engineering proceedings

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Proceeding Paper

Optical Colorimetric Sensing Label for Monitoring Food Freshness †

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† Presented at the 2nd International Electronic Conference on Chemical Sensors and Analytical Chemistry, 16–30 September 2023; Available online: https://csac2023.sciforum.net/.

Abstract: The development of optical sensors to monitor food freshness during storage and transportation helps to increase food security and customer satisfaction by preventing the misinterpretation of food date labeling. In this study, a simple, rapid, and low-cost paper-based optical sensing label was fabricated for the visual detection of food spoilage by the naked eye. The filter paper was coated with electrically conductive polyaniline ink. The pH-responsiveness of the coated polyaniline nanofibers allowed for the colorimetric detection of shrimp spoilage through the transition from the doped green emeraldine acid state to the dedoped blue emeraldine base state. The combination of the flexible filter paper as a substrate and the polyaniline ink as an indicator represents a facile approach for the fabrication of a colorimetric optical sensing label for food freshness monitoring applications.

Keywords: packaging; pH sensor; filter paper; polyaniline; nanofiber; spoilage; shrimp

Citation: Abu-Thabit, N. Optical Colorimetric Sensing Label for Monitoring Food Freshness. *Eng. Proc.* **2023**, *48*, 16. https://doi.org/10.3390/CSAC2023-14932

Academic Editor: Nicole Jaffrezic-Renault

Published: 12 October 2023

1. Introduction

Packaging aims to preserve and protect foods from spoilage and to provide consumers with commodity information such as the production date, shelf life, and expiry date [1]. Smart food packaging systems provide customers with a higher satisfaction level through the direct observation of the food quality and safety during the storage period [2,3]. Multicolor chemical sensors have been proposed for designing and fabricating intelligent sensors to monitor the freshness of different food items [4–6]. Usually, chemical sensor labels/films are fabricated by immobilizing one or more indicators on a selected polymer or composite material. The main shortcoming of using the indicators is their leaching out from the immobilization matrix during the application period [7–9]. Besides that, many of the reported polymeric matrices exhibit low mechanical durability (e.g., high swelling and low tensile strength) which limits their practical applications as optical sensing films [10,11]. Hence, there is a crucial need to find alternative methods or materials that prevent indicators from being leached out during their service period.

Polyaniline (PANI) is one of the Electrically Conductive Polymers (ECPs) that has a high chemical stability and can be coated easily on a variety of conductive and nonconductive substrates via chemical oxidative polymerization. PANI can be polymerized using a variety of methods to produce nanoparticles, nanowires, and other types of nanostructures with controlled morphology [12]. PANI is a pH-responsive polymer that can alter its color and electrical conductivity, which enables its use as a multicolor indicator for different sensing applications, including monitoring food freshness [13,14]. Filter papers are flexible, affordable, and biodegradable materials that have been employed as porous substrates to fabricate optical sensors for various applications [15–17]. However, there is a limited number of studies that have reported the utilization of filter paper as a substrate for the immobilization of colorimetric indicators to monitor food freshness [18]. In this work, we prepared filter paper coated with polyaniline ink for application as a sensing label to monitor the food freshness of shrimp. The fabrication process is simple and rapid, and the coated filter paper exhibits a fast pH response upon switching from an acidic to alkaline medium or *vice versa*.

2. Material and Methods

2.1. Synthesis of Polyaniline Ink

In brief, 0.50 g aniline monomer was dissolved in 50 mL HCl (1 M), and 1.50 g ammonium persulfate was dissolved in 50 mL HCl (1 M). After that, both solutions were mixed quickly, and the polymerization solution was stirred at 1200 rpm for 15 min. The resulting solution was filtered carefully in such a way that the filter cake did not become dry. The resulting polyaniline nanofibers were washed with 20 mL HCl (1 M), followed by 10 mL acetone to remove unreacted monomers, oligomers, or other side products. The filter cake was then dispersed in 100 mL of HCl (1 M), and it was used as PANI ink. The dispersion was stable for one month. However, the dispersion was sonicated before use to break any invisible aggregated particles.

2.2. Fabrication of the Optical Paper Sensor

PANI was deposited on a filter paper by dropping 1 mL PANI ink on a 4×4 cm^2 square piece of filter paper. The filter paper was dried in the oven at 60 °C for 1 h.

2.3. Characterization

The sheet resistance of the filter paper coated with PANI ink was measured as per the detailed procedure provided in reference [19]. Light transmittance of the prepared PANI nanofibers was plotted as a function of wavelength in the range of 400–800 nm using a double-beam spectrophotometer, Cintra 2020 (GBC Scientific Equipment, (Melbourne, MEL, Australia). The color parameters (a*, b*, and L*) of the PANI-coated filter paper were measured using a colorimeter device manufactured by Sheen Instruments (Metamora, MI, USA, model no. 281 SPECTRO–GUIDE 45/0 with a white background. The values of the rectangular coordinates (L*, a*, b*), where (L*) is lightness, a* is the degree of redness or greenness, and b* is the degree of yellowness or blueness, were recorded at different pH levels, and the total color differences, ΔE* was calculated by using Equation (1):

$$\Delta E = \left[(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2\right]^{\frac{1}{2}} \quad (1)$$

where ΔL* = L* − L0*; Δa* = a* − a0*; Δb* = b* − b0* (L0*, a0*, and b0* are the color parameters of the reference PANI-coated filter paper at specific pH level).

2.4. Shrimp Spoilage Sensing Test

The PANI-coated filter paper was evaluated as a smart responsive film for application in the food packaging industry. Shrimp with an average weight of 4–6 g were purchased from local supermarkets. About 15 g of shrimp and the testing PANI-coated filter paper (preconditioned with 1 M HCl) were sealed in a food packaging plastic container, and the color change in the filter paper sensor was recorded at room temperature every 6 h for a total period of 24 h.

3. Results

PANI ink was prepared using a facile rapid mixing strategy as well as low concentration, which resulted in the formation of PANI nanofibers. The use of nanofibers allows for the facile dispersion of the PANI ink, and their high surface area enables shorter response times for the fabricated sensor. Figure 1a displays the spectrogram for the prepared PANI ink in acidic and alkaline media. At pH = 2, the conductive form of the PANI ink exhibits maximum absorption at a wavelength of 770 nm. At pH = 10, the nonconductive form of PANI exhibits maximum absorption at a wavelength of 552 nm. Hence, PANI ink exhibits a clear transition from an acidic to alkaline medium and can be used as an optical chemical sensor. The immobilized PANI ink on the filter paper shows a clear transition from a green color in the acidic medium to a blue color in the alkaline medium (Figure 1b). The filter paper coated with the green PANI, which is known as the doped acid form (emeraldine acid), exhibits a sheet resistance of 1×10^4 ohm/square, while the blue colored dedoped base form (emeraldine base) is nonconductive with a sheet resistance of $>1 \times 10^{10}$ ohm/square (Figure 1b). Therefore, the filter paper coated with PANI ink can be employed as a chemical sensor label for the detection of food spoilage.

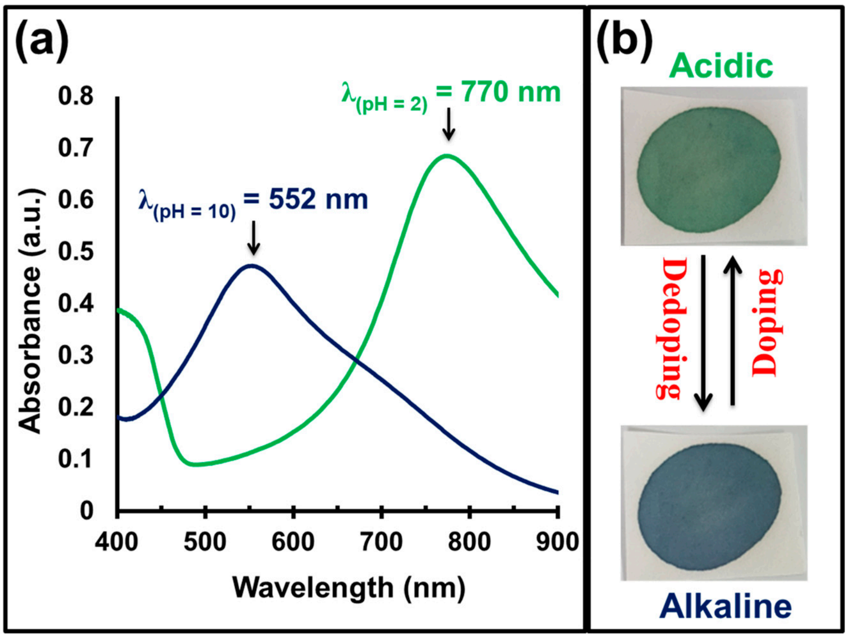

Figure 1. (**a**) Spectrogram for the synthesized polyaniline nanofibers in the doped form (pH = 2) and the dedoped form (pH = 10), and (**b**) digital images fabricated of the sensing label showing the color change in the filter paper coated with polyaniline ink during the doping–dedoping process.

There is a strong correlation between the freshness of some foods and their pH such as meat, chicken, and milk [6,20]. Hence, optical pH chemical sensors have been employed as labels for the visual detection of food freshness through the visual observation of a color change during the storage period. In the current study, shrimp samples were used as a model food to confirm the effectiveness of the pH optical sensor. The PANI-coated filter paper was applied as a pH-indicative film for the assessment of the freshness of shrimp samples (Figure 2a). Fresh shrimp samples were intentionally spoiled in ambient conditions to observe the continuous color change in the filter paper sensor during the testing period. At the initial stage, the green filter paper optical pH sensor was preconditioned with 1 M HCl to ensure a good level of doping. After 12 h, the filter paper optical sensor turned into a light greenish-blue, which indicated that there was a kind of dedoping process due to the increase in the pH ($\Delta E \approx 21$) (Figure 2b). This increase in the pH could be attributed to the release of volatile nitrogenous compounds such as ammonia and triethylamine from the shrimp's proteins when they start to become spoiled due to microbial degradation as well as bacterial growth [21]. A careful inspection of Figure 2b reveals that the observed difference in ΔE is attributed mainly to the decrease in the values of L* and b*, which corresponds to the increased darkness and blueness of the filter paper, respectively. The total spoilage of the shrimp samples was observed after 24 h, which can be inferred from the appearance of the distinctive blue color of the filter paper sensor as well as the high difference in color change ($\Delta E \approx 33$). The inverse of the values of a* and the b* values provide clear evidence for the good performance of the filter paper as an optical sensor for food freshness due to the gradual and obvious color change in the filter paper during the spoilage period of the shrimp samples caused by the corresponding local change in the pH environment.

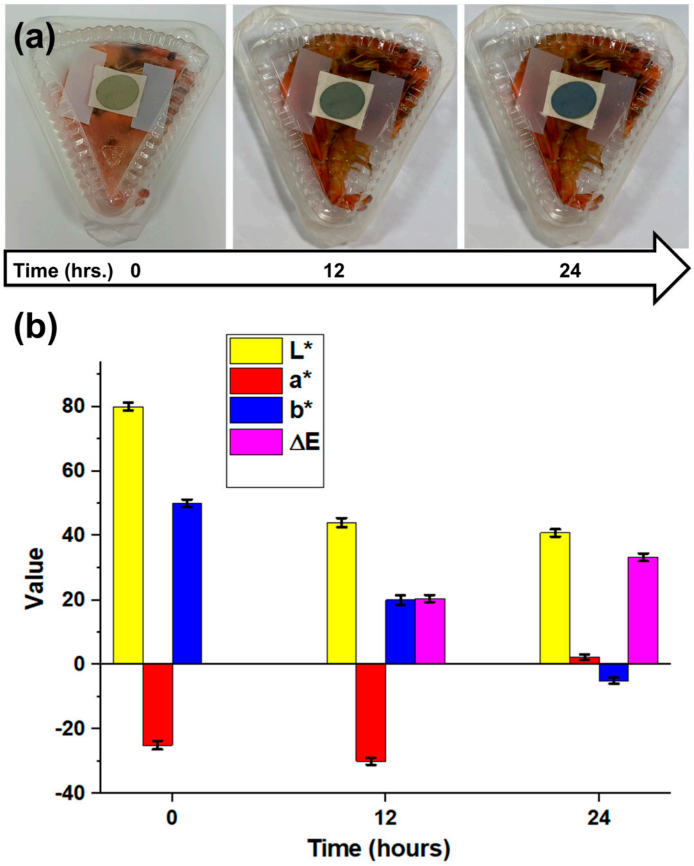

Figure 2. (**a**) Color change in the filter paper optical sensor during the contact with shrimp samples exposed to air at different test intervals. (**b**) The corresponding values for the color parameters (L*, a*, and b*) and color difference (ΔE) for the filter paper optical sensor employed during the shrimp spoilage test for 24 h.

4. Conclusions

The filter paper coated with polyaniline nanofibers presents a facile, quick, and low-cost method for fabricating smart and flexible optical sensing labels to monitor food freshness. In this way, there is no need to use chemical crosslinks to stabilize the indicator and no need to worry about the mechanical properties of the films. The obtained results suggest that the filter paper coated with polyaniline can be used as a sensing label to visualize shrimp spoilage during the storage time due to the strong color transition from green to blue ($\Delta E \approx 33$).

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All the generated data are presented inside the paper.

Conflicts of Interest: The author declares no conflict of interest.

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