Review Article

Ethylene resistance control technologies and applications in regulation of fruit and vegetable preservation

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Abstract: Fruits and vegetables are an indispensable part of a healthy diet due to their rich nutrients. However, fruits and vegetables are not suitable for preservation after harvest, and their losses account for nearly half of the total global food losses. One of the most important reasons is that ethylene is still biosynthesized after fruits and vegetables are picked, accompanied by the respiratory climacteric of fruits and vegetables. As a plant hormone, ethylene can cause fruits and vegetables to overripe, soften, and rot after harvest. Therefore, the control of ethylene in the environment where fruits and vegetables are stored is of great significance to prolong the shelf life of fruits and vegetables and reduce economic losses. This paper reviewed the research progress of ethylene resistance control methods and their applications in the regulation of fruit and vegetable preservation and provides a reference for the further development of green, efficient, safe, and economical ethylene resistance control methods and technical applications.

Keywords: ethylene; catalytic decomposition; resistance control technology; fruit and vegetable preservation

1. Introduction

The Food and Agriculture Organization of the United Nations (FAO) estimates that fruits and vegetables account for up to 45% of total food loss produced globally, with 54% lost during harvest, post-harvest, processing, distribution, and consumption. The resulting losses accounted for 46% of all food losses, totaling US$750 billion per year[1–3]. The post-harvest loss of fruits and vegetables has a significant relationship with the rate of ethylene production[4]. Ethylene (C_2H_4) is a plant endogenous hormone[5] and also a volatile organic compound (VOC), which accelerates plant metabolism by increasing respiration and regulates the growth, development, and aging of fruits and vegetables[6]. It still has biological activity at very low concentrations (ppb, nL/L), affecting the post-harvest storage of almost all fruits and vegetables. Depending on the physiological characteristics of maturity, fruits and vegetables are divided into climacteric and non-climacteric fruits and vegetables[7]. Climacteric fruits and vegetables (such as bananas, mangoes, etc.) experience respiratory peaks and release a large amount of ethylene during ripening. While non-climacteric fruits and vegetables have no respiratory peak, exogenous ethylene will still affect their post-harvest ripening process. Regardless of the type of fruit and vegetable, they will experience a ripening process controlled by ethylene during post-harvest processing and storage, leading to overripening of fruits and vegetables and softening of pulp, eventually causing post-harvest losses due to the quality deterioration of fruits and vegetables[8]. Therefore, the prevention and control of ethylene in fresh-keeping environments is an effective way to prolong the shelf life of fruits and vegetables and reduce the post-harvest loss of fruits and vegetables.

Ethylene resistance control has always been a concern. Ethylene resistance control technologies developed over the years can be roughly divided into the following three categories: 1) physical removal technology[9–11], 2) chemical oxidation technology[12–14], and 3) photocatalytic decomposition technology[15–19].

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This review summarizes the development of different ethylene resistance control technologies in the storage environments of fruits and vegetables from these three aspects, and the applications of ethylene-resistance-control technologies in post-harvest storage of fruits and vegetables are discussed.

2. Ethylene resistance control technologies

2.1. Physical removal technology

Physical removal technology includes modified-atmosphere technology and adsorption technology. Modified-atmosphere technology changes the gas environment in the storage environment of fruits and vegetables (reducing the concentration of oxygen and increasing the concentration of carbon dioxide) to inhibit the respiration of fruits and vegetables, thereby reducing the consumption of internal substances in fruits and vegetables and inhibiting the biosynthesis of ethylene and its effect to prolong the storage period of fruits and vegetables. Adsorption technology uses various porous materials, such as activated carbon, zeolite molecular sieve, alumina, etc.[20], to combine with ethylene molecules through intermolecular forces to reduce ethylene in the storage environment. The porous materials are generally made into individually packaged small bags or used as food active packaging materials to be placed in the storage or packaging spaces in order to remove ethylene from the storage and the transportation environment to achieve the goal of ethylene prevention and control. Its advantage lies in its fast adsorption speed, which can quickly remove ethylene in the short term. However, due to the weak binding force between the porous materials and ethylene, ethylene is easily desorbed[12] and cannot be used for long-term storage. In addition, porous materials have indifferent adsorption, causing them to be replaced frequently.

Cisneros et al.[21] prepared various silver-containing zeolites by the cation exchange method, using silver nanoclusters loaded on microporous zeolites to remove trace amounts of ethylene from the air. By measuring the adsorption effect of different kinds of silver-containing zeolites on ethylene, it was found that the structure of zeolites played an important role in the stabilization of silver cations and demonstrated the potential ability of silver-containing zeolites to eliminate trace amounts of ethylene during low-temperature transportation and storage. Gaikwad et al.[22] carried out alkalization treatment on natural halloysite to increase its pore size and evaluated the ethylene adsorption efficiency in fresh agricultural product packaging. The results showed that in a low-humidity environment (relative humidity of 11%) at room temperature (25 ℃), the ethylene removal rate of halloysite, which is an active food packaging material, was close to 100%. Natural halloysite is generally considered safe for food packaging by the US Food and Drug Administration[23]. It can be completely used as a substitute for traditional ethylene scavengers for fresh fruit and vegetable packaging. Water molecules have a stronger interaction with porous materials compared with ethylene molecules due to strong polarity. Therefore, environmental humidity also has a significant impact on the ethylene adsorption and removal capacity of porous materials. Limlamthong et al.[24] reported a Pd-based MFI composite adsorbent composed of Pd-ZSM-5 and S-1 zeolite and found a synergistic effect between the silicon-rich layer and Pd nanoparticles in terms of moisture resistance and ethylene capture. This synergistic effect enables the composite adsorbent to have high ethylene adsorption capacity even in a high-humidity environment. Compared with the traditional Pd-ZSM-5 adsorbent, the composite adsorbent has twice the removal rate of ethylene. In addition to traditional adsorption materials, natural organic macromolecules, such as proteins, have a large number of active functional groups[25] that can interact with ethylene, and this has greatly attracted the attention of researchers. Fan et al.[26] used zein and *Artemisia sphaerocephala Krasch.* Gum (ASKG) as raw materials and paper fibers as substrates to synthesize ethylene-scavenging films via electrospraying. In the 15-day fruit experiment, the browning rate of bananas wrapped in the ethylene-scavenging film was only 25% of that of the control group, and the ethylene removal efficiency was nearly 10 times higher than that of the control group, proving the

application's potential as an economical, safe, and sustainable fruit ethylene scavenger. In addition, metal-organic frameworks (MOFs), a new class of synthetic porous materials, are widely used in gas storage and separation[27]. Zhang et al.[28] evaluated the ethylene adsorption capacity of several commercial MOFs and then embedded several commercial MOF powders in low-density polyethylene (LDPE), polylactide (PLA) and polyvinyl alcohol (PVA) films. Then they evaluated the biological efficacy of these films in delaying banana ripening and found that the LDPE film embedded with MgF-MOF had the highest ethylene adsorption capacity. Compared with the control group, bananas stored with this film had spots appearing only on the fourth day of storage, and the number of spots on the banana skin in the end were only half of those of the control group. Hence, the method could effectively delay the ripening of bananas and prolong their shelf life.

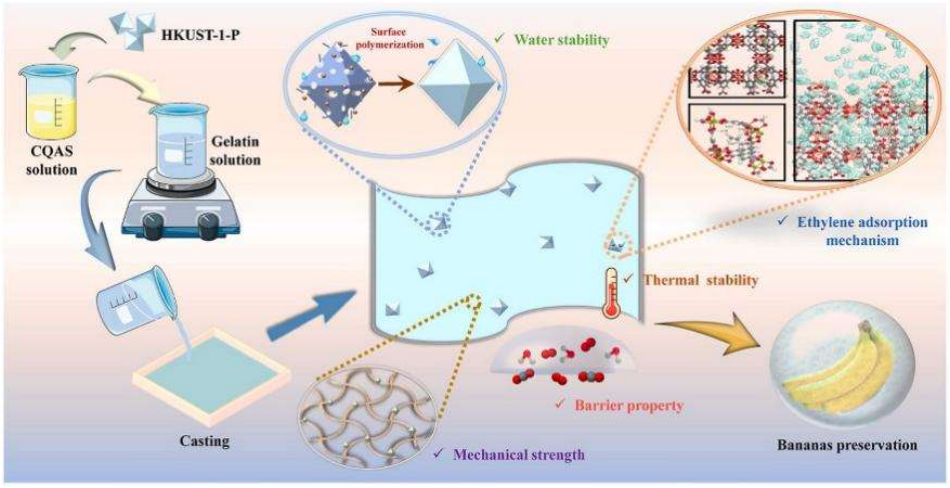

Figure 1. Modified HKUST-1 food preservation packaging with ethylene adsorption properties[29].

2.2. Chemical oxidation technology

Chemical oxidation technology includes the use of strong oxidizing chemicals, such as ozone, to oxidize ethylene and the use of catalysts, such as copper, to catalyze the oxidation and decomposition of ethylene. However, neither the chemical oxidant nor the catalytic oxidant has the adsorption function and contact with the gas. Catalysts such as copper also require medium- or high-temperature catalysis. Therefore, in practical applications, chemical oxidants and catalysts are usually carried by porous materials. Composite materials loaded using different methods are mostly in the form of lumps or powders and, due to the toxicity of most oxidants and catalysts, they are also made into small bags and placed in storage, transportation, and packaging in practical applications. Yang et al.[30] prepared Ag/ZSM-5 catalysts with different SiO_2/Al_2O_3 ratios and found that when the SiO_2/Al_2O_3 ratio was 38, the catalyst exhibited the strongest ethylene catalytic stability at room temperature. The ethylene-scavenging ability of the catalyst was tested at room temperature, and the results showed that the complete conversion rate of the catalyst to ethylene could be maintained for 7 hours and the total duration of ethylene catalytic oxidation reached 16 hours. Saud et al.[31] conducted the adsorption and plasma-catalyzed oxidation of a small amount of ethylene in a pin-type corona discharge coupled with a Pd/ZSM-5 catalyst. Cyclic plasma catalytic oxidation improved the adsorption performance of the catalyst for ethylene. The catalyst combined with plasma catalytic oxidation maintained an ethylene adsorption rate of at least 80% for 8 hours, while the catalyst alone only maintained such an ethylene adsorption rate for 2 hours under the same condition. Saud et al.[32] subsequently combined honeycomb monolith impregnated with palladium, using a honeycomb catalyst (Pd/ZSM-5/monolithic) sandwiched between two perforated electrodes at room temperature to study the effective removal of a small amount of ethylene. The process can be operated

in a low-pressure mechanically stable system and a simple reactor configuration, demonstrating the practicability of this plasma process.

Wei et al.[33] synthesized CeO_2 octahedron-supported Pt catalysts and modified them using capacitively coupled plasma to efficiently catalyze ethylene oxide. Compared with Pt/pure CeO_2, the Pt/plasma-modified CeO_2 catalyst (Pt/CeO_2-P) exhibited significantly higher reactivity. Pt/CeO_2-P induced more than 99.9% ethylene conversion at room temperature for more than 50 hours, even at 0 ℃ for 30 minutes. From the preservation test using bananas as fruit samples, it was found that the bananas treated with Pt/CeO_2-P did not show any yellowing phenomenon after 14 days, while the control group not only turned yellow but also produced a large number of spots, showing the excellent ethylene scavenging of the catalyst for fruit and vegetable preservation.

Figure 2. SiO_2-supported platinum catalysts for perishables preservation[34].

2.3. Photocatalytic decomposition technology

Photocatalytic decomposition technology is an emerging technology that has attracted much attention in recent years. It mainly excites semiconductor compounds using light to generate electrons and holes to oxidize ethylene in the environment. Common catalysts include TiO_2[17], ZnS[18], WO_3[19], etc. The photocatalytic ethylene remover will not be consumed and does not need to be replaced frequently, making them the main direction of the development of ethylene resistance control technologies.

Photocatalytic technology was jointly discovered by Japanese scientists Fujishima and Honda in the 1960s and has been a hot field since the mid to late 20th century[35]. Photocatalytic decomposition technology is developed based on semiconductor-based photocatalysts. Because semiconductor grains contain an energy band structure, usually consisting of a low-energy valent band (VB) and an empty high-energy conduction band (CB)[36], the VB and CB are separated by a forbidden band. The size of this area is called the forbidden band width, and the energy difference is the bandgap energy, The bandgap energy of semiconductors is generally 0.2–3.0 eV. When the catalyst is irradiated with light energy that is equal to or greater than the bandgap energy, the electrons in the VB are excited and cross the forbidden band to enter the CB, generating corresponding holes in the VB, that is, generating electron-hole pairs[37]. Because of its short wavelength and high energy, ultraviolet light has always been the light source of mainstream photocatalytic reactions, but because it is not conducive to practical applications, visible-light photocatalytic reactions have attracted the interest of many researchers. In this subsection, photocatalytic decomposition methods of ethylene dominated by ultraviolet photocatalysts in recent years, as well as photocatalytic ethylene-inhibition methods dominated by visible photocatalysts, are briefly described and discussed.

2.3.1. Ultraviolet photocatalytic decomposition technology

TiO_2 has been most widely studied and used in many applications due to its strong oxidizing ability for the decomposition of organic pollutants, superhydrophilicity[35], chemical stability, durability, and non-toxicity. Due to its high specific surface area and volume ratio, nano-TiO_2 particles have a higher photocatalytic activity than TiO_2 particles. However, both TiO_2 and nano-TiO_2 particles have an electron-hole recombination phenomenon. Studies have shown that doping organic or inorganic components may prevent this phenomenon[37]. Meng et al.[38] synthesized flower-like TiO_2 loaded with Au and Pt nano-ions using the hydrothermal method and photoreduction method, combining the strong surface plasmon resonance (SPR) ability of Au nano-ions and the small work function of Pt nano-ions with TiO_2 to improve the photocatalytic activity of TiO_2 under ultraviolet light. Also, the flower-like microsphere structure formed by TiO_2 increased the specific surface area for gas adsorption. The TiO_2 microspheres loaded with bimetallic alloys showed better photocatalytic decomposition of ethylene due to the synergistic effect of the bimetallic alloys at 19.9 times, 4.64 times, and 2.41 times higher than those of pure TiO_2 microspheres, Au-TiO_2, and Pt-TiO_2, respectively. De Chiara et al.[39] prepared five mixed-phase TiO_2/SiO_2 nanocomposites with different weight ratios via the sol-gel method. Using ultraviolet light as the irradiation source, they studied the degradation efficiency of different catalysts by measuring the ethylene removal rate in the reaction chamber at a given time interval and found that 80Ti-20Si samples showed the best degradation activity. In the experiment, immature tomatoes were stored in atmospheres filled with ethylene-rich gas, with gas treated with 80Ti-20Si nanocomposite materials, and with air. Compared with tomatoes stored in atmospheres filled with gas rich in ethylene and with air, the tomatoes stored in the nanocomposite-treated atmosphere showed no signs of reddening at all for 14 days.

In addition to TiO_2, the application of other semiconductor materials in ethylene scavenging has also attracted extensive attention in the scientific community. Liu et al.[40] prepared four different Ga_2O_3 polymorphs and studied their photocatalytic activities in degrading ethylene under ultraviolet irradiation, finding that the photocatalytic degradation rate constant was mainly determined by the position of the VB and the crystallinity of the samples. Among them, γ-Ga_2O_3 had the highest surface area and exhibited the highest apparent photocatalytic activity in the oxidation of ethylene to CO_2, and its degradation rate constant was ten times that of commercial TiO_2, namely P25. Chen et al.[41] used amorphous Nb_2O_5 nanoparticles as the precursor and water as the solvent to synthesize Nb_2O_5 nanorod bundles by a simple hydrothermal method. Pt-Nb_2O_5-S nanomaterials were prepared by modifying ultrafine Pt nanoparticles on the surface of Nb2O5-S via photodeposition. The nanomaterials completely removed ethylene in the container within 20 minutes after ultraviolet irradiation. Fraga et al.[42] synthesized different ratios of β-Ag_2MoO_4/gC_3N_4 photocatalysts and evaluated their effects on ethylene decomposition under ultraviolet radiation and found that the hybridized sample with a higher proportion of g-C_3N_4 had a better ethylene degradation effect because of better hole-electron separation efficiency and more superoxide radicals participating in ethylene oxidation. Zhu et al.[43] synthesized ZnO porous microclusters using thermally decomposing microflowers as the precursor and then prepared Ag-ZnO microspheres using simple photodeposition on Ag particles. Benefiting from the porous structure, higher separation efficiency and more active species, the photodegradation of ethylene at room temperature exhibited high mineralization ability and stability.

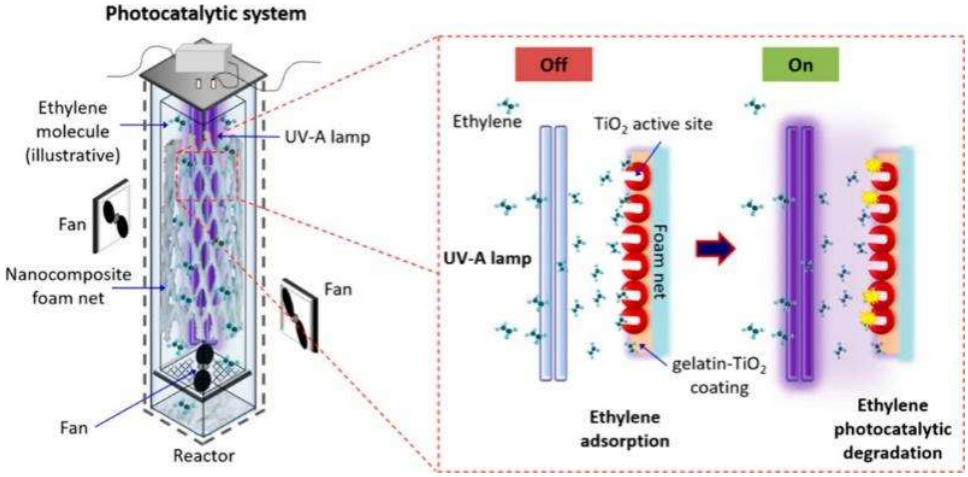

Figure 3. Ethylene-scavenging performance of TiO_2 composites on polyethylene support[44].

2.3.2. Visible-light catalytic decomposition technology

Photocatalysts often only respond to ultraviolet light due to their wide energy bandgap, which limits their practical applications in industries. Catalysts used in the photocatalytic oxidation of ethylene should satisfy the following: the minimum value of the CB is lower than the reduction potential of oxygen, the maximum value of the VB is greater than the oxidation of -OH and the bandgap should be greater than 2.92 eV[45]. Therefore, suitable semiconductor photocatalysts can only absorb ultraviolet light, and it is still a challenging task to explore semiconductor photocatalysts for efficient ethylene oxidation under visible light irradiation. Chen et al.[45] prepared In_2O_3-Ag composites with the Z-scheme configuration for the first time using the in-situ synthesis of Ag_3PO_4 on the narrow-bandgap semiconductor In_2O_3 and the subsequent photoreduction of Ag_3PO_4 to produce nano-Ag as the electron mediator. For the semiconductors, the apparent reaction rate constant, *k*, of photocatalytic oxidation of ethylene was measured. The *k* values of the composite semiconductors were 61 times and 41 times those of In_2O_3 and Ag_3PO_4, respectively, indicating that they have considerable potential in the photooxidation of ethylene. Su et al.[46] prepared a series of single-layer heterostructures containing photocatalyst CdS quantum dots (QDs) and an oxidized photocatalyst Bi_2WO_6 monolayer through a two-step hydrothermal method and successfully constructed an S-scheme semiconductor heterojunction. Both the photocatalytic degradation ability of ethylene and the photostability of CdS were significantly enhanced. The *k* values of the composites were 88 and 194 times those of pure CdS and Bi_2WO_6, respectively. Song et al.[47] synthesized $BiVO_4$/P25 nanocomposites using a modified citric acid complexation method. The results showed that the addition of $BiVO_4$ inhibited the growth of P25 grains and the precipitation of the rutile phase, extended the light absorption of the nanocomposite to about 525 nm and formed an n-n junction heterostructure on the contact interface of the nanocomposite, enhancing the nanocomposite photocatalytic activity of the composite. The catalyst formed with the mass ratio of $BiVO_4$ and P25 at 3:1 exhibited significantly higher photocatalytic activity than those of P25 or $BiVO_4$: the degradation rate of ethylene was more than 7 times that of P25 and more than 3 times that of pure $BiVO_4$. Liu et al.[48] reported for the first time the synthesis of a WO_3 photocatalyst with high photocatalytic activity and stability via synergistic internal Fe^{3+} doping and surface Pt loading for the degradation of ethylene under visible light irradiation. The internal Fe^{3+} doping not only enhanced visible light absorption but also improved the separation efficiency of photogenerated carriers due to the higher positive reduction potential of Fe^{3+}/Fe^{2+} than that of W^{6+}/W^{5+}, and the stability improved to a certain extent. In addition, the efficient transfer of photogenerated electrons was promoted and the photocorrosion of WO_3 was reduced by the photoreduction-loaded Pt on the Fe-doped WO_3 surface. Due to the synergistic effect, the material degraded about 3.3 times faster than pristine WO_3 under visible light irradiation. Thalluri et al.[49] introduced ammonium carbonate in

the synthesis of photocatalyst $BiVO_4$ and found that ammonium carbonate affected the preferential crystal growth of the catalyst along its {040} plane at high pH, thereby increasing the concentration of its surface OH species, significantly improving the photocatalytic activity induced by visible light, and its photoinduced degradation rate of ethylene is 10 times higher than that of P25.

2.3.3. Composites photocatalyst decomposition technology

In order to solve the problems of wide bandgaps, electron-hole recombination, nanoparticle agglomeration, and practical application difficulties in a single photocatalyst system and to improve the catalytic effect of photocatalysts[50], researchers often combine photocatalysts with other materials to increase the specific surface area of the composite material, electron mobility, photocatalyst stability, and application range.

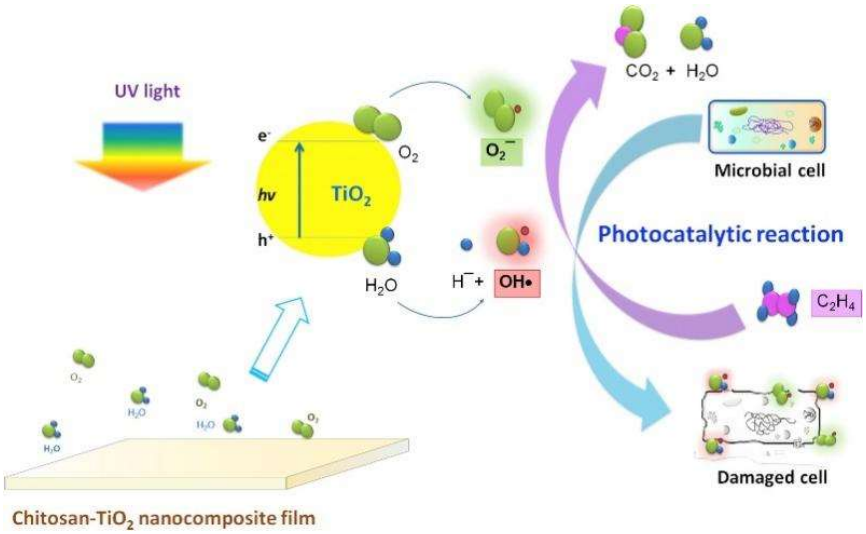

Figure 4. Ethylene-scavenging and antibacterial activity of chitosan-TiO_2 nanocomposite film[51].

Carbon materials have demonstrated that they can produce synergistic effects between phases to enhance the photocatalytic performance of TiO_2[52], which is not only based on stronger adsorption activity but also because the conjugated π bond system of carbon materials can accept photogenerated electrons (i.e., sensitizers) and avoid electron-hole recombination. Graphene oxide (GO) is an oxidation product of graphene. Its structure is similar to graphene but with a planar two-dimensional network structure[53]. Its surface is composed of various oxygen-containing groups[54], such as -OH, C = O, C-OH, and C-COOH, which makes it more reactive than graphene. The special single-atomic-layer structure of GO endows it with unique physical and chemical properties, such as a large specific surface area, great adsorption capacity for pollutants[55], and a large number of active sites. In photocatalytic materials, GO can capture photogenerated electrons, effectively improve the separation of photogenerated carriers, and improve the photocatalytic activity of semiconductors. Lv et al.[56] took advantage of the large specific surface area and the effective built-in electric field of GO to anchor TiO_2/$BiNWO_6$ nanoparticles on a GO sheet to obtain GO/TiO_2/Bi_2WO_6 (GTB) ternary-composite photocatalyst, and its ethylene degradation ability was tested under ultraviolet-visible light irradiation. The results showed that the degradation rate was the highest when the GO content was 0.75% because the addition of GO reduced the average grain size of GTB and created an interfacial interaction with TiO_2/Bi_2WO_6, which inhibited the recombination of electron-hole pairs and improved the photocatalytic activity. The ethylene degradation rate of GTB was 5.7 times, 2.8 times, and 1.3 times those of pure TiO_2, Bi_2WO_6, and TiO_2/Bi_2WO_6, respectively. Reduced graphene oxide[57], which is obtained by partially reducing graphene oxide in a solution, has been widely used as a cheap substitute for graphene, and its similar properties to graphene can also

effectively inhibit the recombination of photogenerated carriers. Xie et al.[58] prepared TiO_2 nanotubes/reduced graphene oxide nanocomposite photocatalysts (rGO-TNTAs) using γ-ray radiolysis and evaluated the rGO-TNTAs by comparing the *k* values of rGO-TNTAs with TNTAs. Compared with TNTAs, the *k* value of rGO-TNTAs increased by about 40.9% in the degradation effect of ethylene under ultraviolet light in a low-temperature environment, which reflected the important role of rGO in improving the photocatalytic activity of materials. Huang et al.[59] found that the GO precursor rGO effectively adjusted the branched chain structure of ZnO nanosheets. The shape of hierarchical ZnO nanosheets can be adjusted by controlling the weight ratio of GO during the synthesis. By optimizing the mass ratio of GO to 2%, the photocatalytic oxidation performance of the ZnO-rGO photocatalyst further improved, and the experimental characterization proved that the close contact between rGO nanosheets and ZnO nanoparticles enhanced light absorption intensity and facilitated the separation and migration of photogenerated carriers. The ZnO-rGO composite exhibited great photocatalytic performance for ethylene oxidation under the simulated sunlight irradiation, and the mineralization rate of ethylene (the ratio of the carbon content of CO_2 in the oxidation product to the carbon content in the original organic matter) was close to 100%.

Metal-organic frameworks (MOFs), as a crystalline material with a periodic network structure composed of organic ligands and metal ions[60], have a large specific surface area, a regular pore structure, and abundant catalytic active sites[61], which are beneficial for photocatalysis and gas adsorption and separation[62]. Chen et al.[63] synthesized a novel nanocomposite photocatalyst containing Fe-MOF, TiO_2, and rGO. The method can be used for the rapid photocatalytic degradation of ethylene in a relatively wide range of photo-response by taking advantage of the adsorption properties, large specific surface area, and abundant pores of Fe-MOF through the efficient photocatalytic reaction between titanium ions and iron ions, the effective separation of electron-hole pairs, and the conductivity of rGO. The photodegradation ability of ethylene was tested under photo-reaction in a simulated closed refrigeration environment. The *k* value reached 2.07×10^{-4} min^{-1}, which was better than other catalysts' constants.

In recent years, the size of developed photocatalysts is usually at the nanometer level, and the problem of nanoparticle agglomeration often occurs in practical applications[64], while air-suspended nanopowders have security risks. Loading photocatalyst nanopowders on solid supports has become a research hotspot of composite photocatalytic systems. Licciulli et al.[65] coated the commercial TiO_2 powder P25 in a glass tube through the drainage method and used the metal-organic dye of copper phthalocyanine (CuPc) as the sensitizer of the TiO_2 powder. With its ability to generate charge carriers and effectively separate electron-hole pairs under visible light, the photo-oxidation rate of gaseous ethylene was improved and the reaction rate of the coated tube decreased by only 5% after four consecutive tests. Chawengkijwanich et al.[66] sprayed TiO_2 onto pleated washable synthetic (PWS) fibers using the spraying method to prepare a TiO_2-coated photocatalytic filter device and determined that the ethylene degradation rate in a $45m^3$ post-harvest storage room was 1.59 ± 0.52 ppm/min. The method is suitable for a large-scale reduction of ethylene at room temperature. Biopolymers and organic polymers are often used in combination with nano-TiO_2 due to their stable chemical properties and easy-to-functionalize chemical groups. Fonseca et al.[44] synthesized gelatin-TiO_2 and hydroxypropyl methylcellulose nanocomposite films with different TiO_2 contents and combined them with EPE foam nets to provide better surface adsorption for photocatalysts and adhesion of nanocomposite coatings to prevent the TiO_2 material from migrating to the fruit surface. The ability of the composite material to photocatalytically degrade ethylene was tested by wrapping papayas loaded with a foam net with a nanocomposite coating. The experiment[67] showed that the ethylene accumulation of the fruit treated with the composite material was reduced by 60% compared with that of the control group after four days of UV light, and the maturity of the papaya was effectively delayed. Böhmer-Maas et al.[68] used zein combined with TiO_2

nanoparticles to produce zein-TiO_2 nanofibers via the electrospinning technology as a bioactive packaging material and evaluated the nanofibers' effect on the ethylene absorption of cherry tomatoes during storage. The nanofibers exhibited photocatalytic activity towards ethylene during 22 days of storage, indicating their enormous great potential as ethylene-modulating active packages.

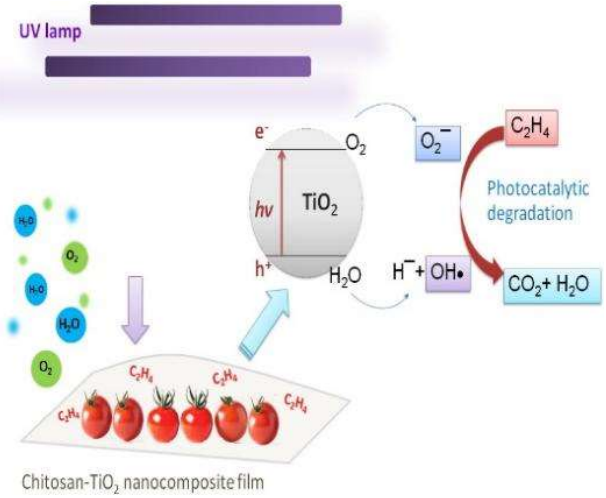

Figure 5. Active packaging of chitosan-titanium-dioxide nanocomposite film to remove ethylene from tomato storage environment[69].

3. Applications of ethylene risk prevention and control technology in fruit and vegetable preservation

Today, the most commercialized and widely used ethylene risk prevention and control technology is still the combination of physical adsorption technology and chemical oxidation technology, which uses powder, granules, and beads in small bags to remove or control ethylene from fresh product packaging during storage, transportation, or packaging of fruits and vegetables. Wang and Ajji[70] used pumice with small particle size and low relative humidity, combined with $KMnO_4$ as a new ethylene scavenger. This scavenger limited the ethylene production rate of avocados to 0 for 9 days, while the CO_2 production rate was below 25 mL/kg/h and the shelf life of the avocados at 25 ℃ was extended by one week. Mori et al.[34] studied the ethylene oxidation activity of SiO_2-supported Pt-based catalysts under semi-realistic conditions, which can be used for ethylene scavenging during the storage of bananas, cucumbers, and apples, while significantly delaying ripening. Commercial ethylene-removal bags include SendoMate (Mitsubishi Gas Chemical Co., Ltd., Japan), Evert-Fresh (Evert-Fesh Corporation Ltd., U.S.), BRYSORBTM 508 (Bry-Air (Asia) Pvt Ltd., India), Super Fresh Media (Ethylene Control, Inc., USA), and Biofresh (Grofit Plastics, Israel)[71]. The pouch size required for packaging is influenced by many variables, including the type of fruit and vegetables, the time required to protect the fresh produce, the weight of the fresh produce, the packaging size to be protected, and sensitivity to the ethylene gas. The main benefit of this format is that ethylene can be eliminated throughout the supply chain, providing continuous protection starting from the packaging process line to the retail backend. However, such pouches are not recommended for long-term storage of fruits and vegetables, as the ethylene scavengers quickly saturate and need to be replaced periodically. Ethylene-removal packaging in the form of polymer films is gaining popularity due to limited consumer recognition of sachet-packed products. Nian et al.[29] added modified HKUST-1 to chitosan quaternary ammonium salt (CQAS)-gelatin matrix to prepare a food packaging film (HPCGF) with ethylene adsorption properties and improved water stability. The verification experiment results proved that the absorption rate of ethylene was above 50%, and the bananas wrapped using HPCGF

still maintained their color and hardness after 7 days. However, this research is still in the laboratory stage and has not been put into application.

There are two most common forms of photocatalytic systems used in the post-harvest preservation of fruits and vegetables. The first type is made of a photocatalyst and an inorganic material, where photocatalyst particles are immersed on the wall of the inorganic material, or inorganic materials are made into loaded photocatalysts. Basso et al.[72] deposited commercial TiO_2 particles inside borosilicate glass tubes to make a continuous photocatalytic reactor for tomato ripening regulation. These reactors can exhibit different designs and modes of operation, such as batch, batch with gas recovery, and continuous flow, allowing storage regulation according to different tomato states. The second type is a combination of polymer and photocatalyst nanomaterials. These materials are mainly used as films and coatings, and photocatalytic reactions for ethylene degradation are usually performed in batch systems. Kaewklin et al.[69] used chitosan-TiO_2 nanocomposite films containing 1wt% TiO_2 to delay the ripening of cherry tomatoes. The fruits were wrapped in nanocomposite films, packed in low-density polyethylene bags, and stored at 20 ℃ and 85% relative humidity for 14 days. Tomatoes encapsulated in nanocomposite films exhibited lower ethylene production rates and their maturity was delayed. During the whole storage period, the firmness of the fruits was better than that of the control fruit, and the respiration rate of the fruits during the transition period decreased. In addition, its soluble solid content and its lycopene and ascorbic acid concentrations were lower than those of the control fruit, and the fruit color was mainly green. Zhu et al.[73] used polyacrylonitrile as a matrix and also fabricated nanocomposite membranes via electrospinning technology for photocatalytic degradation of ethylene. Compared with the banana coated with polypropylene film, the control banana's brown spots appeared on the tenth day and its firmness dropped sharply, while the banana wrapped using the nanocomposite film did not show a similar phenomenon, indicating that the nanocomposite film had better photocatalytic properties of ethylene degradation effect. However, there are almost no photocatalytic ethylene-decomposition products for ethylene removal applied in the storage environments of fruits and vegetables, and most photocatalytic ethylene-decomposition materials have not completed the transformation from the laboratory to the market.

4. Summary

Post-harvest preservation of fresh fruits and vegetables has always been an important topic in the field of fruit and vegetable preservation. Fruits and vegetables continuously release a lot of volatile gas substances from harvest to sale. The composition of these substances is very complex, and ethylene is one of the important components[74]. Post-harvest ethylene resistance control technologies have evolved from single-regulated refrigeration, wax coating, and physical removal technology to chemical oxidation technology, demonstrating the market's demand for faster, better, and more convenient fruit and vegetable preservation technology with the development of the times.

Nowadays, ethylene resistance control technologies are still mainly based on physical removal and chemical oxidation. Although photocatalytic decomposition technology has good development and application prospects in the field of post-harvest preservation of fruits and vegetables, photocatalysts still have drawbacks, such as large bandgap energy and a high electron-hole recombination rate. The new materials developed to break through the drawbacks also have problems, such as low yield, high cost, and safety risk, and most of the new materials are in the laboratory stage. Generally, only one kind of fruit is used in fruit and vegetable experiments, resulting in significant limitations in converting photocatalysts into products to solve practical market problems. Therefore, the focus of future research should not be limited to simply improving ethylene removal efficiency but should start from actual needs and combine multiple resistance control technologies for different types of fruits and vegetables to develop simple manufacturing methods that have stable yields and

low production costs, are easy to use, and will not affect the quality of fruits and vegetables. The focus should also be on accelerating the transformation of new materials and technologies from laboratory to market application and evaluating the new materials' value in practical applications.

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Conflict of interest

The authors of the article declare no conflicts of interest.

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