Green Synthesis of Nano Ag/Cu Hybrid Particles for Repelling Water from Cotton Fabric

Ali Akbar Zolriasatein1*, Mohsen Hosseinkhan1, Shabnam Karimnejad 1

Abstract
Nano Cu and Ag have a lot of applications in various industries. From different methods of nano particle synthesis, reduction of metallic salts in presence of ascorbic acid as stabilizer can lead to fabrication of nano particle with specific dimensions. In addition, because of using environmentally friendly and nontoxic substances their green synthesis are very noteworthy. In this study, nano Cu/Ag hybrid simultaneously was synthesized through reduction of Ag and Cu salts in presence of natural reducing agent like maltose. The effect of different concentrations of salts together with reducing agent and stabilizer on dimension of nano particles were also investigated. Theses nano particles were applied on cotton fabric and then water repellency and physical properties of nano treated fabric were analyzed. Statistical data showed a significant difference between samples which were synthesized with different salt, stabilizer and reducing agents. Moreover, some spectroscopy tests like FT-IR, XRD, EDX and SEM were conducted to analyze the results.

Keywords
Green synthesis, Ag/Cu hybrid nano particles, Water repellency, Wicking test, Drop test, Physical properties

1 Department of Textile Engineering, College of Technical and Engineering, Yadegar-e-Imam Khomeini (RAH) Shahre-rey Branch, Islamic Azad University, Tehran, Iran
*Corresponding author: ali_ziasati@yahoo.com

1. Introduction

Nanotechnology is a new growing field in which production and fabrication of nano particles with specific dimensions are desired. They can be used in various aspects of our lives and synthesized through physical or chemical methods [1]. Amongst different nano particles, metallic ones are very noteworthy and primarily used in industrial and scientific fields [2-3] due to their chemical stability, catalytic, photonic and electrical conductive properties [4]. In general, nano Cu particles shows different behavior in contrast to micro Cu particles [5]. There are various methods for synthesizing these nano particles including electrochemical [6], physical [7], laser pyrolysis [8], micro emulsion [9-10], reduction of metallic salts [11], two dimensional crystal [12], using microwave radiation [13] and green biochemical method [14]. Using reductants can lead to some disadvantages for instance they are relatively expensive and have adverse effect on environment. Therefore, green synthesis of nano particles becomes an attractive issue through which inexpensive and environmentally friendly nano particles can be synthesized. Green synthesis of nano particles using poly saccharides is an alternative method for synthesizing of metallic nano particles [15]. Findings suggested the potential of the proposed method in producing fine fibers with enhanced tensile strength and slight color change [16-17]. Applying these metallic nano particles onto fabric surface can lead to water replant properties. The aim of this study is to achieve a water repellant fabric through treating fabric with Ag/Cu hybrid nano particles.

2. Materials and methods

Plain weave 100% cotton fabric with 25 warps and 25 wefts per cm was used throughout this study. Silver nitrate, copper nitrate, sodium carbonate, maltose, ascorbic acid and dispersing agent were purchased from Merck, Germany. Woven fabrics were pretreated by using 2g/L nonionic detergent and 1g/L soda ash at 70°C for 30 min at a liquor to goods ratio of 50:1. Then, green synthesis of nano Ag/Cu hybrid particles was carried out according to Table 1. Afterwards, ascorbic acid was added to each samples to achieve pH 5 for every samples. Finally, samples were treated by nano Ag/Cu hybrid particles through pad-dry method at 50°C for 60 min. All samples were then dried at room temperature. To analyze the changes in moisture regain wicking test was performed according to AATCC 19720013. Furthermore, drop test was carried out according to ASTM TS-018 to investigate the rate of absorption. Finally, washing fastness tests were performed according to ASTM D435-42(1995).

2.1 Spectroscopic characterization
X-rte color-eye A7000 was used to analyze changes in appearance of samples. Quantitive mineral and glass analyses were carried out using XPMA, XGT-7200 Horia model. FT-IR spectrophotometer (Bruker Tensor 27) was used to analyze the changes in functional groups. In addition some other test
like UV/Vis Spectrometer, spectrophotometer (Brite BT 600), scanning electron microscope (Model Kyky-EM3200), X-ray Diffraction (Equinox), tensile strength (Tensometric Rochdale M500-25CT), Martindale rub test (Nasj sang) were used in this study. Yellowness index of samples was calculated according to ASTM D 1925 standard method and whiteness index of cotton samples was computed under CIE Canz 82 standard method. The color strength (K/S) of the dyed samples was determined from equation 1. The K/S values calculated from the sample reflectance (R), K/S = (1 - R)2 / 2R ————(1)

Color-difference (E) was calculated from equation 2. The three coordinates of CIELAB represent the lightness (L*), its position between red and green (a*), and its position between yellow and blue (b*). E = (L*2 + a*2 + b*2) ————(2)

### 3. Results and Discussion

#### 3.1 Color spectroscopy analysis
Changes in reflectance of untreated and treated samples at 370 nm were summarized in Table 2. It can be seen that L*, a* and b* can be changed as a result of concentration of silver nitrate, copper nitrate, maltose and dispersing agent. Fig. 1 shows that this type of synthesis increases the yellowness of the treated samples. From Fig. 2 it can be concluded that sample A1/C1.M2 was the best sample in respect to the whiteness of fabric. The synthesis of Ag/Cu nano-particles can be formed via chemical methods by using different reductants. Here, the presence of reductant groups in maltose have reduction ability. Therefore, the presence of maltose as a reductant leads to the in situ synthesis of Ag/Cu nanoparticles. Hence, increase in the amount of synthesized Ag/Cu hybrid particles can affect K/S and E (Fig. 3 and Fig 4).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Concentration of silver nitrate (W/V %)</th>
<th>Concentration of copper nitrate (W/V %)</th>
<th>Concentration of maltose (W/V %)</th>
<th>Concentration of dispersing agent (W/V %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1/C1.M1</td>
<td>0.5</td>
<td>0.5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>A2/C2.M1</td>
<td>0.5</td>
<td>0.5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>A1/C1.M2</td>
<td>0.5</td>
<td>0.5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>A2/C2.M2</td>
<td>0.5</td>
<td>0.5</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

#### 3.2 Wicking test
The results of wicking test of samples were demonstrated in Fig. 5. It can be seen that samples which were treated by nano synthesized Ag/Cu hybrid particles showed lower water absorption. The lower water absorption results in the higher water repellency. Fig. 6 shows the water absorption of samples after 35 min. Presumably, silver and copper salts reduced easily due to the presence of functional groups in maltose. Here, nano-particles were synthesized simultaneously on the surface of the cotton fabric, which led to water repellent property. It seems that A1/C1.M1 was the best sample in respect to the water repellency of fabric.

#### 3.3 Drop test
The results of drop test were shown in Table 3. It can also be seen that A1/C1.M1 showed the lowest water adsorption. The micrographs of drop test on treated fabric were shown in Fig. 7.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Time (second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>4</td>
</tr>
<tr>
<td>A1/C1.M1</td>
<td>145.5</td>
</tr>
<tr>
<td>A2/C2.M1</td>
<td>38.71</td>
</tr>
<tr>
<td>A1/C1.M2</td>
<td>12.21</td>
</tr>
<tr>
<td>A2/C2.M2</td>
<td>14.08</td>
</tr>
</tbody>
</table>

#### 3.4 Washing fastness
Table 4 demonstrates that washing of samples can lead to a decrease in water repellency property. However, after once or twice of washing, samples kept their water repellency property.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Time (second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>4</td>
</tr>
<tr>
<td>A1/C1.M1</td>
<td>80</td>
</tr>
<tr>
<td>A2/C2.M1</td>
<td>15.33</td>
</tr>
<tr>
<td>A1/C1.M2</td>
<td>4.49</td>
</tr>
<tr>
<td>A2/C2.M2</td>
<td>3</td>
</tr>
</tbody>
</table>

#### 3.5 FTIR analysis
FT-IR test were carried out in the range of 500 - 3500 cm⁻¹ to analyze the changes in functional groups. Hydroxyl groups can be seen around 3440.02 cm⁻¹ in Fig 8a and 8b. After treatment with nano particles this peak shifted to 3507.96 cm⁻¹ due to the synthesis of nano particles on the surface of cotton fabric which affects functional groups to the significant difference.

#### 3.6 SEM analysis
Fig. 9 shows the surface morphology of untreated sample. It can be seen that surface of treated sample (A1/C1.M1) is fully covered with nano particles (Fig. 10). Furthermore, using maltose as a reducing agent can lead to Ag/Cu hybrid nano particles with average of 77.14 nm (Fig. 11).

<table>
<thead>
<tr>
<th>Mass[%]</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>Ag2O</td>
</tr>
<tr>
<td>0.15</td>
<td>CuO</td>
</tr>
</tbody>
</table>

Table 7. Tensile strength of untreated and treated fabrics

<table>
<thead>
<tr>
<th>Sample code</th>
<th>%Force at break</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1/C1.M1</td>
<td>2.81</td>
</tr>
<tr>
<td>A2/C2.M1</td>
<td>10.56</td>
</tr>
<tr>
<td>A1/C1.M2</td>
<td>3.52</td>
</tr>
<tr>
<td>A2/C2.M2</td>
<td>6.69</td>
</tr>
</tbody>
</table>

3.7 XRD analysis

Fig.12a shows the XRD results before and after nano treatment. It can be seen that a prominent peak attributed to cellulose can be observed between 10 and 30 of 2. After simultaneous synthesis and treatment, new peaks at 38 and 43 can be attributed to Ag and Cu respectively (Fig. 12b). The Scherrer equation, in X-ray diffraction and crystallography, is a formula that relates the size of sub-micrometre particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern (equation 3). 

\[ \frac{K}{\cos \theta} = \frac{\lambda}{b} \]

where:
- \( \theta \) is the Bragg angle.

3.8 EDX analysis

The presence of Ag2O and CuO on the surface of fabric was characterized by EDX analysis and results were illustrated in Fig. 13. The EDX results confirm the presence of Ag2O and CuO particles on the treated sample (Table 6).

3.9 Tensile strength

Tensile test was performed according to ASTM D1445-95 and results were summarized in Table 7. Higher concentration of maltose leads to increase in concentration of acidic ions. These acidic ions can be produced from decomposition of Ag and Cu salts. As a result, an increase in acid concentration brings about a decrease in tensile strength. Amongst, treated samples, A2/C2.M1 showed higher tensile strength.
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**Figure 4.** Color difference (E) of untreated and treated fabrics

**Figure 5.** Results of Wicking test

**Figure 6.** Wicking results at 35 min

**Figure 7.** Micrographs of drop test on treated fabric

**Figure 8a.** FT-IR spectrum of untreated and treated samples
- (a) untreated sample

**Figure 8b.** FT-IR spectrum of untreated and treated samples
- (b) nano-treated sample
Figure 9. SEM micrograph of untreated sample at different magnifications

Figure 10. SEM micrographs of treated sample (A1/C1.M1) at different magnifications

Figure 11. SEM micrographs of treated sample A1/C1.M1 with size of nano particles

Figure 12a. The XED results before and after nano treatment (a) Before Treatment

Figure 12b. The XED results before and after nano treatment (b) After nano treatment

Figure 13. EDX results of (A1/C1.M1) sample
4. Conclusion

In general, the goal of this research was to achieve a water repellant fabric through treating fabric with Ag/Cu hybrid nano particles. Surface of treated samples is fully covered with nano particles. Treated samples, which were treated by nano Ag/Cu hybrid particles showed lower water absorption. Higher concentration of maltose led to an increase in concentration of acidic ions, which brought about tensile strength loss.

References


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