straightforward and efficient technique to create a MWCNT functionalized compressible carbon aerogel flexible sensor [96]. CB has the ability to connect multiwalled CNTs into continuous lamellas, creating robust 3D structures. Even after 50,000 cycles of strain-release, the MWCNTs/CB hybrid aerogel could experience a high compression strain of 90% with just 8% deformation at 50% strain. New electrically conductive multifunctional nanocomposites with self-healing properties based on micro-structured chitosan fibers and MWCNTs have also been reported [97]. Studies summarized in this section can also be found as a list in Table 2.

In electrochemical sensors biopolymer substrates are usually combined with conductive nanoparticles to produce conductive biopolymer nanocomposite anchoring platforms for efficient capture of targets. The chemistry behind the immobilization capabilities of zein and other green compounds have not been extensively studied. With more research, protein-based biopolymers like zein and other types of biopolymers can serve as an integral part in sensors for immobilization loading, efficiency, and stability.

5. Conclusions

In this review, some of the most recent studies focusing on fabricating nanomaterials from greener polymers are summarized in three main categories. Nanodelivery systems were categorized as coacervate nanoparticles, layer-by-layer nanotubes, hollow nanoparticles and nanofibers. The studies that synthesized nanodelivery systems as coacervate nanoparticles, and layer-by-layer nanotubes showed the importance of optimizing the pH to maximize the attraction between the proteins to ensure higher encapsulation of bioactives. Also, the molar charge ratio and the order of addition were shown to greatly impact the size of the nanoparticles and the enthalpy of reaction. With hollow nanoparticles, a novel sacrificial template method was introduced and the superiority of hollow nanoparticles to solid nanoparticles were shown. Electrospun nanofibers were also shown

as another branch of green nanodelivery systems, where surface properties can be easily modified as desired. Nanophotonic film or nanofiber-based biosensors were also summarized, where the platforms were either fabricated from biodegradable corn protein-based films or fibers, paper or cellulose. The results of these studies showed that plant-based polymers show great potential to replace synthetic polymers and the biosensors created with them have comparable sensitivities. Lastly, synthesis of nanocomposite films was discussed where a plant-based protein was coupled with nanofillers, such as graphene oxide, carbon nanotubes, Laponite® or carbon black. The characterization of these films with various techniques showed that highly sensitive electrochemical sensors can be created using the green nanocomposite films. Overall, this review aims to provide an understanding of the science behind creating green nanomaterial-based systems and show their applications in food, pharmaceutical and agricultural industries.

Abbreviations Used

AFM	Atomic Force Microscopy
CNT	Carbon nanotube
DSC	Differential Scanning Calorimetry
EF	Enhancement Factor
EIS	Electrochemical impedance spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
FT-Raman	Fourier Transform Raman Spectroscopy
LbL	Layer-by-layer
LOD	Limit of detection
MWCNT	Multiwalled carbon nanotubes
PDMS	Polydimethylsiloxane
SEM	Scanning Electron Microscopy
SERS	Surface Enhanced Raman Spectroscopy
TEM	Transmission Electron Spectroscopy
TGA	Thermogravimetric Analysis

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Author Contributions

Hazal Turasan: Contributed to the conception and design of the article, reviewed the relevant literature, drafted the article, and revised it critically for important intellectual content. Tahrima B. Rouf: Reviewed the relevant literature, drafted the article, and revised it critically for important intellectual content. Tuncay Yilmaz: Reviewed the relevant literature and contributed to drafting the article. Jozef Kokini: Lead supervisor of the article, contributed to the conception, design, review and editing of the article.

Competing Interests

The authors declare no conflict of interest.

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