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Research article

Application of plasma-activated hydrogen peroxide solution synergized with Ag@SiO_2 modified polyvinyl alcohol coating for strawberry preservation

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ABSTRACT

To extend the postharvest storage time of strawberries, this study aims to prepare a composite coating using plasma-activated hydrogen peroxide solution (PAH) synergized with nano-Ag@SiO_2 by blending method to modify polyvinyl alcohol (PVA) solution. Results showed that the viscosity and the swelling rate of PVA significantly decreased with the addition of Ag@SiO_2 at 0.18 %. Meanwhile, the elongation at break and the tensile strength of PVA increased to 0.87 MPa and 214 %. When the addition of Ag@SiO_2 was 0.18 % and the composite ratio of PAH to PVA was 1:1, the composites could inactivate the pathogenic bacteria at 2 h. During the storage of strawberries, the initial colony counts on the surface of strawberries could be reduced by about 1 lg CFU/g after coating with the composite film. Moreover, with the extension of the storage time to 7 d, the respiratory intensity, colony counts, and rot index in the strawberries were 65.7 mg/(kg•h), 4.05 log CFU/g, and 38.7 %. Meanwhile, the superoxide dismutase activity and Vc content were 944 U/g and 690 μg/g, respectively. Overall, this study provides ideas and the theoretical basis for applying composite films in fruit preservation.

1. Introduction

Strawberries are widely popular among consumers due to the high nutritional value, rich in vitamins, anthocyanins, and dietary fiber. However, the high moisture content of strawberries makes them susceptible to microbial infestation, which limits the marketing of strawberries [1]. The main microorganisms that cause strawberry rot are *Botrytis cinerea* [2], *Rhizopus stolonifer* [3], and *Aspergillus niger* [4] (spoilage microorganisms). Additionally, it is worth noting that studies have found that the contamination of pathogenic bacteria, such as *Escherichia coli* and *Staphylococcus aureus*, presents a serious threat to consumer health [5,6]. Meanwhile, strawberries are less likely to be detected when contaminated by pathogenic bacteria compared to gray mold. Therefore, in order to reduce foodborne disease outbreaks, this study will further focus on the effectiveness of novel preservation techniques against pathogenic bacteria.

Cold plasma sterilization technology has attracted more attention in recent years due to its easy operation and no chemical residue. Plasma is a fourth state of matter consisting of a variety of reactive species, such as free radicals, ions, electrons, and excited state molecules, as a result of the ionization of the neutral gas after the application of high energy [7]. Plasma-activated solution is prepared by treating the liquid with plasma generation device. Highly reactive species generated in the plasma interact with water molecules to

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ultimately produce a variety of reactive species in the liquid phase [8,9]. Our previous study found that plasma-activated hydrogen peroxide solution (PAH) exhibited a strong bactericidal effect on pathogenic bacteria on the surface of fresh food [10]. Moreover, the plasma-activated solution acts in a gentle manner, avoiding the damage to food color and nutrients caused by heat, electric fields, and ultraviolet light, which are found in other sterilization methods [11]. Furthermore, Sharma et al. found that plasma activation solution can remove the surface microorganisms of fruits or vegetables and enhance the SOD activity to extend the shelf life [12]. However, plasma-activated liquid treatment is unable to isolate the product from the outside environment, which can lead to secondary contamination during storage and distribution. Thus, the plasma-activated solution treatment should be considered in conjunction with other preservation methods to address the above drawback.

Polymer-based nanocomposite coatings are extensively investigated for the application in the preservation of fruits [13]. Alas et al. applied multicolor emitting carbon dot as nanofillers in the polyvinyl alcohol (PVA)-based composites, meanwhile, the mixture was used as the coating material to avoid the mold growth and the moisture loss of strawberries during storage [14]. In recent years, various kinds of metal nanoparticles have been added to PVA, such as Ag, ZnO, TiO_2, SiO_2, among which Ag nanoparticles (AgNPs) have been given great importance for showing better spectral antimicrobial properties [15]. In contrast to pure PVA films, which show high water vapor permeability and high oxygen permeability [16], polyvinyl alcohol modified with nanomaterials leads to improved hydrophobicity and barrier properties, as well as bactericidal properties [17,18]. For the toxicity, Biswas et al. found that when higher silver (1.5 %) loaded silica-carbon-silver ternary blend nanocomposite film was immersed in distilled water for one week, no silver trace in the water was detected [19]. What's more, Domínguez et al. found that the cytotoxicity of AgNPs was significantly attenuated when AgNPs were immobilized on SiO_2 at the same concentration [20]. Meanwhile, Ag@SiO_2 was also found to be used for seed coating against crop pathogenic fungi (*Fusarium oxysporium and Rhizoctonia solani*) [21]. This further confirms the feasibility of using Ag@SiO_2 in this study.

Therefore, in this study, PAH synergistic nano Ag@SiO_2 was applied to modify PVA by blending method, to further enhance the bactericidal properties and improve the film-forming properties of PVA solution. The viscosity and antibacterial activity (against *E. coli* and *S. aureus*) of modified PVA solution, as well as the swelling rate, elongation at break, tensile strength, micromorphology of the PVA-based films were analyzed. Furthermore, changes in the qualities (respiration ratio, weight loss, firmness, rot index, color, malondialdehyde content, superoxide dismutase activity, vitamin C, and anthocyanin content) of strawberries after modified PVA solution coating were investigated.

2. Materials and methods

2.1. Preparation of core-shell nano-Ag@SiO_2 materials

Firstly, 5 mL of 1 % PVP and 0.6 mL of 0.1 % $NaBH_4$ solution were added to 20 mL of deionized water in an ice-water bath. Then, 5 mL of 1 % PVP and 5 mL of 0.1 % $AgNO_3$ are added dropwise to the solution at a rate of 30 mL/h to form a silver colloid. The color of the solution immediately changed from colorless to pale yellow. To remove the remaining $NaBH_4$, the solution was heated to 80 °C for 2 h. After the solution turned bright yellow, the mixture was centrifuged at 13000 r/min for 20 min at 4 °C, and the precipitate was washed repeatedly with deionized water to obtain nano-Ag. To adsorb SiO_2 onto the surface of the silver colloid, the nano-Ag was resuspended with 20 times the volume of anhydrous ethanol. And 10 mL of the mixture was taken in the beaker, then 5 mL of ammonia (25 wt%) was added as the catalyst and 0.3 mL of TEOS (tetraethyl orthosilicate) as the precursor of SiO_2, respectively. The mixture was stirred for 2 h and then centrifuged at 13000 r/min for 20 min at 4 °C. The precipitate was washed three times with deionized water and ethanol, respectively, and then 10 mL of anhydrous ethanol was added and resuspended to obtain the nano-Ag/SiO_2 material [22].

2.2. Preparation of plasma-activated hydrogen peroxide solution (PAH)

Briefly, 0.8 mL of H_2O_2 was added to 100 mL of deionized water, and then the mixture was transferred to a polypropylene packaging box (178 mm × 126 mm × 35 mm, oxygen permeability: 10 $cm^3/m^2/24$ h, water permeability: 10 $g/m^2/24$ h). The packaging box was sealed with the polyamide/polyethylene composite film, and then treated by the dielectric barrier discharge plasma apparatus (BK130/36, Phenix, USA). For treatment parameters, the voltage was 60 kV, the treatment time was 4 min, and the PE plate was used as the dielectric material. The plasma-activated water prepared without adding H_2O_2 was chosen as the control group.

2.3. Preparation of PAH combined with Ag@SiO_2 modified PVA solution

For the PVA solution preparation, 4 g PVA was added to 100 mL of deionized water, then heated at 90 °C and stirred continuously for 1 h, and cooled to room temperature.

For the preparation of Ag@SiO_2 modified PVA solution (PVA/Ag@SiO_2), nano-Ag@SiO_2 materials were added to the PVA solution at 90 °C with continuous stirring for 1 h and cooled to room temperature.

For the preparation of the PAH-modified PVA/Ag@SiO_2 solution, PAH was added to the PVA/Ag@SiO_2 solution, and the final PVA concentration in the mixture was 4 %. The mixture was stirred continuously for 10 min at room temperature.

2.3.1. Effect of nano-Ag@SiO_2 addition content on composite properties

The nano Ag@SiO_2 addition content was 0, 0.06 %, 0.12 %, 0.18 %, 0.24 %, and 0.30 %, and PAH and PVA were added at the weight ratio of 1:1. The compound coating materials were prepared as mentioned in Section 2.3.

2.3.2. Effect of PAH content on composite properties

The nano Ag@SiO_2 addition content was 0.18 %, meanwhile, PAH and PVA were added at the weight ratio of 3:1, 2:1, 1:1, 1:2, 1:3, and 0:1. The compound coating materials were prepared as mentioned in Section 2.3.

2.4. Properties of PAH-modified nano-Ag@SiO_2

2.4.1. Viscosity determination

To determine the viscosity, various groups were measured using a rotational viscometer (NDJ-79, Kunshan Shun Debbi Instrument Co., Ltd., China). The prepared film solutions were placed in the viscometer at room temperature.

2.4.2. Swelling rate determination

For the determination of the swelling rate (SR), different film solutions were poured onto a flat glass plate (90 mm), and the cast plates were dried at 60 ± 2 °C for 6 h. The films were then peeled from the glass plates. The PVA-based films of different treatment groups were then immersed in 100 mL of deionized water and left to stand at 25 °C for 24 h. The SR was calculated according to formula (1) [23]:

$$\text{Swelling rate }(\%) = \frac{m_2\text{-}m_1}{m_1} \times 100 \tag{1}$$

where m_1 is the weight of the film after drying, and m_2 is the weight of the film after immersion in water.

2.4.3. Elongation at break and tensile strength measurement

To determine the elongation at break and tensile strength, the differently treated PVA solutions were poured onto flat glass plates (90 mm), and the cast plates were dried at 60 ± 2 °C for 6 h. The films were then peeled from the glass plates. The film material was cut into 80 mm × 10 mm cross strips and placed on the electronic tensile tester (KD-05, Shenzhen Kaiqiangli Machinery Co., China). The experiments were conducted at an elongation rate of 60 mm/min.

2.4.4. Antibacterial activity analysis

For the antibacterial activity of film solutions against *E. coli* and *S. aureus*, bacteria were incubated in the nutrient broth medium at 37 °C until the logarithmic phase. The cultured bacteria were then collected by centrifugation and diluted to about 10^7 CFU/mL with the sterile 0.85 % saline solution. Then, 9 mL of PVA solution with different treatments was added to 1 mL of bacterial suspension and mixed well. The mixture was incubated at 37 °C for 0, 0.5, 1.0, 1.5, and 2.0 h. Subsequently, 0.5 mL of the bacterial suspension was serially diluted with saline and calculated. After incubation at 37 °C for 24 h, the number of surviving bacteria was counted.

2.4.5. Morphological analysis

For the morphological observation, the surface gold-plated sections were obtained using liquid nitrogen embrittlement fracture, and the composite films were placed in a scanning electron microscope (SEM, S-4800, Hitachi High-Technologies, Ltd., Japan) to observe the apparent morphology of the sections with an accelerating voltage of 5.0 kV.

2.5. Qualities of strawberries

Strawberries (*Fragaria* × *Ananassa* Duch.) were harvested from the Moling Strawberry Plantation in Nanjing, Jiangsu Province, and the strawberries were selected to be free of mechanical damage, pests, and diseases, and transported to the laboratory immediately after picking. Strawberries were stored at 4 ± 1 °C for subsequent experimental analysis. Samples were divided into four groups, the CK group represents the sample without any treatment, meanwhile, the PVA, Ag@SiO_2+PVA, and PAH + Ag@SiO_2+PVA group represents the sample coating with the corresponding solution. Twenty strawberries were used for each treatment.

2.5.1. Determination of respiration ratio

Strawberries were randomly selected and stored in airtight containers for 20 min to detect the concentration of CO_2. The gas concentration was determined from the top of the container using the portable carbon dioxide gas detector (Shenzhen Wandi Technology Co., China). The intensity of strawberry respiration is the rate of CO_2 production and is calculated by formula (2):

$$\text{Respiration ratio }(\text{mg} / (\text{kg} \bullet \text{h})) = \frac{C \times 44 \times t \times 60}{22.4 \times m \times (t + 273)} \tag{2}$$

C: increase in CO_2 concentration per minute (ppm/min), m: the weight of the sample (g), t: the ambient temperature (°C), 44/22.4: the ratio of molar mass to molar volume of ozone.

2.5.2. Weight loss

Strawberries were weighed during storage and the rate of weight loss of strawberries was calculated according to formula (3):

$$\text{Weight loss } (\%) = \frac{W_i\text{-}W_s}{W_i} \times 100 \tag{3}$$

W_i is the initial weight of the strawberry, and W_s is the weight of the strawberry during storage.

2.5.3. Firmness

Strawberries were tested using a fruit hardness tester (GY-1, Shanghai Huqin Instrument Co., China) equipped with a 3.5 mm diameter cylindrical probe. The samples were penetrated 10 mm.

2.5.4. Rot index

Calculation of rot index of strawberries after grading strawberries according to Table 1. The rot index of strawberries is calculated according to formula (4) [24]:

$$\text{Rot index } (\%) = \sum \frac{\text{rot grade} \times \text{number of fruits at that level}}{\text{highest rot grade} \times \text{total number of fruits}} \times 100 \tag{4}$$

2.5.5. Color measurement

To quantify the color difference of strawberries after processing, a color difference meter (Chroma Meter CR-410, Konica Minolta, Japan) was used using the CIE (L^*, a^*, and b^*) system. The CIE system is a standard system for evaluating color change, the L^*, a^*, and b^* values represent the brightness, greenness/redness, and blue/yellowness degree of the sample, respectively. ΔE^* as an indication of the total color difference after water and PAH treatment is calculated according to formula (5) [25]:

$$\Delta E^* = \sqrt{(L_c\text{-}L_t)^2 + (a_c\text{-}a_t)^2 + (b_c\text{-}b_t)^2} \tag{5}$$

L_c, a_c, and b_c is the color on day 0, L_t, a_t, and b_t is the color during the storage.

2.5.6. Malondialdehyde (MDA), superoxide dismutase (SOD), Vc, and anthocyanin measurement

Changes in the MDA, SOD activity, Vc, and anthocyanin were measured using the malondialdehyde (MDA) content assay kit (BC0025, Solarbio), superoxide dismutase (SOD, Solarbio) activity assay kit (BC0175, Solarbio), vitamin C assay kit (BA1722, Saint-Bio), and micro plant anthocyanin assay kit (BC1385, Solarbio).

2.6. Statistics analysis

Each experiment was independently repeated three times. The experimental data were analyzed by analysis of variance (ANOVA, one-way ANOVA) using SAS 8.2 (SAS Institute Inc., Cary, North Carolina, USA), and the means between the different treatment groups were tested for the significance of the differences using the Duncan test ($P < 0.05$).

3. Results and discussion

3.1. Effect of PAH synergistic nano Ag@SiO_2 modification on the performance of PVA

3.1.1. Changes in viscosity and swelling rate

Effects of different nano Ag@SiO_2 additions and the mixing ratio of PAH and PVA on the viscosity and swelling rate of the composite films were exhibited in Fig. 1. It showed that the viscosity of the material significantly decreased ($P < 0.05$) with the increasing addition of Ag@SiO_2 (Fig. 1A). While there was no significant change in the viscosity when the addition exceeded 0.18 %. The decrease in solution viscosity was mainly due to the stable binding of nano Ag@SiO_2 to the molecular groups of PVA, which reduced the interaction of hydrogen bonds between PVA molecules. As the nanoparticle addition increased, the interaction between nano-Ag@SiO_2 and PVA reached saturation. In contrast, since PVA and PAH were compounded with a final PVA concentration of 4 % (w/v), there was no significant ($P > 0.05$) effect of the compounding ratio on the viscosity and swelling rate of the material (Fig. 1B and D). The water-blocking ability of different PVA-based coating materials can be determined by measuring the swelling rate of the composite film materials, which can reflect the filling effect of nano Ag@SiO_2 on the molecular gap of PVA. With the increasing Ag@SiO_2 addition, the swelling rate of the materials gradually decreased (Fig. 1C). This is mainly attributed to nano-SiO_2 dispersed in an orderly arrangement in the polymer matrix, through the bridge role of Si, it can form a tightly bonded polymer-nanocomposite

Table 1
Evaluation criteria of strawberries rot grade.

Grade	Standard
0	Bright red, no mechanical damage
1	Deep red, mechanical damage, less than 25 % rotted area
2	Mechanical damage, 25%–50 % rotted area
3	Greater than 50 % rotted area, inedible

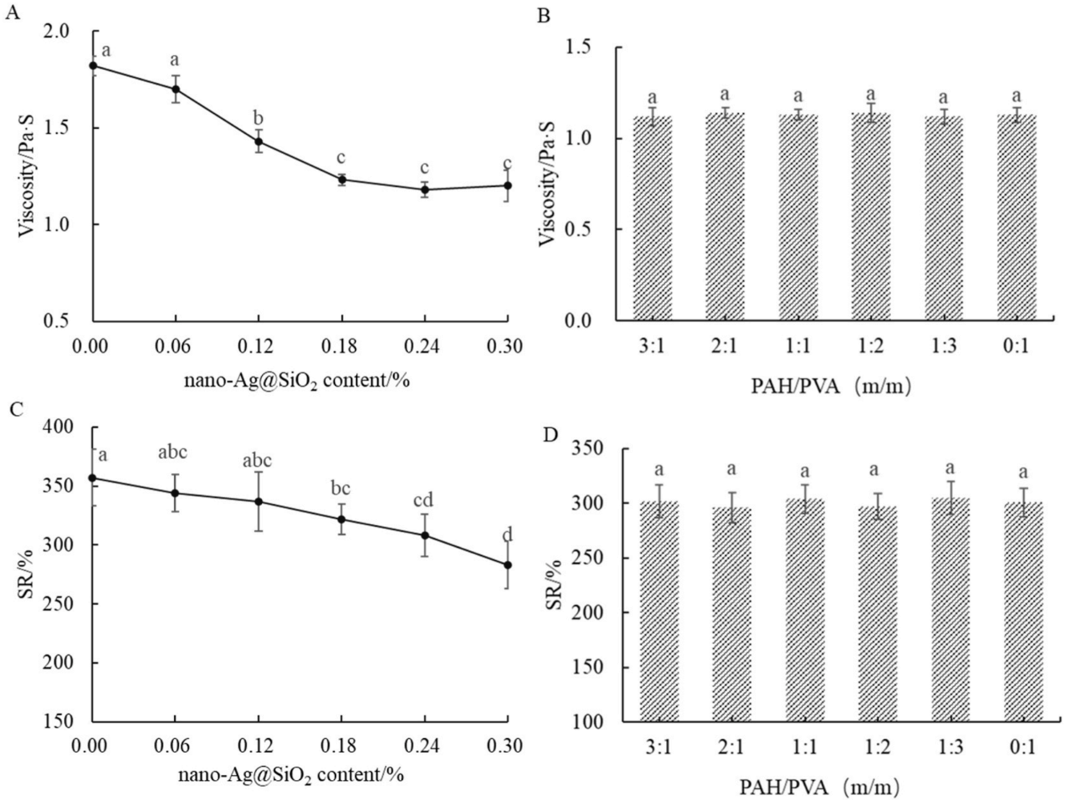

Fig. 1. Changes in the viscosity (A and B) and swelling rate (C and D) of the composites prepared with different nano-Ag@SiO_2 additions and mixing ratios of PAH and PVA. Different lowercase letters indicate significant differences ($P < 0.05$) between samples from different groups.

construction [26]. Meanwhile, SiO_2 will form strong interactions with the PVA molecular groups and bind together to prevent water molecules from penetrating. In addition, there was no significant change in the viscosity and swelling rate of the PAH-modified PVA, mainly due to the high acid and alkali resistance of the PVA solution.

3.1.2. *Changes in mechanical properties*

The tensile strength (MPa) and elongation at break (%) were measured to determine the changes in the mechanical properties of composite film (Fig. 2). The ability of the film to maintain integrity and withstand environmental stresses in food preservation applications can be reflected from them. There was a significant increase ($P < 0.05$) in tensile strength and elongation at break of the composite film with the increasing nano Ag@O_2 addition (Fig. 2A and **C**). This phenomenon is ascribed to the fact when SiO_2 is uniformly dispersed in the polymer, the molecular interstices of PVA could be filled by SiO_2 through hydrogen bonding, ionic bonding, and other interaction forces [27]. Moreover, the tensile strength of the polymer increased by taking advantage of the specific surface area and elasticity of the nanomaterials [28]. However, the compounding ratio of PVA and PAH had no significant ($P > 0.05$) effect on the mechanical properties of the composites after film formation (Fig. 2B and **D**).

3.1.3. *Changes in antibacterial activity*

The effects of PAH synergistic nano Ag@SiO_2 modification on the antibacterial activity of PVA solution were shown in Fig. 3. With the increasing Ag@SiO_2 addition, the antibacterial activity of modified PVA solution against *E. coli* and *S. aureus* was gradually enhanced, especially when the nano Ag@SiO_2 addition was more than 0.18 % (Fig. 3A and **C**). Moreover, the bactericidal effect of the modified PVA solution against two pathogenic bacteria increased gradually with the increasing PAH percentage, and when the PAH compounding ratio was more than 50 % (1:1), the bacteria in the system could ultimately be killed in 2 h. Meanwhile, the SEM results (Fig. 3E–H) showed that the modified PVA solution had a significant lethal effect on *E. coli* compared with the control group, which could significantly destroy the cell structure of the bacterium. And *S. aureus* appeared to be wrinkled and deformed. These phenomena indicated that PAH synergized with Ag@SiO_2 modified PVA solution is a new method that could effectively improve the bacterial inhibition effect of PVA, when the Ag@SiO_2 addition was 0.18 % as well as the compounding ratio of PAH and PVA was 1:1. In this study, by preparing core-shell Ag@SiO_2, the silver nanoparticles are less sensitive to agglomeration, thus improving the stability of the nanoparticles. Moreover, the silver nanoparticles can be released slowly through the porous structure of SiO_2, thus exhibiting long-lasting antibacterial properties.

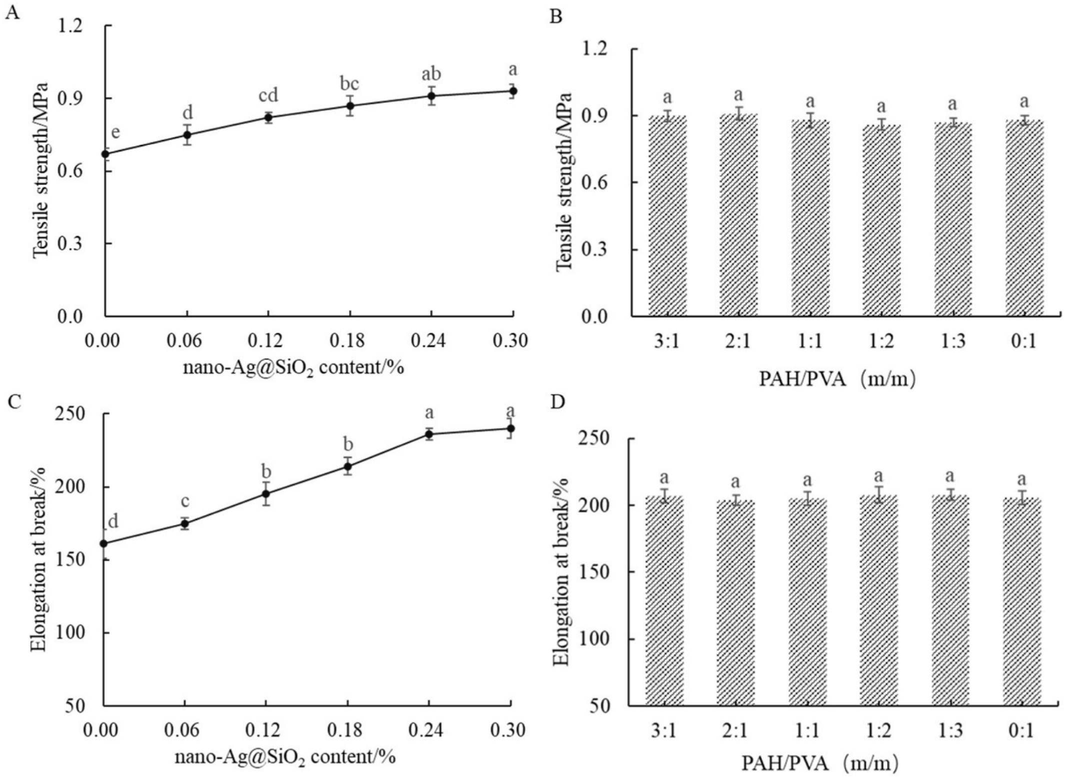

Fig. 2. Changes in tensile strength (A and B) and elongation at break (C and D) of the composites prepared with different contents of nano-Ag@SiO_2 and mixing ratios of PAH and PVA. Different lowercase letters indicate significant differences ($P < 0.05$) between samples from different groups.

3.1.4. The morphology of the composite film

The SEM image of the composite film, prepared with the composite ratio of PAH to PVA at 1:1 and the addition of Ag@SiO_2 at 0.18 %, is shown in Fig. 4. Nano Ag@SiO_2 is uniformly filled in the molecular voids of PVA, which exhibited the smooth and flat surface without noticeable lumps. Moreover, there were no voids in the dense cross-section.

3.2. Effects of PAH synergized with nano Ag@SiO_2 modified PVA on the preservation of strawberry

3.2.1. Changes in weight loss rate, respiratory strength, hardness, and putrefaction indices

Dehydration is an essential aspect during postharvest storage, mainly due to water transpiration and respiration consumption. It can be applied to evaluate the preservation effect of preservation materials on strawberries, meanwhile, the control of strawberry storage water loss can directly enhance the quality of strawberries [29]. As observed in Fig. 5A, the weight loss of strawberries in all groups increased during the storage. However, the change in weight loss of strawberries in the three coated groups (PVA, Ag@SiO_2+PVA, PAH + Ag@SiO_2+PVA) was lower than that of the control group. The coating material attached to the surface of strawberries serves as a barrier to gas and water, which could decrease the respiration and water loss, thus reducing the dehydration and shrinkage of strawberries [30]. Moreover, there was no significant difference between the Ag@SiO_2+PVA and PAH + Ag@SiO_2+PVA group, which were 1.77 ± 0.16 % and 1.41 ± 0.28 %, respectively, significantly lower than that of the control group at storage up to the 5th day. Modification of PVA further enhanced the hydrophobicity of the coating (Fig. 1C), leading to an improvement in the barrier properties [18]. Meanwhile, the effects of different coating materials on the respiratory strength of strawberries during storage were shown in Fig. 5B. The respiratory intensity of strawberries in all groups decreased slightly during the first 2 days of storage. With the extension of storage time, the respiratory intensity of strawberries increased significantly, especially in the control group, where the respiratory intensity of strawberries increased from 49.8 mg/kg/h to 92.4 mg/kg/h, indicating that strawberries continued to ripen after picking. Furthermore, the microbial metabolism during the post-storage period could promote the respiration to a certain extent [31]. For the other treatment groups, the effect of PVA coating on strawberry respiration was weak, while the Ag@SiO_2+PVA and the PAH + Ag@SiO_2+PVA group significantly inhibited the respiratory intensity of strawberries during storage. It may be due to the fact that the nanomaterials were dispersed in the pores of PVA, which increased the densification of the PVA material, thus reducing the air permeability, and altering the respiratory pathway of strawberry cells to inhibit respiration by affecting the metabolic activities of strawberries [32]. Combined with the results in Fig. 5A, it further indicated that the modified PVA material could reduce the change in the weight loss rate of strawberries during storage by inhibiting strawberry respiration.

Strawberry textural characteristics are critical attributes that determine consumer purchases and can reflect the overall sensory

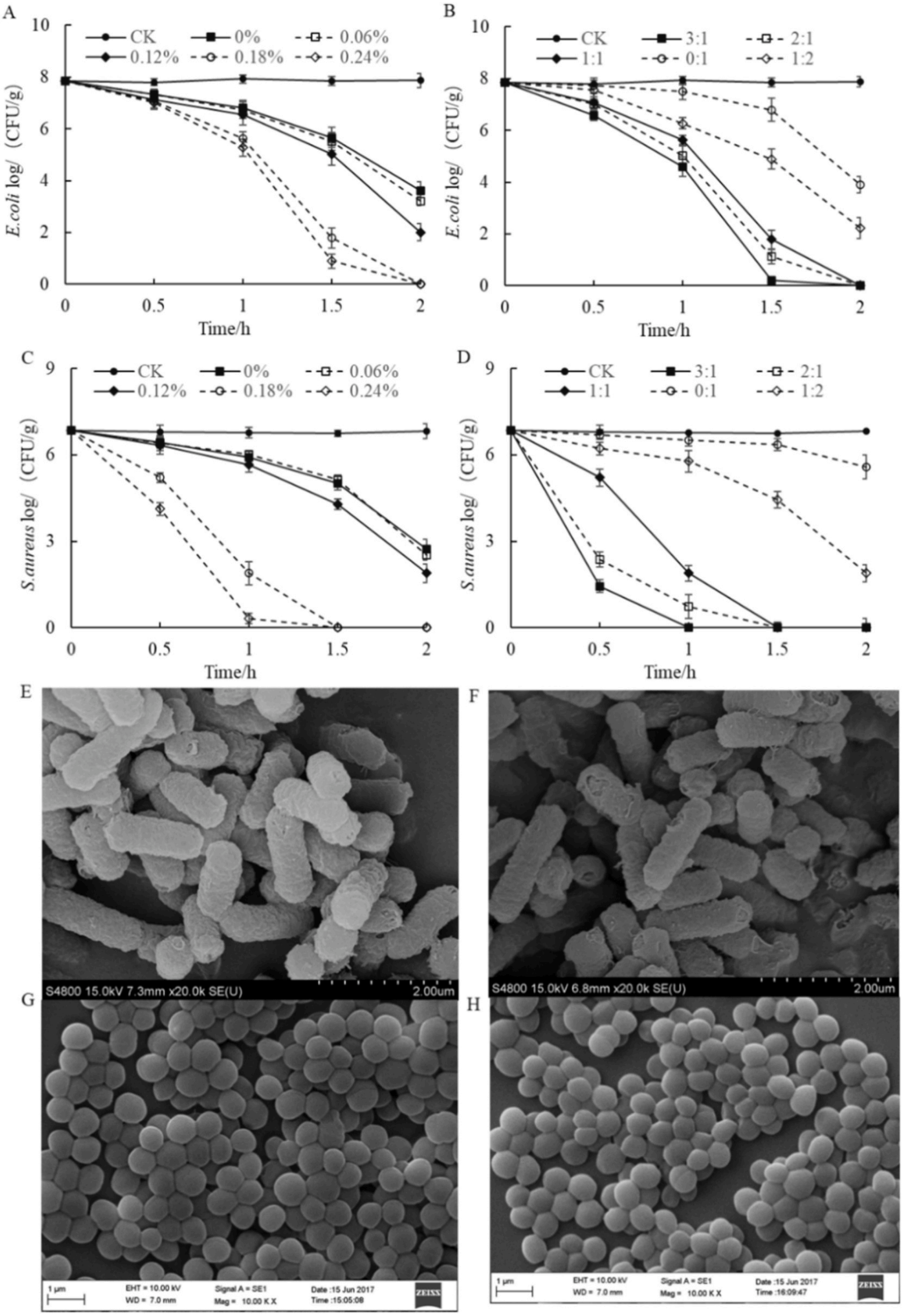

Fig. 3. The antibacterial activity of modified PVA solution against *E. coli* (A and B) and *S. aureus* (C and D). Changes in the morphology of *E. coli* (E and F) and *S. aureus* (G and H). CK represents the sample without any treatment.

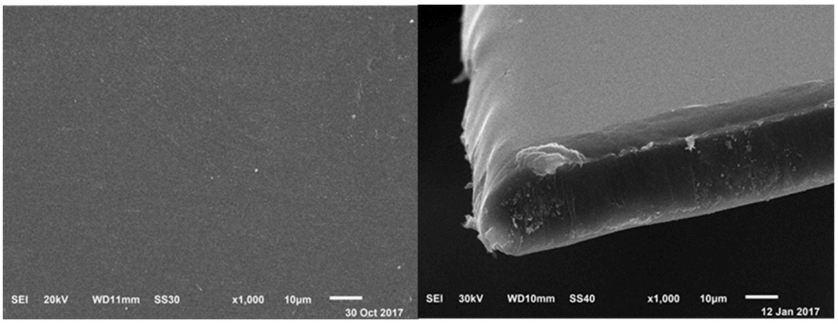

Fig. 4. Microscopic morphology of the surface and cross-section of the modified composite film.

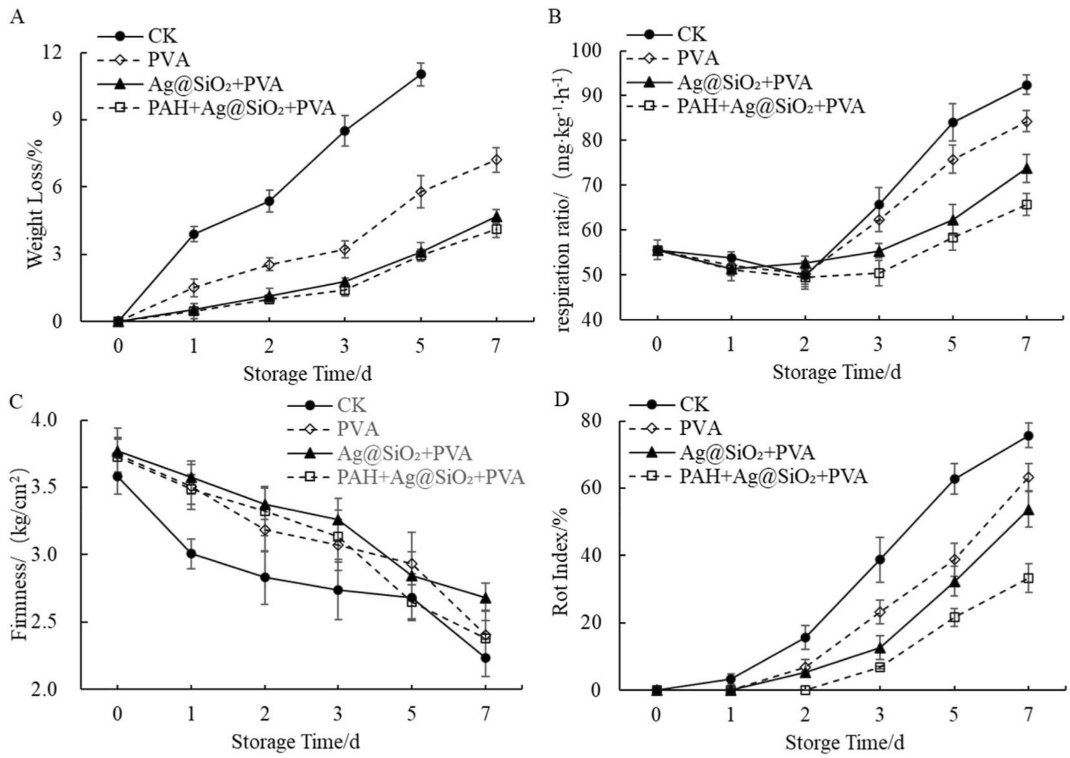

Fig. 5. Changes in (A) weight loss, (B) respiration ratio, (C) firmness, and (D) rot index of strawberries after treatments during the storage. CK represents the sample without any treatment, PVA, Ag@SiO_2+PVA, and PAH + Ag@SiO_2+PVA represent the sample coating with the corresponding solution.

quality [33]. During the storage of strawberries, the cell wall is damaged by the increased growth of microorganisms and endogenous autolytic enzyme activity, leading to cell collapse and the softening of strawberries. In Fig. 5C, it can be observed that strawberries of different treatment groups gradually softened during storage, which was manifested as the hardness index of strawberries gradually decreased with the prolongation of storage time. Changes in the hardness of strawberries in the three coating groups (PVA, Ag@SiO_2+PVA, and PAH + Ag@SiO_2+PVA) were lower than those in the control group. It was attributed to the fact that the composite coating could act as a protective film to reduce mechanical damage. Meanwhile, the barrier properties of the film could slow down the metabolism of strawberries, thus minimizing the softening of strawberries during storage.

Previous studies have shown that the respiration intensity of strawberries is positively correlated with the spoilage index of strawberries ($r = 0.916$, $P < 0.01$) [34]. As observed in Fig. 5D, the rot index of strawberries in the control group continued to increase during storage, increasing to 75.7 % ± 3.7 % at 7 d, followed by the PVA and Ag@SiO_2+PVA group. For the PAH + Ag@SiO_2+PVA treatment group, there was no significant ($P > 0.05$) change in the rot index of strawberries during the first two days of storage, and it was only 6.7 % at 3 d. As the storage time increased to 7 d, the rot index of strawberries was 38.7 % ± 6.7 %, which was significantly lower than the other treatment groups ($P < 0.05$). This result indicated that the modified PVA material could significantly reduce the decay rate of strawberries during storage.

3.2.2. Changes in the surface color

Changes in the L^*, a^*, b^*, and ΔE^* values of strawberries in different treatment groups during storage were shown in Table 2. It can be found that the a^* and b^* values of strawberries in treatment groups increased slightly during storage (0–5 d), but there was no significant difference ($P > 0.05$). For the difference in perceptible color (ΔE^*), it can be summarized as a highly significant difference ($\Delta E^*>3$), significant difference ($1.5<\Delta E^*<3$), and slight difference ($\Delta E^*<1.5$) [35]. In this study, the ΔE^* value of strawberries in each treatment group gradually increased compared with fresh strawberries. The ΔE^* value of most strawberry samples was in the range of 1.6–3.0, and only strawberries in the PVA and the PAH + $Ag@SiO_2$+PVA group had obvious and perceptible differences in color at 3–5 d of storage. Still, there was no significant difference from that of 0 d of storage ($P > 0.05$). Combined with the non-significant differences in L^*, a^*, and b^* values, it can be inferred that the main reason for the differences in the perceptible results is the intrinsic variability of the product color. Therefore, it can be concluded that PAH synergized with nano $Ag@SiO_2$ modified PVA had no significant effect on the color of strawberries during storage.

3.2.3. Changes in MDA, SOD, Vc, and anthocyanin measurement

During the storage of strawberries, the cells can be damaged due to microorganisms, endogenous enzymes, and external forces, which can cause the oxidation of lipids in the cell membrane. Besides, the accumulation of lipid peroxidation products also leads to cell membrane leakage and accelerates cellular senescence [36]. The levels of lipid peroxidation products in strawberries in the experiment were expressed as MDA content, as presented in Fig. 6A. The MDA content of strawberries increased gradually throughout the postharvest storage period. The MDA content of strawberries in the $Ag@SiO_2$+PVA and PAH + $Ag@SiO_2$+PVA groups was significantly higher than that of the other groups during the first three days of storage. It is mainly due to the fact that the lipid peroxidation could be triggered by the ROS generated by PAH and $Ag@SiO_2$. With the extension of storage time, there was no significant change in the MDA content in strawberries of the PAH + $Ag@SiO_2$+PVA group compared with the control group.

The antioxidant system is crucial in the ripening process of strawberries. SOD is considered as a critical antioxidant in the response of strawberries to stress factors and is the first line of defense against damage by superoxide radicals. Maintaining high SOD activity might be an essential indicator of strawberry tolerance to unfavorable environmental conditions. As observed in Fig. 6B, the SOD activity in the control group showed a trend of initial increase and then decrease with the extension of storage time, achieving the highest at 3 d. Meanwhile, the rate of strawberry decay gradually increased with increasing storage time, resulting in complete damage to the antioxidant environment of strawberries. For the $Ag@SiO_2$+PVA and PAH + $Ag@SiO_2$+PVA group, the SOD activity increased continuously during the storage. It was significantly higher than that of the control group ($P < 0.05$), which was 921 and 944 U/g, respectively, when stored for 7 days. This result indicated that the composite film could enhance the SOD activity of strawberries during storage and inhibit the damage caused by unfavorable conditions during the storage process.

Vitamin C in strawberries is a crucial portion of the antioxidant system and is able to synergize with SOD to counteract the damage caused by ROS in strawberries [37]. The Vc content of strawberries in all groups continued to decrease with the increasing storage time (Fig. 6C), with the greatest decrease in the control group, probably due to metabolic activities such as respiration and oxidation of strawberries. Strawberry in the PAH + $Ag@SiO_2$+PVA group had the lowest change in Vc content during the storage, which was only reduced by 149 μg/g on the 3rd day, which was significantly ($P < 0.05$) lower than other groups. Therefore, it can be found that PAH synergized with nano $Ag@SiO_2$ modified PVA can reduce the loss of Vc in strawberries during storage. With the metabolism, such as

Table 2
Changes in the surface color of strawberries after treatments during the storage.

	Storage time/day	CK	PVA	$Ag@AiO_2$+PVA	PAH + $Ag@AiO_2$+PVA
L^*	0	39.92 ± 1.21^a	39.80 ± 1.51^a	40.32 ± 1.11^a	38.78 ± 1.35^a
	1	39.76 ± 1.52^a	39.52 ± 1.02^a	40.66 ± 1.22^a	38.08 ± 1.32^a
	2	39.22 ± 1.16^a	38.68 ± 0.94^a	39.66 ± 1.03^a	37.72 ± 1.15^a
	3	38.78 ± 1.46^{ab}	38.26 ± 1.23^{ab}	39.76 ± 1.01^a	36.32 ± 1.14^b
	5	37.95 ± 1.23^a	38.52 ± 1.23^a	38.52 ± 1.28^a	36.66 ± 1.28^a
a^*	0	42.22 ± 1.57^a	42.52 ± 0.92^a	43.02 ± 0.80^a	42.82 ± 1.02^a
	1	42.98 ± 1.12^a	42.58 ± 0.67^a	42.78 ± 1.09^a	42.22 ± 0.74^a
	2	42.86 ± 0.85^a	43.02 ± 0.71^a	43.12 ± 0.67^a	42.52 ± 0.70^a
	3	43.06 ± 0.81^a	43.77 ± 0.74^a	43.32 ± 1.07^a	43.22 ± 0.89^a
	5	43.26 ± 0.66^a	44.03 ± 0.82^a	43.66 ± 0.65^a	43.49 ± 0.85^a
b^*	0	23.32 ± 0.68^a	24.21 ± 0.77^a	23.87 ± 0.93^a	23.67 ± 0.74^a
	1	23.35 ± 0.55^a	24.62 ± 0.54^a	23.89 ± 0.65^a	23.86 ± 0.65^a
	2	23.43 ± 0.57^a	24.85 ± 0.52^a	24.08 ± 0.57^a	23.72 ± 0.65^a
	3	24.01 ± 0.69^{ab}	25.05 ± 0.59^a	23.95 ± 0.59^{ab}	23.47 ± 0.41^b
	5	23.32 ± 0.53^b	25.68 ± 0.81^a	24.69 ± 0.58^{ab}	23.52 ± 0.45^b
$\triangle E^*$	0	1.80 ± 0.84^a	1.83 ± 0.89^a	1.65 ± 0.88^a	1.92 ± 1.07^a
	1	1.83 ± 0.57^a	1.83 ± 0.77^a	1.82 ± 0.77^a	2.38 ± 0.74^a
	2	1.60 ± 0.67^a	2.43 ± 0.61^a	1.61 ± 0.69^a	2.51 ± 0.87^a
	3	2.24 ± 0.58^a	3.11 ± 0.70^a	1.73 ± 0.93^a	3.01 ± 0.86^a
	5	2.54 ± 0.67^a	3.52 ± 0.96^a	2.41 ± 0.53^a	3.10 ± 0.88^a

Note: Different lowercase letters indicate significant differences ($P < 0.05$) between samples from different treatment groups at the same storage time. CK represents the sample without any treatment, PVA, $Ag@SiO_2$+PVA, and PAH + $Ag@SiO_2$+PVA represent the sample coating with the corresponding solution.

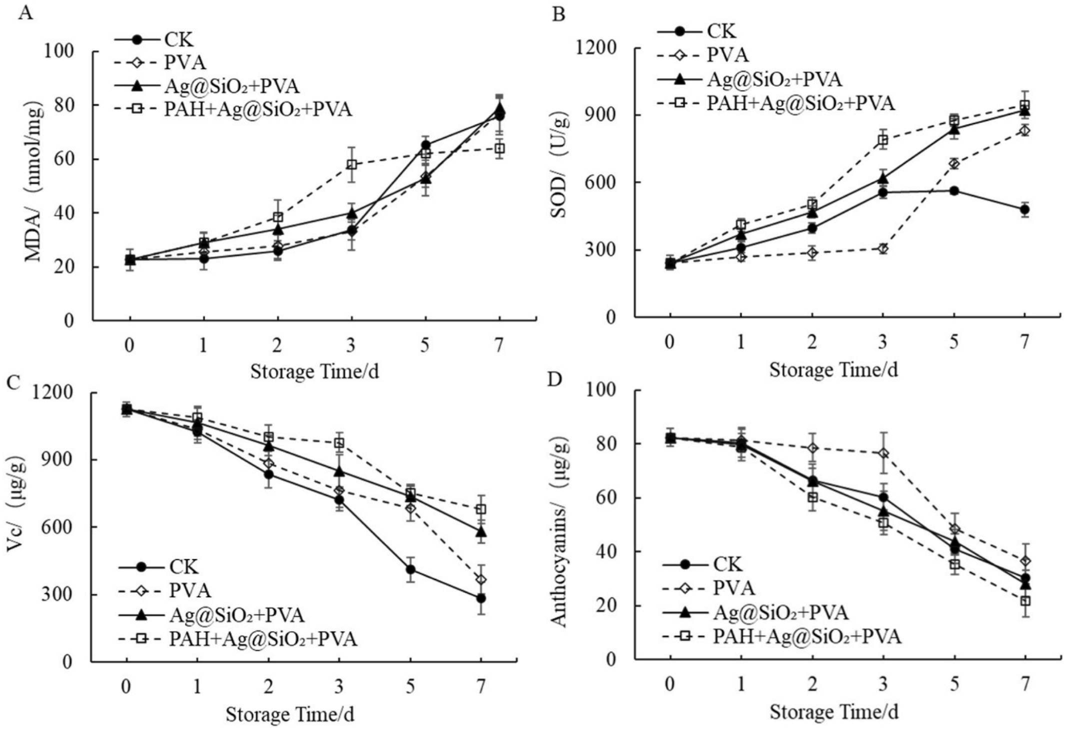

Fig. 6. Changes in (A) MDA, (B) SOD, (C) Vc, and (D) anthocyanins of strawberries after treatments during the storage. CK represents the sample without any treatment, PVA, $Ag@SiO_2$+PVA, and PAH + $Ag@SiO_2$+PVA represent the sample coating with the corresponding solution.

respiration during postharvest storage of strawberries, the anthocyanin in strawberries is gradually oxidized and decomposed, resulting in a continuous decrease. As shown in Fig. 6D, the anthocyanin content of strawberries in all groups decreased with the prolongation of storage time. Meanwhile, there was no significant difference ($P > 0.05$) among the control, PVA, and $Ag@SiO_2$+PVA groups; all were lower than the PAH + $Ag@SiO_2$+PVA group.

3.2.4. Changes in the total bacterial count

Changes in the total bacterial count of strawberries after various treatments during the storage were shown in Fig. 7. The count in the control and PVA groups exceeded 10^6 CFU/g when the storage time increased to 5 days. Meanwhile, the count in $Ag@SiO_2$+PVA and PAH + $Ag@SiO_2$+PVA group was significantly lower. This phenomenon is mainly due to the antibacterial activities of PAW and $Ag@SiO_2$ present in the modified PVA film. They led to the inactivation of microorganisms on the surface of strawberries during the film-forming process. When the storage increased to 7 days, the total bacterial count in the PAH + $Ag@SiO_2$+PVA only reached to 4.01 lg CFU/g. This phenomenon further indicated that PAH synergized with nano-$Ag@SiO_2$-modified film could inhibit microbial

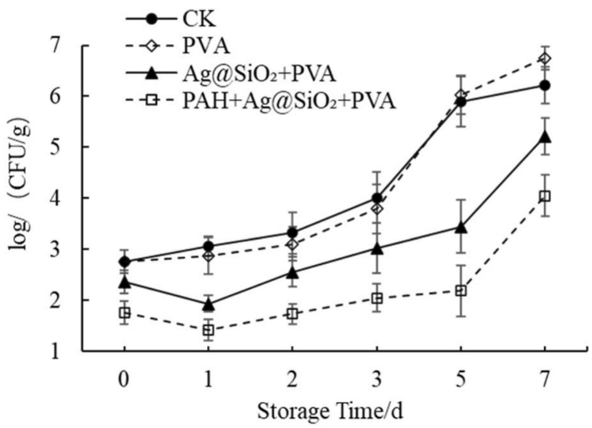

Fig. 7. Changes in the total viable bacteria of strawberries after treatments during the storage. CK represents the sample without any treatment, PVA, $Ag@SiO_2$+PVA, and PAH + $Ag@SiO_2$+PVA represent the sample coating with the corresponding solution.

colonization of strawberries during storage by reducing the initial colony count of strawberries.

4. Conclusion

In conclusion, this study mainly focuses on preparing novel composite films by modifying the PVA solution with PAH and Ag@SiO_2. Meanwhile, the effects of the composite modification on the physicochemical properties of the films were analyzed. It was found that the presence of Ag@SiO_2 enhanced the mechanical properties of the PAH film, while the addition of PVA improved the bactericidal properties of the composite film. When the composite film is applied to the preservation of strawberries, the presence of the composite film also inhibited the respiratory strength of strawberries and the growth of microorganisms on the surface, reduced the weight loss rate, softening rate, and rot index of strawberries during the storage, and had no significant effect on the critical nutrients of strawberries. This study provides a basis for the research of composite-modified films on fruits. Meanwhile, in future research, it may be possible to consider the addition of other active substances, being able to realize the real-time monitoring of the freshness of the fruits.

Data availability statement

This manuscript contains all the results from our work, thus, there was no data sharing in any available public repository. Data will be made available on request.

CRediT authorship contribution statement

Wenlong Hong: Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Chunqin Xie:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Data curation. **Jianying Zhao:** Writing – review & editing, Validation, Investigation, Conceptualization. **Zhaoqi Dai:** Writing – review & editing, Software.

Declaration of competing interest

There is no conflict of interest exists in "**Application of plasma-activated hydrogen peroxide solution synergized with Ag@SiO_2 modified polyvinyl alcohol coating for strawberry preservation**".

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