Extending Shelf Life of Fruits Using UV-Activated TiO_2 Nanoparticle Coatings on Cardboard Packaging

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Abstract. Over-ripening of fruits due to ethylene emission has resulted in significant fruit waste during the production and transportation processes. Thus, titanium dioxide nanoparticles (TiO_2 NPs) have been chosen for coating onto cardboard to degrade ethylene produced by fruits, thereby increasing their shelf life. TiO_2 NPs were precipitated onto cardboard using ammonium hydroxide and titanium chloride. Pieces of banana peels were placed in cardboard boxes with coatings that were activated by UV light and then monitored for days. TiO_2-coated packaging showed visible improvements in reducing ethylene effects on the banana peels' ripening process.

Keywords: Shelf life, TiO_2 Nanoparticle, Cardboard Packaging, UV activation, Fruit preservation technology.

1. Introduction

Fruits are a major part of most people’s lives, whether it’s for food or medicine. However, the transportation of fruits has been very troublesome as ethylene production and turbulence can cause fruits to over-ripen very easily. This problem occurs in every method of transportation, whether it's through air, on land, or at sea. Poor packagings significantly increase the risk of damaging fruits, resulting in them being rendered unsaleable. Although fruits are biodegradable and more disposable than other products, this still results in a huge financial loss and waste. Extending the shelf life of fruits can allow for more efficient and cost-effective allocation. It is estimated that 30% of mangoes are wasted annually by the world's largest producers [1]. Additionally, it is estimated that 5 billion bananas are wasted annually in the U.S. alone.[2] These fruits, along with many others, share two common traits: they are highly popular globally and produce a significant amount of ethylene. Today, although ethylene absorbers have already been on the market, such packets need to be replaced regularly and aren’t as cost-effective when used for mass transportation.

This project aims to develop an alternative, cost-effective, and nanoscale solution to this problem. Fruits go to waste in such significant amounts due to a variety of reasons. However, ethylene emission is the main problem. Fruits either emit ethylene themselves or absorb it from the atmosphere. Ethylene is a hormone that triggers the ripening of fruits. As a result, to increase the shelf life of fruits, ethylene has to be removed. The use of titanium dioxide nanoparticle coatings is also employed. The mechanism behind this approach relies on the photocatalytic activity of titanium tetrachloride nanoparticles. Absorbing ultraviolet light, TiO_2 NPs on coated surfaces, electrons are released. Thus, the TiO_2 NPs are positively charged. They then take electrons from moisture in the air and form hydroxyl radicals. These hydroxyl radicals can break down organic substances and form harmless compounds. In this case, ethylene is broken down into carbon dioxide and water. In theory, if TiO_2 NPs are coated onto commonly used packaging materials, such as cardboard, ethylene would not function as well as it normally would. TiO_2 NPs are also chosen for this purpose due to their antibacterial properties, low cost, and ease of production. We hypothesize that titanium dioxide nanoparticle-coated packaging should slow the spoilage rates of fruits equally effectively as commercial ethylene absorbers, but at a lower price.

2. Methods

2.1 Synthesis of Titanium Dioxide Nanoparticles

TiO_2 NPs were synthesized by a protocol modified from the method developed by Rab, Chong, Mohamed, and Lim [3]. Although they presented various methods of hydrolysis with different ratios of distilled water and glycerol, this experiment used only distilled water to maximize efficiency and accuracy. Under a fume hood, 10mL of distilled water was placed in a beaker with a magnetic stirrer and a thermometer. Approximately 1mL of pure titanium tetrachloride was then carefully extracted from the container with a syringe and added to the distilled water. The magnetic stirrer was then turned on at high speed to allow the titanium tetrachloride to dissolve completely. As the solution was being prepared, 30mL of 2.5M ammonium hydroxide was measured out in another beaker. After the titanium tetrachloride had been fully dissolved in distilled water, ammonium hydroxide was added to the solution with the stirrer still running at high speed. As the mixture was allowed to fully mix and react, when the pH reached 10, a white precipitate should form. To isolate the TiO_2 NPs, the precipitate was filtered using filter paper and transferred to a plate, where it was left to dry overnight. After that, the white to slightly yellow powder was placed into a filter, and ethanol was slowly poured onto it to wash away the residual reactants. Repeat the drying and washing process at least two more times to ensure purity. After this, only pure TiO_2 NPs should be left.

2.2 Coating of Titanium Dioxide Nanoparticles On Cardboard

To ensure efficiency and reduce costs, TiO_2 NPs weren’t coated onto cardboard through typical coating methods, such as chemical vapor deposition or spin coating. Still using the protocol for synthesizing TiO_2 NPs, the volume of each reactant was scaled up proportionally. The total volume of the reaction should be scaled up until the cardboard to be coated can be fully immersed in the reaction. The cardboard was initially introduced to the reaction after the titanium tetrachloride was mixed with the water. Then, the protocol was followed, and precipitate formed. After the pH was at around 10, the cardboard was removed from the solution and left to dry. It was then washed with ethanol to ensure purity.

2.3 Testing Using Banana Peels

A control cardboard box and a titanium dioxide nanoparticle cardboard box were made with the respective pieces of cardboard. As the photocatalytic activity of TiO_2 NPs requires activation by ultraviolet light to function, the titanium dioxide box was placed in a dark closet, and ultraviolet light was shone on the box using a Germ Reaper for two hours. A banana bought from a local grocery store was peeled, and two identical pieces of peel from the same side of the banana were cut out. After the boxes were ready, each piece of banana peel was placed inside each box. Pictures of each piece of banana peel were taken before being put into the boxes. The boxes were then stored in the same closet, in a dry atmosphere, and without any direct contact with light. Pictures of both peels were taken at intervals of time until both banana peels were completely turned black. If the black area of banana peels in the coated cardboard box is comparatively less than that of the control box, then the testing would be considered positive.

3. Results

3.1 Titanium Dioxide Nanoparticles

According to the Dynamic Light Scattering (DLS) scan, the precipitate from the three trials was found to have diameters of 20 nm, 17 nm, and 28 nm. Electron Dispersive Spectrometry (EDS) confirmed that the precipitate was made of titanium and oxygen. With an average size of 21.67 nm, the TiO_2 NPs were considered successfully synthesized at the desired size. Through Scanning Electron Microscopy (SEM), images of particles with diameters of 17 nm and 28 nm were taken, and the particles appear to be spherical (see Figures 1 and 2). Sizes likely varied due to a slightly different amount of volume of titanium chloride. The pH of the solution in the first two solutions was found to be around 10 when white precipitate formed. However, the third trial's solution at precipitation had a pH of 11, likely due to a few minor human errors.

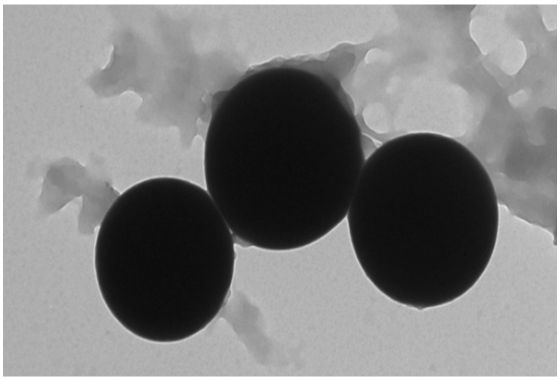

Figure 1: SEM image of TiO2 NP's in trial 2 of size 17 nm

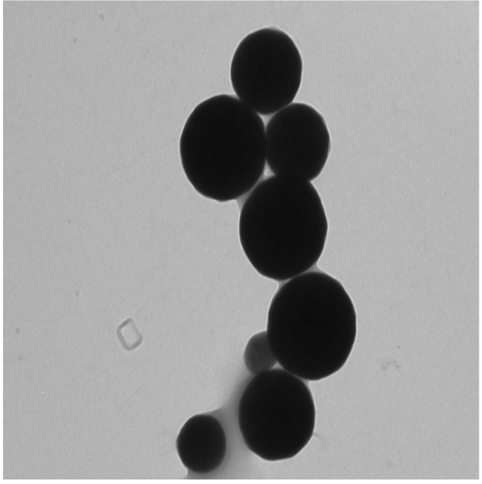

Figure 2: SEM image of TiO2 NP's in trial 3 of size 28nm

3.2 Titanium Dioxide Nanoparticles Coated on Cardboard

Two pieces of cardboard were made under the same protocol to make a box. After the cardboard was soaked in the precipitation solution and washed with ethanol, there were no visible differences from a regular wet cardboard. However, when characterized by EDS, both pieces were found to have titanium and oxygen present on their surfaces. Through SEM images, there are visible clusters of TiO_2 NPs (See Figure 3). Although there are also similar small chunks as found in normal, uncoated cardboard, the textures differ, and no titanium or oxygen was detected in regular cardboard through EDS (See Figure 4).

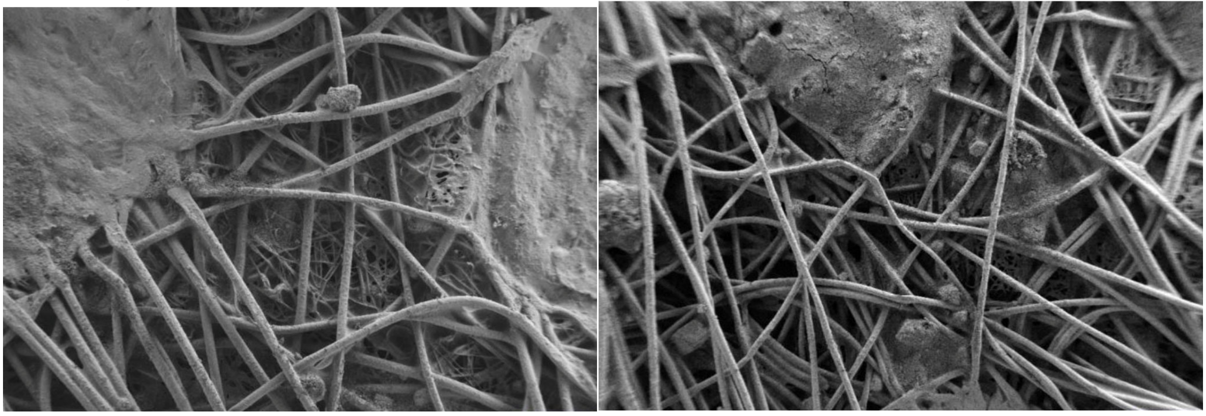

Figure 3: SEM images of both TiO2 NP coated cardboard

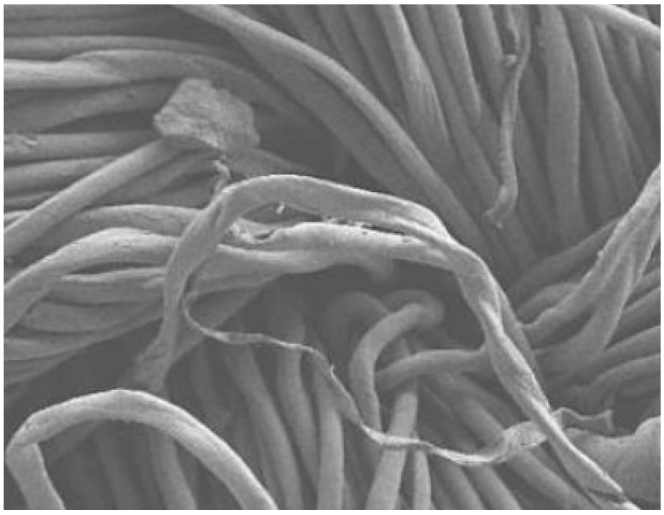

Figure 4: SEM image of a regular piece of cardboard

3.3 Banana Peel Testing

Two trials of the same test were done. Both used the same protocol and lasted around 70 hours. In the first trial, both banana peels looked relatively similar to each other before hour 42 (See Figure 5). However, between hours 42 and 51, the control banana peel had a darker corner than the banana peel with TiO_2 NPs (See Figure 5). In trial 2, where the banana peels were comparatively fresher than those in the first trial, the effects of TiO_2 NPs were more obvious. The freshness of the peels in this trial starter ranged from 44.5 hours to 61.5 hours, with a greater number of black spots present on the control peel.

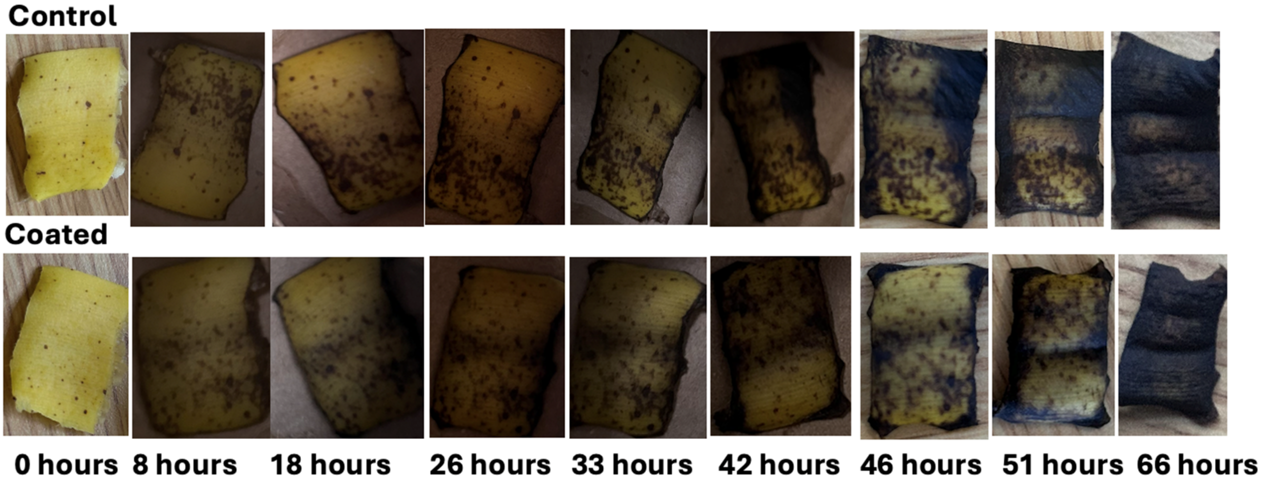

Figure 5: Timeline of banana peels kept in a control cardboard box and a TiO2 NP coated cardboard box over different periods of time in trial 1.

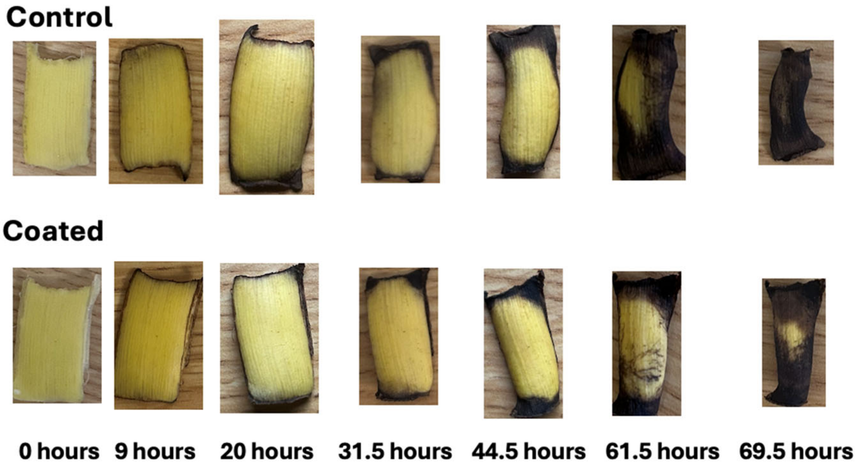

Figure 6: Timeline of banana peels kept in a control cardboard box and a TiO2 NP coated cardboard box over different periods of time in trial 2.

4. Discussion

Through the testing with banana peels, it can be concluded that the TiO_2 NPs were able to preserve fruits by degrading ethylene. However, the effectiveness of the nanoparticles has to be improved for real-world applications. The nanoparticle-coated cardboard was only able to preserve the banana peels better than the control for an average of less than 12 hours. This is insufficient for the regular transportation of fruits or for extending their shelf life. A range of reasons could likely cause this problem. First of all, the coating, despite being quick and easy, might not be as effective or optimal for degrading ethylene. This is evident due to the clusters present in the SEM images of the cardboard. As a result, to improve the effectiveness of TiO2 NPs, other coating methods are recommended for use. Another factor that could have contributed to the decrease in effectiveness is the coated cardboard's duration of exposure to UV light. The duration in this experiment was two hours, longer than in prior studies. The last problem this experiment has to address is the toxicity of the cardboard coatings. As titanium tetrachloride is highly toxic and can be fatal if it is absorbed into the human body, no residual reactants can remain in the cardboard after it is washed and dried to ensure the safety of use on food.

5. Conclusion

The results indicate that this method could be a cost-effective approach to preserving fruits. Using the method, TiO_2 NPs with an average diameter of 21.67 nm were synthesized. The TiO_2 NPs coatings were successful in reducing the ripening rate of banana peels. If the weaknesses addressed in the discussion can be resolved, this technology could be a more cost-effective alternative to fruit preservatives currently available on the market. Overall, this is a unique technology that has yet to be developed and could be revolutionary in the transportation and storage of fruits.

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