



Green Synthesis of Silver Nanoparticle Color Range as a Potential Colorant in Textile Materials

¹Anuradha M.H.T.S, *²Siriwardana, K.

^{1,2}Department of Chemistry, Faculty of Science, University of Ruhuna, Matara, Sri Lanka Email address of the corresponding author - * wkkdsiriwardana@chem.ruh.ac.lk

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ABSTRACT

Coloration of textile materials is achieved using a wide variety of synthetic and natural dyes and pigments with desired fastness. However, colorfastness is adversely affected by several factors, including exposure to UV light, repeated washing, and surface abrasion from wearing. Hence, the overall quality of the fabrics and textiles will be affected. A novel approach in textile coloration can be achieved using silver nanoparticles (AgNPs), since AgNPs are stable upon UV exposure. AgNPs of different sizes and shapes exhibit different colors due to the surface plasmon resonance effect. Herein, we describe a simple, rapid, and green method to synthesize AgNPs with range of colors using the same precursors. AgNPs were synthesized by using irradiation. Lime juice acts as both a reducing and stabilizing agent. Different colored AgNPs were formed by changing the concentrations or volume ratios of Ag⁺ ions, lime juice, and pH values. AgNP formation was confirmed by characteristic UV-Vis spectra. A color range of yellow, brown, gray, maroon, and malachite green was synthesized, and poplin yarn was colored. Instead of chemical binders, the possibility of using vinegar and lime was studied. The washability and UV stability of the colored yarns were studied. The color did not fade even after 10 washing cycles. In the absence of any binder or stabilizer on the fabric surface, initial color did not fade during the washing with deionized water. However, a different color was observed after exposing to sunlight for three weeks. A dark color was observed for vinegar-treated fabric. The method reported herein provides a simple, rapid, and eco-friendly approach to obtain a range of colors using the same precursors which can be used in the coloration of textile materials with a suitable binding agent.

1. INTRODUCTION

The textile industry uses natural and synthetic dyes for the coloration process. Different types of plants, minerals, animals, and insects are used to form natural dyes. Synthetic dyes were synthesized using a number of chemicals or organic molecules such as azo dyes, anthraguinones, oxazines, etc. There are some drawbacks with the natural and synthetic dyes including health issues, environmental problems, cost-effectiveness, and the problem with energy consumption. However, fading of these textile colors has become a major problem. Colorfastness can be varied depending on the type of dye and the nature of the fabric material and unfavorably influenced by several reasons such as repeated washing, UV light, and surface abrasion because of often wearing (Shamey, 2020).

Nobel metals such as gold and silver have long been known to form stable colloids of nanosize particles. Such nanoparticles exhibit different colors due to surface plasmon resonance effects. Different particle size and shapes will result in different colors. These colors are stable upon exposure to UV light. Here we report the novel development and use of silver nanoparticles (AgNPs) of different sizes with different colors as stable colorfast colorants on fabrics for high value fashion fabrics and textiles. AgNPs are well known antibacterial agent, hence fabrics with antibacterial property also can be prepared.

In this study, lime juice extract was used as the reducing agent and stabilizing agent in AgNP synthesis. Sun light was used as the energy source. Hence, the synthesis procedure presented here is a greener method. Different colors were obtained using the same precursors.

There are some studies on using lime extract to AgNP synthesis (Mosae, 2016). Some studies have investigated coloration of textiles using AgNPs with greener method using different plant extracts and mechanical heating (Kahrilas, 2014). Tang *et al* used AgNPs for coloration of cotton (Riaz, 2018). Simple dip coating method, in-situ coating method and spraying methods have been reported in many studies for assembling AgNPs on the textile materials. In the dipping method, several binders (PDDA) have been used to enhance the binding of AgNPs with the fabrics rapidly (Jeyapragasam, 2016).

To the best of our knowledge, there is no literature report on green synthesis of AgNPs color range using same precursors and lime extract in the presence of solar irradiation. The synthesized AgNPs have different colors and desired fastness after the coloration of fabrics using dip coating method.

2. MATERIALS AND METHODS

Silver nitrate $(AgNO_3)$ and sodium hydroxide (NaOH) were purchased from Organic Traded (Pvt) Ltd and utilized without further purification. Good quality lime fruits were purchased from a local market. A UH5300 HITACHI spectrophotometer was used for UV-Vis measurements. Deionized water was used in sample preparations.

Lime fruits were squeezed, filtered and centrifuged twice at 3000 rpm for 10 minutes. Collected lime juice was refrigerated and used in further analysis. Working lime juice solution was prepared by diluting the stock solution ten times.

2.1. AgNP SYNTHESIS

A series of $AgNO_3$ solutions with different concentrations (1, 2, 3, 4, 5, 10, and 15 mM) was prepared. $AgNO_3$ solution was kept under sunlight while stirring. Different volumes of lime juice were added to the $AgNO_3$ solution. The mixtures were stirred for different time periods under sunlight. UV-vis spectra of each solution were acquired. The effect of pH on AgNP synthesis was studied by changing pH of the medium.

2.2. COLORATION OF FABRIC YARNS USING AgNPs

Fabrics were washed with deionized water twice and dried at room temperature. Yarns of fabric were dipped in four fold diluted vinegar (for 1 h) and lime extract (for 1 h) while heating. Then yarns were washed with deionized water and dried at room temperature. Yarns were immersed in prepared AgNP solutions for 30 min while stirring (at room temperature, 40 and 80 °C). Colored yarns were washed with deionized water and dried under sunlight and at room temperature.

Washability of colored yarns were tested by washing yarns with deionized water and tap water for 10 min at 40 °C. The UV-Vis spectrum of washing solution was studied to test the presence of AgNPs. Washing was repeated in the presence of detergent. Similarly, the color stability was studied with different washing cycles (1, 5, 10, 15, and 20).

The UV stability was tested by exposing the colored fabrics to sunlight for different period of time (1, 5, 24 hours, and 1 and 3 weeks).

3. RESULTS AND DISCUSSION





Figure 1. (a) (A) Photographs and (B) UV- vis spectra of synthesized AgNPs with different Ag+ concentrations. (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 10, and (g) 15 mM. (b) (A) Photographs and (B) UV- vis spectra of synthesized AgNPs solutions with 10 fold diluted lime and (a) 3, (b) 10, and (c) 15 mM Ag+ solutions. (c) (A) Photographs and (B) UV- vis spectra of synthesized AgNPs in the presence of NaOH and (a) 3, (b) 10, and (c) 15 mM Ag+ concentrations. Lime: Ag+ were mixed in 6:1 volume ratio in all samples.

AgNPs show characteristic UV-Vis peak around 400 nm due to the localized surface plasmon resonance (LSPR) effect. Hence, the formation of AgNPs can be confirmed by the formation of yellowish color solution and characteristic λ_{max} around 400 nm. According to Figure 1 different colors of AgNPs were formed when the Ag⁺ concentration was changed. LSPR peak intensity was increased with the increase of the Ag⁺ ion concentration. Also, small shift in $\lambda_{_{max}}$ confirmed the formation of different size particles. Broad UV-Vis peak might be resulted due to the formation of polydisperse AgNPs. Greenish (Figure 1 b (A), intense red and orange (Figure 1 c (A)) colored AgNP solutions were formed when diluted lime juice and NaOH were used in AgNP synthesis. However, the intensity of UV-Vis peaks was lowered compared to the concentrated lime juice (Figure 1 a (B)). Citrate concentration has an impact on nanoparticle growth, size distribution, and shape, hence peak position and intensity can be changed. Growth of nanoparticles is slow down as a result of high concentration of citrate in lime. It can be the reason of having low intensity, broad peaks when citrate concentration is lowered. When adding NaOH, free carboxylic groups of citrate is deprotonated as it creates a basic condition. This

spherical.



Different colors of AgNPs were obtained by changing reaction time and pH of the medium (Figure 2). LSPR peak intensity was increased with increasing reaction time as the formed AgNP concentration was increased (Figure 2 a. (B)). By changing the pH value of the medium, malachite green (377 nm) and maroon (432 nm) colors (Figure 2 b. (A), (B)) were obtained. LSPR peak intensity was lowered with increasing pH.

Different size and the shape of the particles absorb different wavelengths of visible light. Low pH helps to form larger particles and reduction rate is low. Here, AgOH can be formed during the addition of NaOH. These facts affect to reduce formation of more AgNPs and give single sharp peak at more basic conditions. Reaction rate of the formation of AgNPs is rapid at the low molar ratios of lime: silver. Aggregation of AgNPs to certain extent is possible in low citrate amounts by destabilization as ionic strength is high in reaction medium [(citrate)³⁻] (Jiang X. C., 2010) and during the redox reaction, oxidizing product of citrate can adsorb to change the AgNPs size and shape. Positively charged dimer formation of silver after the reduction and complexes can be formed with citrate ions to reduce the formation of clusters is also possible. It shows the stabilizing ability of citrate.

When these colored AgNPs solutions kept away

has an ability to take hold of silver clusters on the for several weeks the color of some solutions surface of AgNPs and formed particles are not has become changed (Figure 3 (A)). Continuous stirring was important to mix both reducing agent and metal precursor uniformly throughout the reaction time and usage of clean glassware help to control or prevent nanoparticle aggregations. Peak intensity and the frequency of LSPR absorption peak for nanoparticles depends on the electron density on the nanoparticle surface. If uniform distribution of electrons result a sharp and single absorption band with symmetric shape (Jiang X. C., 2010). By changing the reaction conditions λ_{max} of absorption peaks can be changed. Well penetration of colored AgNPs solutions into the fabrics results in light colors of fabrics (Figure 3 (B), (C). Heating during the coloring process has not cause a huge difference in colors. The color was slightly dark at the 80 °C. Since sunlight contributes to the further stabilizing process to control the size of AgNPs by developing a final AgNPs solution without utilizing any chemical stabilizing agents colors are changed slightly. When the entire fabric material subjected to dyeing, the dye is completely penetrate into fabric fibers and it gives the maximum colorfastness properties and usage of binder will result to increase the stability for washing by creating crosslinks with cellulose molecules (Riaz, 2018).

> There was no color difference observed before and after the washing of the fabrics with deionized water and it was confirmed by the UV-Vis spectra by the absence of peak around 400 nm. When tap water was used for washing, color was faded with detergent and soap. In absorption spectra there is a peak around 400 nm for both detergents and soap. AgNPs were leached from the fabric even after 10 cycles of washing in very small amounts. Tap water can be change the color more as change the environment of the AgNPs on fabrics while washing than deionized water. When AgNPs fabricated fabrics exposure to sun light until 3 weeks, color change was observed. It may be due to these penetration of colored AgNPs

may have not occur properly in to fabric while **REFERENCES** coloration. If there are any unreacted Ag⁺ ions and lime adsorbed on to the fabric material, AgNPs formation can be continued with the prolonged exposure to sunlight or synthesized AgNPs can be aggregate in the absence of good stabilizer on fabric surface and to overcome these issues, fabric material should be washed well before testing the UV stability in order to remove any unreacted precursors. Surface functionalization of AgNPs using a polymer can be done to enhance the stability of AgNPs for washing and sun light.

While most of the AgNPs are dispersed on the fabric in equal way some particle aggregation also can be happened. Therefore this may be a reason that AgNPs treated fabrics shows different or light colors after drying than the AgNPs included final solution.



Figure 3. Photograph of (A) different colors of synthesized AgNPs, (B) colored popline yarns and (C) cotton (amuredi) fabrics using synthesized AgNPs

CONCLUSION Δ.

Different colors of AgNPs were obtained by changing experimental conditions using the same precursors. Sunlight was used as the energy source leading the synthesis process to more green.

There is a potential to use vinegar and lime juice as fabric binders eliminating the use of chemical binders. Reasonable colorfastness against washing and UV light was achieved after the dying process. The synthesis method was quick, easy, and eco- Riaz, S. A. (2018). Functional finishing and friendly. The green synthesized AgNP color range can be used as a colorant in high fashion fabrics with desired colorfastness.

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