Time temperature indicators (TTIs) based on silver nanoparticles for monitoring of perishables products.

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Abstract. This work presents the results of the production and characterization of silver nanoparticles (AgNPs) to applications in Time Temperature Indicators (TTIs). AgNPs were synthetized by chemical processes. The suspensions (AgNPs in water) were characterized for different temperatures (4°C and 22°C) and time (0 to 5h). The AgNPs were characterized by energy dispersive X-ray spectrometry (EDS), UV–vis spectrophotometry and dynamic light scattering (DLS). AgNPs with diameters between 40 to 160nm were produced. The UV-Vis spectra reveal a characteristic absorption peak of the Ag in 420nm. This suspension shows shifts in the emission wavelength when exposed to room temperature compared to when exposed to a temperature of 4°C for different periods of time. ∆λ = 20nm in the absorption spectra were found. Size distribution showed that the nanoparticles size decreases from 164 ±8 nm to 44±3 nm in the period of time studied. Suspension with nanoparticles concentration of 1.26·10⁻¹⁰M were obtained. TTIs manufactured with nanomaterials base its operation on the variations of the characteristics of nanoparticles suspended due to absorbing heat.

Introduction

The perishables products spoilage and its shelf life are associated with external environmental parameters such as temperature, humidity, mechanical stress, carbon dioxide production, respiratory behavior, ethylene production, and sensitivity[1]. In order to increase the shelf life of this products, currently news kinds of packaging with the ability to monitor variables such as temperature are being used. Packaging with this communication capacity are called Intelligent Packaging (IP) and are defined as packaging that contains an external or internal indicator to provide information about the traceability of the package. Furthermore, IP allows the monitoring of the product quality from the production process until it reaches the consumer [2]. Product quality is determined by a series of devices and indicators including barcode labels, radio frequency identification tags, time-temperature indicators, gas indicators, and biosensors [3-7]. Time-temperature indicators (TTIs) are systems for temperature monitoring which can be placed in packages as a small self-adhesive label. Temperature variations in a TTI produce an optical response like a change of color. This change is due to physical, chemical or biological changes in the systems. Recent studies show that metal nanoparticles with plasmonic properties have been applied successfully in the production of these types of indicators [8-11].

Metal nanoparticles have interesting optical attributes when they interact with light, since free electrons of nanoparticles that interact with the electromagnetic field experience a collective coherent oscillation. This oscillation is resonant at a particular frequency of the light and causes that emission of light is generated in a specific wavelength according to the characteristics of the nanoparticles and the medium.
in which they are suspended [12-17]. For application in TTIs, usually silver and gold nanoparticles suspended in a liquid are used. When the temperature of the system increase, changes in the size, shape and distribution of the nanoparticles can be produced (figure 1), which results in a shift of wavelength emission. In this work, we present the synthesis and characterization of silver nanoparticles AgNPs suspended in water to be used in the manufacture of time temperature indicators.

![Figure 1](image)

**Figure 1.** Time temperature indicator based on nanoparticles. a) Representation of the change in size, shape or distribution that nanoparticles may experience due to temperature. b) Photograph of suspended nanoparticles exposed to 22 °C for three different periods of time.

**Methods**

**Synthesis of nanoparticles**

AgNPs were synthesized chemically according to the protocol used by Zeng et. al. which involves the reduction of silver nitrate (AgNO₃) by L-ascorbic acid in the presence of Ag seeds, poly vinyl pyrrolidone (PVP), and sodium citrate [8]. In this process, under magnetic stirring, 100 mL of milli-q water was mixed with a solution of 2.5 mL of AgNO₃ in water at 5 mM, a solution of 7.5 mL of vinyl pyrrolidone in water at 0.8 mM, a solution of 7.5 mL of sodium citrate in water at 30 mM, 0.2 mL of the of Ag seed solution, and finally (by slow dropping) 62.5 mL of L-ascorbic acid in water at 1 mM. Seed solution was prepared with silver nitrate and trisodium citrate in 11 mL of water at 0.1 mM and 2 mM respectively. Following, under magnetic stirring, 0.3 mL of a solution of sodium borohydride (NaBH₄) in water at 5 mM was added all at once.

**Sample preparation and characterization**

The suspension of the synthesized nanoparticles was placed in two capped beakers, and then one was aged at room temperature and another in an ice bath at 4°C (relevant temperature in the cold chain) for different periods of time (0h to 5h). Samples of 2 ml of suspension in quartz cuvettes were taken out from the beakers at a specific time for its characterization. The particle suspensions were studied by energy dispersive X-ray spectrometry (EDS), UV-visible absorbance spectroscopy (UV/Vis) and dynamic light scattering (DLS) in order to do compositional analysis of the nanoparticles synthetized and quantify the optical properties of the suspension exposes to two temperatures for different periods of time. The compositional analysis was carried away by EDS attached with a SEM JEOL JSM 64890-LV. To acquire the absorption data, the 10S UV-Vis Spectrophotometer equipment of the Thermo Scientific brand was used. Finally, the DLS measurements were taken with a Malvern Zetasizer Nano ZS.
Results and Discussion

In figure 2, scanning electron microscopy shows that the synthetized nanoparticles present a relatively spherical in shape. The EDS pattern indicates that AgNPs were synthesized, since Ag metal with 67.92% of presence in the sample used was found. The EDS spectrum also reveals two other peaks. The first peak (C) is due to the carbon tape used in the assembly of the sample. The second peak (Na) might be coming from residues of the synthesis process. UV/Vis absorption spectra from the silver nanoparticles synthetized are showed in figure 3. Shortly after the synthesis process, the spectra reveals a characteristic absorption peak of the silver located at around 420 nm due to surface plasmon resonance[18].

![Figure 2](image.png)

Figure 2. a) SEM image of the synthesized silver nanoparticles. b) EDS analysis of synthesized AgNPs.

![Figure 3](image.png)

Figure 3. UV/Vis absorption spectra from the Ag nanoparticles synthetized. a) Samples in ice bath at 4°C. b) Samples at room temperature (22°C) c) Photograph of the samples at room temperature for different periods of time.
After one hour of elapsed time, the samples at 4°C and at room temperature (22°C) increased the intensity of the absorption peak. There is a difference between the dispersions exposed to low and those exposed to room temperature in the absorption spectrum having elapsed two hours. For the case of nanoparticles exposed at 4°C, the maximum absorption peak was maintained in a wavelength of 399 nm (Figure 3-a) for the following periods of time measured. In a different way, samples that were exposed to room temperature experienced a change in the wavelength and intensity of the absorption spectra as time increased (Figure 3-b). The presence of a new absorption peak in these spectra is caused by changes in the characteristics of the nanoparticles. The optical properties of AgNPs depend on their morphology [16] and variations in the emission wavelengths of the dispersion are a consequence of change of shape and size when exposed to room temperature. This produces a change in the distribution charge making the plasmonic interaction different. Changes in the optical properties of the nanoparticles are showed macroscopically as a color change in the dispersion (Figure 3-c).

The absorption peaks of silver nanoparticles on UV/Vis spectra can be used to calculate the nanoparticle concentration via Beer-Lambert law $A = eLc$ where $A$ is absorbance, $e$ is the molar extinction coefficient (M$^{-1}$ cm$^{-1}$), $L$ is the path length of the sample (cm), $c$ is the concentration of nanoparticles in solution (M). The molar extinction coefficient $e$ of silver nanoparticles is estimated by theoretical calculations. Calculation of the extinction coefficients of AgNPs is based on Mie theory (power-law) [19]. The relationship between the extinction coefficients and the diameters of silver nanoparticles is $e = Bd^\gamma$ with $d$ in nm. To $d \leq 38$nm, $B = 2.3 \times 10^5$ M$^{-1}$cm$^{-1}$, $\gamma = 3.48$ and to $d > 38$nm, $B = 4.2 \times 10^8$ M$^{-1}$cm$^{-1}$, $\gamma = 0.77$ [19].

DLS measurements were used to determine the diameter of the nanoparticles. The DLS size distribution image of silver nanoparticles is shown in figure 4. For distributions, a Gaussian analysis was performed for each peak. It is observed that the size distribution depending on the exposure time of the dispersion at room temperature. For 1h, 2h and 4h, suspensions with nanoparticles size average of 113.7 nm, 45nm and 22nm, respectively, were found. To calculate the concentration of nanoparticles with the size of greater presence in the suspensions exposed at room temperature, values of higher intensity peaks of the UV/Vis absorption spectra and the DLS size distribution was used. The concentration was calculated from the Beer-Lambert law [20] for which, the molar extinction coefficient was determined of the Mie theory[21]. In table 1, the results of the concentration found are presented. The decrease in the concentration of the nanoparticles with the size of greater presence in the dispersion and the generation of a second peak in the UV/Vis absorption spectra shows that features such as the size and/or shape of the nanoparticles are changing.

![Figure 4. Size distribution image of silver nanoparticles at room temperature for 1, 2 and 3 hours.](image-url)
Table 1. Concentrations of nanoparticles with the size of greater presence in the suspensions exposed at room temperature. The absorption values are taken from the UV/Vis absorption spectra from figure 3-b.

The absorption values are taken from the UV spectrum of the figure

| t(h) | d (nm) | ε (M⁻¹ cm⁻¹) | A   | ε (M)       |
|------|--------|--------------|-----|-------------|
| 1    | 164 ±8 | 2.1·10¹⁰    | 1.12| 5.25·10⁻¹¹ |
| 2    | 91±7   | 1.4·10¹⁰    | 0.79| 5.83·10⁻¹¹ |
| 4    | 44±3   | 7.7·10⁹     | 0.98| 1.26·10⁻¹⁰ |

Conclusion

In summary, suspension of silver nanoparticles to applications in time temperature indicators was synthetized and characterized. UV/Vis spectral studies and DLS measurement were used to determine the difference in optical response of two sets of samples, the first set of samples was exposed at 4°C and the second at room temperature. Silver nanoparticles exposed at 4°C did not show significant optical changes. For samples exposed to room temperature (22°C) the UV / Vis spectra reveal changes in the absorption peaks of the suspension, Δλ = 20nm, as the time increases. With DLS, the size distribution showed that the nanoparticles size decreases from 164 ±8 nm to 44±3 nm in a period of time from 1h to 4h, and the concentration of nanoparticles increases from 5.25·10⁻¹¹ M to 1.26·10⁻¹⁰ M. These changes in the size of the nanoparticle and its concentration produce differences in the plasmonic interaction, and in consequence, differences in the optical properties of the samples. In this work, we have demonstrated that dispersion of silver nanoparticles can be used successfully to TTIs manufacture.

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