Green synthesized nanomaterials as an alternative to restricted chemicals in postharvest preservation of horticultural crops: a review

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Abstract. Synthetic chemicals have been successfully used to control economic postharvest pathogens such as *Botrytis cinerea*, *Penicillium* spp., *Rhizopus* spp., etc., thus reducing postharvest losses. However, their active ingredient and co-formulants have resulted in their use being restricted internationally due to health concerns and consumers' requests for safe and natural alternatives. As an alternative to chemicals, green synthesized nanomaterials incorporated with edible coatings in a polymer matrix have been successfully applied on horticultural crops to improve their shelf-life. Due to their known antimicrobial activities, plant extracts and nanoparticles such as silver and zinc oxide have been successfully used in food processing applications. Green sources are used as stabilizer and reducing agents to synthesize shape and size-controlled metal and metal oxide nanoparticles. Thus, eco-friendly nanoparticles are produced without using toxic materials and are cost-effective. Edible coatings form a thin layer that prevents oxidation, maintains the product quality, can be safely eaten as part of the product, and does not add unfavourable properties. Studies showed that edible coatings with or without green nanomaterials have been successfully used to control postharvest losses and improve the shelf-life of fruit crops such as plums, raspberries, etc.

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1 Introduction

Postharvest losses of fruits and vegetables are mainly caused by decay brought about by fungal plant pathogens [1]. According to the Food and Agricultural Organisation [2], one of the most feasible options for meeting future food needs is reducing postharvest losses. Postharvest losses pose a serious threat to the storage and marketability of fruits and vegetables, leading to nutrient loss and the spread of microorganisms responsible for degradation, leading to huge fresh produce losses[3-4]. Therefore, innovative technologies such as edible coatings (EC)[5] and controlled atmosphere (CA) are suggested as possible solutions for maintaining the quality of agricultural products during storage [3]. The spread of harmful microorganisms and the use of chemicals in postharvest preservation of horticultural crops poses a severe threat to the environment, crop quality and human health [6]. The application of green synthesized nanomaterial to control postharvest losses of horticultural crops has been generally regarded as safe [GRAS] to both the environment and human health [7-8]. The exceptional properties of green nanomaterials make them a practical choice for sustainable horticulture in general and in particular postharvest diseases of fruit and vegetable at the scientific and industry level[9]. The objective of this review was to document the application of green synthesized nanomaterials as an alternative to restricted chemicals in postharvest preservation of horticultural crops.

2 Economic importance of postharvest losses of horticultural crops

In the developing world, fruit and vegetable losses significantly impact poor and vulnerable people [2]. This comes in the form of social (health and livelihoods), environmental and economic costs[10]. According to FAO [11], about one-third of the edible parts of food produced for human consumption gets lost or wasted globally, which is about 1.3 billion tons per year. Food waste at the consumer level in industrialized countries (222 million tons) is almost as high as the total net food production in sub-Saharan Africa (230 million tons). Losses and waste in fruits and vegetables are the highest categories of losses among all types of foods, with up to 60 percent of all fruits and vegetables making their way to the landfill [2]. Horticultural losses impact food security for poor people, food quality and safety, economic development, and the environment [11]. Economically, postharvest losses of fruits and vegetables have a direct and negative impact on the income of both farmers and consumers [2], thus making food insecurity a question of access (purchasing power and prices of food) than a supply problem[10]. Improving the efficiency of the horticultural supply chain and reducing postharvest losses could reduce the high costs of fruits and vegetables and help bring down their cost and increase access for the consumers [10-11]. Given the high perishability of horticultural crops, the use of green nanomaterials, as an alternative to control postharvest losses, could be one way of reducing the economic cost of horticultural crops, improving their availability and increasing farmer income [9].

3 Green nanomaterials as a viable alternative to control postharvest losses of horticultural crops

The application of nanotechnology is largely promoted to develop active food packaging materials with excellent performance to protect horticultural crops and extend their shelf-life [12]. Promising performances of antimicrobial nano-coatings have been reported when they were applied on fresh fruits and vegetables [13-14]. Traditionally, nanoparticles (NPs) have been synthesized using physical and chemical methods and have high toxic residues, are expensive to produce, and are environmentally unfriendly [15]. Recently, green methods to synthesize metal-oxide nanoparticles have attracted much attention because they are simple, low cost and environment friendly [16-17]. These methods involve the use of plant, fruits, and vegetable extracts, which are used as stabilizers and reductant agents to control the crystal growth, and for scale-up and industrial production of NPs [18]. These plant extracts have organic compounds, such as polyphenols that act as reductants and amino and carboxylic groups that may help as stabilizers, favouring the conversion of metal compounds into specific NPs [19]. The application of green nanomaterial to control postharvest losses of horticultural crops is summarised in Table 1.

Table 1. Application of green nanomaterial to control postharvest losses of horticultural crops

Green material	Synthesized nanoparticles	Fruit/vegetable	Focus of the study	Key findings	Reference
Citrus sinensis peel extract	Zinc-oxide NPs	Strawberries	Application of Citrus sinensis nano-coatings on fresh strawberries to evaluate the preservation effect	Strawberries coated with citrus peel nanoparticles incorporated into carboxymethylcellulose sodium (CMC) had decreased weight loss, rate of rotting, and the storage quality was improved	[20]
α -pinene	Chitosan	Bell pepper	α -pinene chitosan nanoparticles in controlling to Alternaria alternata on bell pepper	The chitosan nanoparticles and edible coating inhibited A. alternata during the cold storage period of bell pepper and preserved the physicochemical quality.	[21]
chitosan/gum arabic (CH/GA)	ZnONPs	Banana	ZnO NPs incorporated into chitosan/gum Arabic (CH/GA) for the preservation of bananas	Banana coated with the CH/GA/ZnO maintained freshness for more than 17 d in comparison with the less than 13 d for the control banana at 35 °C and 54 % RH.	[22]
Olive and marjoram leaf extract	ZnO-NPs	Bell pepper	Evaluating disease management of gray and black mold of pepper fruits (artificially inoculated with the tested two fungi)	Results showed significant reduction to the appearance of both diseases of pepper fruits treated with any of the two green synthesized ZnO nanoparticles compared with chemically synthesized ZnO-NPs and control.	[23]
Bergamot essential oil (BEO)	Titanium-NPS	Mango	Effects of polylactic acid (PLA)/BEO/nano-TiO ₂ film and PLA/BEO/nano-TiO ₂ + nano-Ag in maintaining the quality of mangoes.	Results with PLA and PLA/BEO films indicated that PLA NC films successfully restricted adverse changes in total acidity, vitamin C content, and color. At the same time, firmness retention in the mangoes was enhanced. Results showed that the shelf life of these fruits was extended up to 15 d.	[24]
Carrageenan	ZnO-NPS	Mango	The effect of carrageenan/ZnO-NPs (CZ) coating in maintaining the storage quality of mango	On d 13 of storage, the decline in the total acidity of mangoes exposed to CZ 0.5 and CZ 1 NP coating treatments was significantly lower than that in the control samples. The CO ₂ production peak occurred after 7 d of storage, where the mangoes in the control sample produced the highest level of CO ₂ . Until day 33, minimal degradation was evident in the	[25]

				mangoes with CZ 0.5 coatings compared to samples without coatings.	
Beeswax	beeswax solid lipid nanoparticles (BSLN)	strawberry	Nano-coatings with BSLN-with xanthan gum (XG) as an alternative in the shelf life of strawberries stored in refrigeration.	The coating with 10 g/L of BSLN, 4 g/L of xanthan gum, and 5 g/L of propyleneglycol contributed positively to preservation while also decreasing decay rates; reflected in less fungal growth, weight loss, and physiological damage to the end of storage.	[26]

4 Antimicrobial and mechanism of action

The efficacy of NPs in reducing microbial growth on fruits/vegetable surface is mainly dependent on the type, concentration and properties of coating films, as well as the type, size, shape, concentration, chelation, release and photocatalytic properties of the applied NPs [27-28]. The synergistic effect of coating materials and NPs in the barrier, the types and structure of tested microorganisms and the tested conditions could also influence antimicrobial activity of the applied green nanomaterial edible coatings [27, 29]. A study by Cano *et al.* [30] revealed that Ag-loaded films exhibited antimicrobial activity against postharvest pathogens such as *Aspergillus niger* and *Penicillium expansum*. However, the result appeared to be concentration dependent. Jia *et al.* [31] reported that silver/CS NPs exhibited a high effect on *Botrytis cinerea* fungi by suppressing the growth and germination at a concentration of 0.02 mg/mL in vitro and in vivo. Similarly, El-Sherbiny *et al.* [32] indicated that 100 µl/ml Ag-NPs and the in-situ development of Ag-NPs on the surface of poly(ε-caprolactone)/curcumin/grape leaf extract-Ag hybrid NPs controlled *Aspergillus flavus*. These antimicrobial activities could significantly contribute to controlling the decay and quality loss of horticultural crops during storage or when exported [3, 14]. Otoni *et al.* [33] and Goudarzi *et al.* [34] reported that nanoparticles and edible coatings (EC) act directly on the pathogen by inhibiting spore germination and mycelium growth and altering morphological structures and reactive oxygen species (ROS) generation, spore mitochondrial membrane potential (MMP) and adenosine triphosphate (ATP) content. The preservation mechanism includes gas modification and induction defence properties of EC with NPs by forming a thin coating film on the surfaces of fresh products after being treated and dried, thus, modifying the concentrations of O₂, CO₂, and ethylene produced by horticultural crops [3, 14, 35].

Gao *et al.* [36] reported that strawberries coated with carboxymethylcellulose (CMC) enriched with ZnO nanoparticles synthesized from *Citrus sinensis* peel extract (CMC/CSP) had higher efficacy in controlling *Botrytis cinerea* compared to CMC enriched with commercial ZnO nanoparticles (CMC/CZN). Strawberries coated with CMC/CSP showed a lower rate of rotting and increased the storage period by 2 d compared to the other treatments. The higher antifungal activity of the CMC/CSP damaged the DNA and protein of the postharvest pathogen resulting in their cells death, thus reducing its severity and preserving the quality of the fruit for a longer time. An in vitro study by Saekow *et al.* [37] found that ZnO-NPs synthesized from pineapple peel extracts in CMC coating delayed the severity of *Alternaria alternata* persimmon and tomato fruit. After 3d, results showed that control fruit had a progressive higher disease development in the early stage of the storage period. Contrary to the control, CMC+ZnONPs coated persimmon and tomato had a lower level of disease development started showing signs of diseases development at 6 d of storage. Sing [38] reported that zinc oxide nanoparticles have a strong good antifungal activity against selected strains of bacteria and fungus compared to conventional zinc oxide particles.

5 Conclusion and future prospects

Green nanomaterials have emerged as an alternative to fungicides and have proven cost-effective and have high efficiency in maintaining fruit/vegetable quality. The low cost, environmentally benign, low-toxicity, and good performance green nanomaterials show a

great potential to be applied in postharvest preservation of horticultural crops. For this reason, research efforts are needed to enhance our knowledge in the application of nanotechnology in postharvest technology. Currently, there is a dearth of knowledge on how the synthesis of green nanomaterials could be optimized for high yield and efficacy in the protection of horticultural crops. In addition, long term risks and hazards of the use of nanomaterial remain unknown. There is a need to investigate this area and be cautious with the use of certain metal oxides such as TiO₂ and ZnO, which have been studied to cause detrimental adverse factors such as colon cancer in humans. Finally, factors, including dose, kind of nanomaterials, application timing, and fruit/vegetable physiology, can affect the efficacy of nanomaterials; therefore, this area also requires further investigation.

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