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Chitosan–Agar Biopolymer Nanocomposites with Ag and Zr-Doped ZnO: A Comprehensive Review of Synthesis, Characterization, Functional Properties and Emerging Applications

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ABSTRACT

The integration of naturally derived biopolymers with functional nanoparticles has emerged as an important strategy for developing sustainable and multifunctional materials. Chitosan and agar are particularly attractive because of their biodegradability, biocompatibility, film-forming ability and abundance of reactive functional groups. Silver (Ag) nanoparticles provide strong antimicrobial and antioxidant functionality, whereas zirconium-doped zinc oxide (Zr–ZnO) offers tunable optical, photocatalytic, electrochemical and antibacterial properties. This review discusses the scientific basis for developing chitosan–agar biopolymer nanocomposites containing Ag and Zr–ZnO, with emphasis on synthesis approaches, polymer–nanoparticle interactions, characterization, functional properties and emerging applications. Previous studies have demonstrated that chitosan and agar form compatible blended films and that Ag nanoparticles can be generated in situ within chitosan–agar matrices using a green approach, with chitosan acting as a stabilizing component and agar contributing to reduction of silver ions. Related agar–ZnO and chitosan–ZnO systems further demonstrate the ability of natural polysaccharide matrices to accommodate metal-oxide nanoparticles while modifying mechanical, barrier, optical and antimicrobial properties. Zr doping provides an additional route for tuning the physicochemical characteristics of ZnO, including defect chemistry, optical response, surface activity and photocatalytic performance. The review critically compares reported preparation and characterization approaches and highlights the potential complementary functions of Ag and Zr–ZnO within a chitosan–agar matrix. Literature-derived performance data demonstrate strong antimicrobial activity in Ag/ZnO-containing agarose-based films and substantial photocatalytic activity of Zr–ZnO nanoparticles. Potential applications include active food packaging, antimicrobial coatings, wound-care materials, environmental remediation and multifunctional biodegradable films. Challenges related to nanoparticle dispersion, loading optimization, release, mechanical stability, scalability and environmental safety are also discussed. The combination of renewable biopolymers with Ag and Zr–ZnO represents a promising platform for the development of sustainable multifunctional nanocomposites...

Keywords: Chitosan; Agar; Silver nanoparticles; Zr-doped ZnO; Biopolymer nanocomposite; Antimicrobial activity; Photocatalysis; Green synthesis; Active packaging; Sustainable nanomaterials..

INTRODUCTION

The development of sustainable materials capable of replacing or reducing the use of conventional petroleum-derived polymers has become an important research priority. Natural polysaccharides have attracted particular attention because they combine renewable origin with biodegradability, biocompatibility and chemical functionality. Among these materials, chitosan and agar are particularly useful for the preparation of films, hydrogels and nanocomposites.

Chitosan is a partially deacetylated derivative of chitin and contains amino and hydroxyl functional groups that can participate in hydrogen bonding, electrostatic interactions and coordination with metal ions. It possesses film-forming ability and intrinsic antimicrobial characteristics, making it attractive for biomedical, agricultural and food-packaging applications. However, pure chitosan films can suffer from moisture sensitivity and limitations in flexibility and mechanical stability.

Agar is a seaweed-derived polysaccharide with strong gel-forming ability and good film-forming characteristics. When combined with chitosan, it can modify water affinity, swelling and surface characteristics. Elhefian et al. reported that chitosan and agar form compatible blended films with homogeneous morphology, while increasing agar content increased swelling and water affinity of the films.

The incorporation of nanoparticles into these biopolymer matrices provides an opportunity to overcome some limitations while introducing additional functions. Silver nanoparticles (AgNPs) are especially attractive because of their broad-spectrum antimicrobial activity. The antimicrobial behavior of AgNPs has been attributed to interactions with microbial membranes, release of silver ions and oxidative mechanisms (Rai et al., 2009)..

Importantly, Ag nanoparticles can be generated directly within a chitosan–agar matrix. Shi et al. demonstrated a green *in situ* synthesis of AgNPs using a chitosan/agar hydrogel. Agar acted as a reducing component, while chitosan stabilized the resulting particles. The AgNPs were spherical, predominantly monodispersed and approximately 10–15 nm in diameter, with an average size of about 12.25 nm.

Metal oxides provide another important class of functional nanofillers. ZnO nanoparticles are widely investigated because of their antimicrobial, optical and photocatalytic characteristics. ZnO has also been incorporated into agar and chitosan matrices. Kumar et al. developed agar–ZnO nanocomposite films and demonstrated their potential for active packaging, while chitosan/ZnO films have shown improved antimicrobial properties compared with unmodified chitosan films.

The incorporation of zirconium into ZnO provides an additional method for modifying the properties of the semiconductor. Zr-doped ZnO can exhibit changes in lattice structure, optical response, defect states, surface properties and photocatalytic behavior. Recent studies have demonstrated promising photocatalytic and antibacterial activity of Zr-modified ZnO nanoparticles.

The combination of chitosan, agar, Ag and Zr–ZnO is therefore scientifically attractive because each component can contribute a different function. Chitosan and agar provide a renewable polymeric framework; Ag provides strong antimicrobial activity; and Zr–ZnO can provide photocatalytic, optical and additional antimicrobial functionality.

However, it is important to distinguish between **reported component systems** and the **proposed integrated four-component composite**. The exact chitosan–agar/Ag/Zr–ZnO formulation remains comparatively underexplored. Therefore, this review integrates evidence from closely related systems to establish the scientific rationale, expected interactions and application potential of the proposed multifunctional nanocomposite.

2. Chitosan–Agar as a Biopolymer Platform

2.1 Chemical Characteristics

Chitosan contains amino groups that can become protonated under acidic conditions, together with hydroxyl groups that participate in hydrogen bonding. These groups make chitosan chemically versatile and capable of interacting with metal ions and nanoparticles.

Agar contains abundant hydroxyl groups and possesses strong gel-forming ability. The combination of the two polymers can produce a continuous matrix with modified swelling, wettability and mechanical characteristics.

Elhefian et al. demonstrated that chitosan–agar films exhibited compatibility and homogeneous morphology. Thermal and surface studies further indicated that blending agar with chitosan increased water affinity and swelling relative to pure chitosan.

2.2 Role of the Matrix in Nanoparticle Stabilization

The polymer matrix can act as more than a passive support. Functional groups in chitosan and agar can bind metal ions and nanoparticle surfaces, thereby helping to prevent aggregation.

In the AgNP@CS/Agar system reported by Shi *et al.,* the chitosan–agar hydrogel provided electron-rich functional groups capable of facilitating reduction of Ag ions and stabilizing the generated nanoparticles. The polymer coating also reduced nanoparticle aggregation.

This property is particularly important for multifunctional composites because excessive nanoparticle aggregation can reduce active surface area and create defects in the polymer film.

3. Green Incorporation of Silver Nanoparticles

Silver nanoparticles can be incorporated into biopolymer matrices through ex situ blending or in situ synthesis.

The *in situ* approach is particularly attractive from a green chemistry perspective because nanoparticle generation and stabilization occur within the polymer matrix. Shi et al. prepared chitosan/agar hydrogel using chitosan and agarose and subsequently introduced $AgNO_3$. Following heating, Ag nanoparticles were generated within the matrix. FTIR, SEM, TEM, EDX and XRD confirmed the formation and stabilization of Ag nanoparticles.

The reported AgNPs were spherical and approximately 10–15 nm in diameter. XRD showed characteristic metallic Ag reflections corresponding to the (111), (200), (220) and (311) planes.

This study provides strong evidence that chitosan–agar can function as a green nanoparticle-forming and stabilizing platform rather than simply serving as a structural polymer.

4. Incorporation of ZnO and Zr–ZnO into Biopolymer Matrices

ZnO nanoparticles have been extensively incorporated into natural polymer systems. Agar–ZnO films are a particularly relevant example because they directly demonstrate the ability of an agar matrix to stabilize ZnO nanoparticles.

Kumar et al. prepared ZnO nanoparticles using a green synthesis approach and incorporated them into agar films at 2 and 4% w/w. The resulting films showed increased thickness and elongation, although tensile strength and transparency decreased as ZnO loading increased. The films also demonstrated potential for extending the shelf life of green grapes under ambient storage.

The same study reported ZnO nanoparticle sizes of approximately 14–48 nm, with an average size of 24.75 ± 0.78 nm. The nanoparticles were incorporated into the agar matrix through solution casting.

Chitosan–ZnO systems provide complementary evidence. Chitosan/nano-ZnO films have demonstrated improved antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*, with smaller ZnO nanoparticles producing stronger bacteriostatic effects in the reported study.

More recent work has shown that chitosan films containing phytosynthesized ZnO nanoparticles can exhibit substantial antimicrobial activity. A 2025 study reported that 5% w/v ZnO provided an effective balance of antimicrobial performance and material usage, with inhibition zones of 33, 31 and 27 mm against *E. coli*, *S. aureus* and *Candida albicans*, respectively.

These results support the broader feasibility of using polysaccharide matrices for ZnO nanoparticle incorporation.

5. Why Zr-Doped ZnO is Relevant to the Composite

Zr doping provides a method for modifying the physicochemical characteristics of ZnO without abandoning the fundamental advantages of the ZnO semiconductor.

Naik et al. investigated Zr-doped ZnO nanoparticles prepared through a sol–gel method and reported changes in structural, optical, electrochemical and antibacterial properties with Zr concentration. Their results demonstrate that Zr can modify the functional behavior of ZnO and potentially broaden its application range.

Recent work has further demonstrated that Zr-modified ZnO nanoparticles can provide strong photocatalytic and antibacterial performance. A 2025 study reported successful Zr incorporation, a reduction in band gap from 3.11 to 3.05 eV and nearly complete degradation of Reactive Red 120 using 3 wt% Zr-doped ZnO under both UV-A and sunlight conditions. The material also showed enhanced bacterial inhibition against several bacterial species.

Embedding Zr–ZnO within chitosan–agar could therefore provide a flexible and biodegradable support for a semiconductor nanomaterial with photocatalytic and antimicrobial functionality.

Table 1. Reported biopolymer–nanoparticle systems relevant to chitosan–agar/Ag/Zr–ZnO composites

Reported system	Main preparation approach	Important findings	Relevance to proposed system
Chitosan–agar blend	Solution blending	Compatible films, increased swelling and water affinity	Provides polymer matrix
AgNP@chitosan–agar	In situ green synthesis	Spherical AgNPs, ~10–15 nm; strong polymer interaction	Direct evidence for Ag incorporation
Agar–ZnO	Green ZnO + solution casting	Improved film functionality; active packaging potential	Direct evidence for ZnO in agar
Chitosan–ZnO	Solution blending/casting	Improved antibacterial properties	Supports ZnO incorporation into chitosan
Chitosan–AgNP	Green Ag synthesis + film formation	Antimicrobial, antioxidant and barrier improvements	Supports Ag functionality
Sericin–agarose/Ag/ZnO	Layer-by-layer assembly	Strong antibacterial activity and good film properties	Supports combined Ag/ZnO–agarose concept

Zr–ZnO nanoparticles	Sol–gel/hydrothermal/other routes	Modified optical, structural, antibacterial and photocatalytic properties	Provides multifunctional oxide component
Chitosan–agar/Ag/Zr–ZnO	Emerging concept	Expected multifunctional biodegradable nanocomposite	Research opportunity

The literature therefore provides evidence for each major component and for closely related hybrid systems, but the complete four-component system remains an emerging research direction. Related Ag/ZnO–agarose work has demonstrated synergistic antimicrobial behavior when Ag and ZnO were assembled on an agarose-containing film.

6. Preparation Strategies for the Proposed Composite

Several preparation routes can be considered for chitosan–agar composites containing Ag and Zr–ZnO.

6.1 Solution Blending

In a conventional approach, chitosan and agar are separately dissolved or dispersed and then mixed. Pre-synthesized Ag and Zr–ZnO nanoparticles can subsequently be dispersed into the polymer solution before casting.

The main advantage is process simplicity. However, nanoparticle aggregation must be carefully controlled.

6.2 In Situ Ag Formation

A greener strategy would first prepare the chitosan–agar matrix and then introduce Ag^{+} ions, allowing AgNPs to form directly within the matrix.

The Shi et al. study provides a direct precedent for this strategy.

6.3 Ex Situ Zr–ZnO Incorporation

Because Zr–ZnO requires controlled inorganic synthesis conditions, it may be preferable to synthesize the nanoparticles separately and subsequently introduce them into the chitosan–agar solution.

This approach provides better control over Zr concentration, crystallinity and particle size.

6.4 Sequential Assembly

A sequential approach could combine:

Chitosan + agar matrix → Ag nanoparticle formation → Zr–ZnO dispersion → film casting/crosslinking

This approach may allow independent optimization of Ag and Zr–ZnO concentrations.

7. Structural and Physicochemical Characterization

A comprehensive characterization strategy is essential because the performance of the composite depends strongly on nanoparticle dispersion and polymer–nanoparticle interactions.

7.1 FTIR

FTIR can identify changes in O–H, N–H, C–O and other functional groups following nanoparticle incorporation. Shi et al. reported shifts in characteristic bands after Ag incorporation into chitosan–agar, indicating interactions between polymer functional groups and Ag nanoparticles.

7.2 XRD

XRD can identify the crystalline phases of Ag and Zr–ZnO while also determining whether the polymer matrix remains predominantly amorphous or semicrystalline.

The AgNP@CS/Agar system exhibited characteristic metallic Ag reflections, confirming successful Ag formation.

7.3 SEM and TEM

SEM can provide information about film morphology, cracks and nanoparticle distribution. TEM is useful for measuring individual nanoparticle dimensions.

For AgNP@CS/Agar, TEM demonstrated approximately 10–15 nm spherical particles.

7.4 EDS and Elemental Mapping

EDS can confirm the presence of Ag, Zn and Zr, while elemental mapping can determine whether the nanoparticles are distributed uniformly.

7.5 UV–Visible Spectroscopy

Ag nanoparticles exhibit surface plasmon resonance, while Zr–ZnO contributes semiconductor absorption. Changes in absorption may therefore provide evidence of nanoparticle formation and optical interaction.

7.6 Thermal Analysis

TGA and DSC are useful for evaluating whether nanoparticle incorporation modifies thermal degradation and polymer transitions.

7.7 Mechanical and Barrier Testing

For films intended for packaging or coatings, tensile strength, elongation, water-vapor permeability, water absorption and contact angle should be measured.

Agar–ZnO films have demonstrated clear loading-dependent changes in tensile strength and elongation. At 2% ZnO, tensile strength decreased from 51.02 MPa for control agar to 29.19 MPa, while elongation increased from 27.90% to 32.63%. At 4% ZnO, tensile strength was 20.68 MPa and elongation increased to 37.23%.

8. Antimicrobial Functionality

Antimicrobial activity is expected to be one of the most important functions of the proposed composite.

Ag nanoparticles are well established as broad-spectrum antimicrobial materials. Their activity can involve membrane disruption, Ag^+ release, interaction with proteins and nucleic acids and oxidative stress (Rai *et al.,* 2009).

Chitosan itself contributes antimicrobial activity through interactions between protonated amino groups and negatively charged microbial surfaces.

ZnO nanoparticles can contribute through reactive oxygen species, Zn^{2+} release and nanoparticle–cell interactions. Raghupathi et al. demonstrated that antibacterial activity of ZnO nanoparticles is strongly dependent on particle size and associated surface processes.

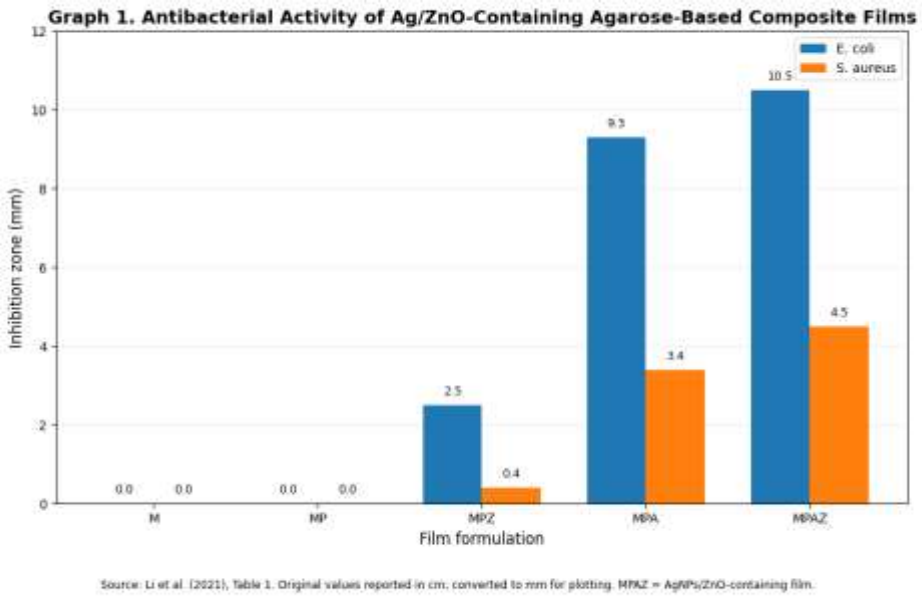
Zr modification can further alter the surface and defect properties of ZnO. Recent Zr–ZnO research has demonstrated enhanced antibacterial performance against several bacterial species.

The combination of Ag and Zr–ZnO may therefore provide multiple antimicrobial mechanisms. However, **synergistic activity should be experimentally demonstrated rather than assumed**.

9. Literature-Based Antimicrobial Comparison

A closely related study by Li et al. (2021) assembled AgNPs and ZnO nanoparticles onto a sericin–agarose composite film. Although the polymer matrix was sericin–agarose rather than chitosan–agar, it provides useful evidence for the behavior of Ag/ZnO combinations on agarose-containing biopolymer films.

The AgNP/ZnO-containing film showed the largest bacteriostatic zones among the tested film formulations. Against *E. coli*, the AgNP/ZnO film produced a zone of approximately 1.05 cm, while against *S. aureus* the zone was approximately 0.45 cm.



Graph 1. Antibacterial activity of Ag/ZnO-containing agarose-based composite film

The reported results demonstrate that the combined Ag/ZnO system can produce stronger antibacterial behavior than the corresponding individual nanoparticle-containing films in that particular agarose-based system. The study attributed the improved performance partly to the interaction between AgNPs and ZnO and reported potential applications in antimicrobial biomaterials, wound dressing and tissue engineering.

This evidence is relevant to the proposed chitosan–agar/Ag/Zr–ZnO system, but it should not be interpreted as direct experimental evidence for the exact proposed formulation.

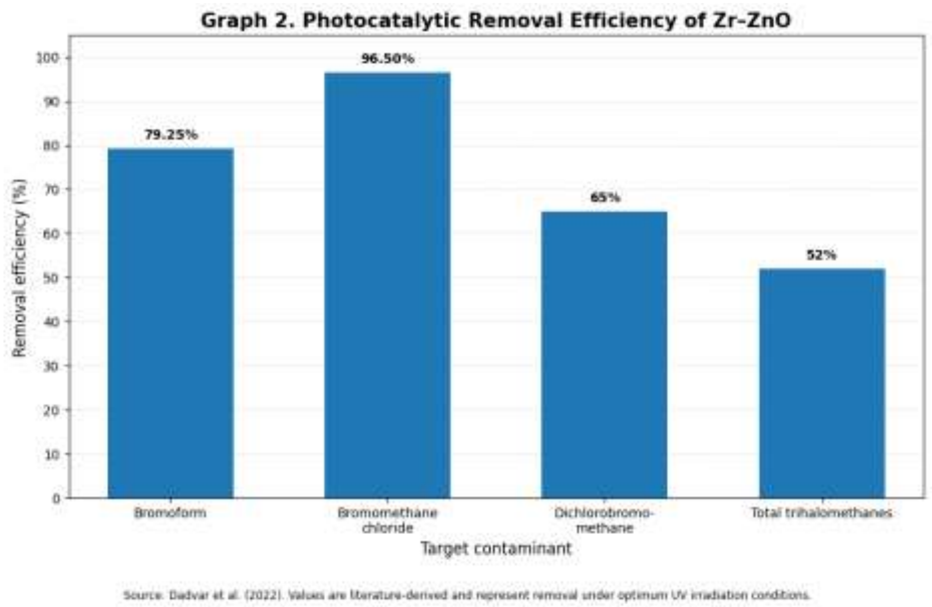
10. Photocatalytic Functionality of Zr–ZnO

The second major functionality expected from the proposed composite is photocatalytic activity.

ZnO can generate electron–hole pairs under irradiation. Zr incorporation may modify charge separation, surface defects and adsorption behavior. The photocatalytic activity therefore depends on both the semiconductor properties and the accessible surface area.

Recent Zr-modified ZnO research demonstrated nearly complete degradation of Reactive Red 120 using 3 wt% Zr-doped ZnO under UV-A and sunlight irradiation. The reported study attributed the improvement to reduced band gap and enhanced charge separation.

A related hydrothermal Zr–ZnO study reported substantial removal of trihalomethanes, including 79.25% bromoform, 96.5% bromomethane chloride, 65% dichlorobromomethane and 52% total trihalomethanes under optimum UV conditions.



Graph 2. Photocatalytic removal efficiency of Zr–ZnO

The highest removal was observed for bromomethane chloride at 96.5%, whereas total trihalomethanes showed 52% removal under the reported optimum UV conditions.

When Zr–ZnO is embedded into a chitosan–agar matrix, the polymer can provide a flexible support and prevent nanoparticle aggregation. However, excessive polymer coverage could also shield active semiconductor surfaces. Therefore, an optimum balance between polymer content and Zr–ZnO loading will be essential.

11. Packaging and Environmental Applications

11.1 Active Food Packaging

Agar–ZnO films have already demonstrated potential for active food packaging. Kumar et al. reported that green grapes packaged with agar–ZnO films maintained fresh appearance for up to 14 and 21 days for 2% and 4% ZnO formulations, respectively, under ambient conditions.

Chitosan–ZnO films have similarly demonstrated antibacterial activity, supporting the possibility of combining chitosan and agar to obtain biodegradable active packaging.

Ag incorporation could provide additional antimicrobial protection, while Zr–ZnO could potentially contribute photocatalytic and UV-related functions.

11.2 Antimicrobial Coatings

The combined antimicrobial effects of chitosan, Ag and Zr–ZnO make the composite attractive for antimicrobial coatings on surfaces, packaging materials and biomedical devices.

11.3 Wound-Care Materials

Agarose-based Ag/ZnO films have already been investigated for wound dressing and tissue-engineering applications. The reported Ag/ZnO–sericin/agarose system exhibited desirable hydrophilicity, water absorption and antibacterial behavior.

Chitosan provides additional relevance because of its biocompatibility and intrinsic antimicrobial properties.

11.4 Environmental Remediation

Zr–ZnO provides the strongest rationale for environmental applications because of its photocatalytic capability. A polymer-supported Zr–ZnO system could potentially be developed as a recoverable film or coating rather than using free nanoparticles in suspension.

Table 2. Functional roles, advantages and limitations of the proposed components

Component	Main functional role	Potential advantage	Main limitation/consideration
Chitosan	Biodegradable matrix; antimicrobial support	Biocompatible, film-forming, reactive amino groups	Moisture sensitivity
Agar	Gel/film-forming matrix	Renewable, strong gel formation, hydrophilic	Can alter mechanical strength at high content
Ag nanoparticles	Antimicrobial/antioxidant	Strong broad-spectrum antimicrobial activity	Release and toxicity require control
Zr–ZnO	Photocatalytic/antimicrobial/optical	Tunable semiconductor properties	Dopant concentration must be optimized
Chitosan–agar	Integrated matrix	Compatible renewable polymer blend	Swelling and water sensitivity
Ag + Zr–ZnO	Multifunctional nanophase	Potential complementary antimicrobial and photocatalytic activity	Possible aggregation and interfacial shielding
Complete composite	Sustainable multifunctional material	Packaging, coatings, biomedical and environmental applications	Exact formulation remains underexplored

12. Proposed Interaction Mechanism

The expected behavior of the composite can be summarized as:

Chitosan + Agar

↓

Hydrogen bonding / polymer-network formation

↓

Ag^+ reduction and AgNP stabilization

Zr–ZnO nanoparticle dispersion

↓

Polymer–nanoparticle interfacial interactions

↓

Antimicrobial + photocatalytic + barrier functionality

The chitosan–agar matrix can provide functional groups for nanoparticle interaction and a flexible support structure. Ag nanoparticles can contribute direct antimicrobial action, whereas Zr–ZnO can generate reactive species under irradiation and contribute additional antimicrobial and photocatalytic functionality.

This conceptual mechanism should be treated as a **literature-supported proposed model**, not as an experimentally demonstrated mechanism for the complete four-component system.

13. Challenges and Research Gaps

Several important challenges need to be addressed before the proposed composite can be considered practically mature.

13.1 Limited literature on the exact four-component system

The strongest limitation is that relatively few studies directly investigate chitosan–agar containing both Ag and Zr–ZnO. Therefore, the present review integrates evidence from related systems.

13.2 Nanoparticle dispersion

Both Ag and Zr–ZnO can aggregate at high concentrations. Aggregation reduces available surface area and may weaken the polymer matrix.

13.3 Optimization of nanoparticle loading

Increasing nanoparticle concentration does not automatically improve performance. Agar–ZnO studies demonstrate that higher ZnO loading can improve elongation while reducing tensile strength.

13.4 Controlled release

Ag release must be controlled for biomedical and food-related applications. A 2019 chitosan–AgNP film study demonstrated pH-dependent sustained release of AgNPs and Ag^+ ions, highlighting the importance of release behavior.

13.5 Photocatalytic accessibility

If Zr–ZnO nanoparticles become deeply embedded within the polymer matrix, the active surface available for light and pollutant interaction may decrease.

13.6 Safety

The toxicity and environmental fate of Ag and metal-oxide nanoparticles must be considered. The final composite should therefore be evaluated for nanoparticle migration, cytotoxicity, ecotoxicity and degradation behavior.

14. Future Perspectives

Future research should focus on systematic optimization of chitosan–agar ratio, Ag concentration and Zr–ZnO loading. Rather than changing several variables simultaneously, factorial or response-surface approaches could be used to determine interactions between polymer composition and nanoparticle loading.

Green synthesis is another promising direction. The ability of chitosan and agar to participate in Ag nanoparticle formation provides a useful basis for reducing dependence on conventional chemical reducing agents. Plant-derived reducing agents may also be incorporated into the synthesis strategy where appropriate.

For environmental applications, immobilized chitosan–agar/Zr–ZnO films could provide a recoverable photocatalytic platform. For packaging applications, Ag concentration and release should be optimized to achieve antimicrobial protection without unacceptable migration.

The combination of Ag and Zr–ZnO may also support multifunctional materials capable of both microbial control and contaminant degradation. However, synergistic effects should be established experimentally through direct comparison of individual and combined components.

15. Conclusion

Chitosan–agar biopolymer matrices provide a promising renewable platform for incorporating multifunctional nanoparticles. Their compatibility, film-forming ability and reactive functional groups allow them to interact with metallic and metal-oxide nanomaterials.

Published evidence demonstrates that Ag nanoparticles can be generated and stabilized directly within chitosan–agar matrices through a green *in situ* approach. The resulting AgNPs were spherical and approximately 10–15 nm in diameter, confirming the suitability of the polymer matrix for nanoparticle stabilization.

Related agar–ZnO and chitosan–ZnO systems demonstrate that metal-oxide nanoparticles can be incorporated into natural polymer films while modifying mechanical, optical, antimicrobial and packaging properties.

Zr-doped ZnO provides an additional functional dimension because Zr incorporation can modify the structural, optical, surface and photocatalytic characteristics of ZnO. Recent literature demonstrates promising photocatalytic and antibacterial performance of Zr–ZnO nanoparticles.

The integration of Ag and Zr–ZnO into a chitosan–agar matrix therefore represents a promising emerging concept for multifunctional biodegradable materials. Potential applications include active food packaging, antimicrobial coatings, wound-care materials and environmental remediation. Nevertheless, the exact four-component formulation remains comparatively underexplored. Future studies should therefore concentrate on nanoparticle dispersion, composition optimization, controlled release, photocatalytic accessibility, mechanical stability, scalability and comprehensive safety evaluation.

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