Functional modification of Nylon fabrics based on noble metal nanoparticles

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Abstract. In situ synthesis of gold nanoparticles was realized on Nylon fabrics through heat treatment with assistance of citrate. The synthesized gold nanoparticles imparted bright colors to Nylon fabrics due to its localized surface plasmon resonance (LSPR) features. Optical properties of the treated fabrics were analyzed by recording color strength (K/S) curves of fabrics. Scanning electron microscopy (SEM) was employed to observe the surface morphologies of Nylon fabrics with gold nanoparticles. The influence of pH value on the in situ synthesis of gold nanoparticles was discussed. Moreover, the coloration with gold nanoparticles improved the UV protection of Nylon fabrics.

1. Introduction
Functional modification of textiles based on nanoparticles has attracted intensive interests of scientists and engineers in recent years. Lots of strategies have been developed to endow textiles with different functions, such as antibacterial activity, self-cleaning, and UV protection enhancement [1-3]. Noble metal nanoparticles, including gold and silver nanoparticles, have drawn extensive attention in virtue of their unique optical property, i.e. localized surface plasmon resonance (LSPR) [4, 5]. LSPR generates from local oscillation of conduction electrons around metal nanoparticles at a certain frequency when light irradiates these nanoparticles. Gold and silver nanoparticles display bright colors because of their particular LSPR properties. Noble metal nanoparticles were used to produce colorful glass and ceramics in ancient times [6]. Recently, gold and silver nanoparticles as novel dyestuffs have been used to colorate textile. In our previous research, many natural fibers/fabrics, such as wool, bamboo, ramie and cotton, were treated with gold and silver nanoparticles to achieve the multifunctionalization of fibrous materials [7-10]. Gold nanoparticles with good stability endowed fabrics with colors, UV protection, antibacterial properties and improved heat conductivity [7-9]. Nylon (polyamide) as one of the most popular synthetic polymers has been applied to apparel, flooring and rubber reinforcement. Developing functional modification of Nylon materials is significant to commercial applications of Nylon.

In this study, the functionalization of Nylon fabrics was realized by in situ synthesis of gold nanoparticles. The gold nanoparticle treated Nylon fabrics exhibited red and purple colors. Trisodium citrate was used to assist the in situ reduction of gold ions on fabrics. The influences from citrate concentration and pH value were investigated. The color strength (K/S) of different fabric samples was measured to analyze the colors changes of fabrics resulting from in situ synthesized gold nanoparticles. The surface morphologies of Nylon samples after coloration were characterized by scanning electron microscopy (SEM). The improvement effect of UV protection property of fabrics from gold nanoparticle coloration was discussed.
2. Experimental section

2.1. Materials
Tetrachloroauric (III) acid (HAuCl₄·3H₂O, >99%), trisodium citrate (>99.0%) and acetic acid (>99.7%) were purchased from Aladdin (Shanghai, China). All chemicals were analytic grade reagents, and used without further purification. Nylon fabrics were obtained from a local retailer. They were used as received.

2.2. Instruments
SEM measurements were performed with a Supra 55 VP field emission SEM. UV protection factor (UPF) of fabrics was measured by UV spectrophotometer (HD902C). The color strength (K/S) of Nylon fabrics colored with gold nanoparticles was calculated using the Kubelka–Munk equation as follows:

$$K/S = \frac{(1-R)^2}{2R}$$

where $K$ is the absorption coefficient of the substrate, $S$ is the scattering coefficient of the substrate, and $R$ is the reflectance of the fabric at maximum absorption, measured using a X-rite Color i7 spectrophotometer.

2.3. In situ synthesis of gold nanoparticles on Nylon fabrics
Nylon fabrics were washed for 3 min with warm water (40 °C), followed by rinsing with deionized water at room temperature. The washed fabrics were immersed in different concentrations of HAUCl₄ solutions with (0.05, 0.10, 0.15 and 0.20 mM), at a weight ratio of aqueous solution to fabrics of 100:1. The HAUCl₄ solutions containing Nylon fabrics were shaken for 5 min at room temperature and then heated at 90 °C for 60 min in a shaking water bath. The treated fabrics were rinsed with running deionized water and dried in an oven at 50 °C. The samples corresponding to 0.05, 0.10, 0.15 and 0.20 mM of HAUCl₄ solutions were denoted by Ny-Au-1, Ny-Au-2, Ny-Au-3 md Ny-Au-4. Pristine Nylon fabric was designated as Ny-0.

To improve the reduction of gold ions on Nylon fabrics, trisodium citrate was used as a reducing agent to reduce gold ions and prepare gold nanoparticles on fabrics. The washed Nylon fabrics were immersed in 0.20 mM of HAUCl₄ solution at a weight ratio of aqueous solution to fabrics of 100:1. Subsequently, different amounts of trisodium citrate was added into the HAUCl₄ reaction solutions and the final concentrations of citrate were 0.4, 0.8, 1.0 and 1.4 mM, respectively. The mixing solutions with Nylon fabrics were shaken for 5 min at room temperature and then the solutions were heated at 90 °C for 60 min in a shaking water bath. The treated fabrics were rinsed with running deionized water and dried in an oven at 50 °C. The samples corresponding to 0.4, 0.8, 1.0 and 1.4 mM of citrate were denoted by Ny-Au-5, Ny-Au-6, Ny-Au-7 md Ny-Au-8.

2.4. Color fastness to washing
Color fastness to washing was evaluated according to AATCC Test Method 61-2A. The Nylon fabrics colored with gold nanoparticles were washed for 30 min at 40 °C in the presence of standard soap (5 g/L) with liquor ratio of 50 using the SW-12A washing fastness tester (Changzhou Dahua Electronic Instrument Co., Ltd). AATCC gray scale for color change and staining of undyed fabrics were used to judge the washing fastness rating from 1 to 5 in steps of 0.5 unit. Grade 5 indicates no color change.

2.5. Colorfastness to rubbing
The rubbing colorfastness of treated Nylon fabrics was evaluated according to AATCC Test Method 8-2007 by a Gellown G238BB electronic crockmeter. The fabrics colored with gold nanoparticles were rubbed using an undyed cotton cloth. The staining of the cotton cloths was assessed using the standard Grey Scale for staining. Both dry and wet rubbing fastness tests were performed.
3. Results and discussion

Figure 1 shows the photograph of Nylon fabrics after heat treatment in the presence of HAuCl₄. The treated fabrics exhibited purple red, indicating that the gold nanoparticles were synthesized on Nylon fabrics. As can be seen from Figure 1, the colors of the treated fabrics changed slightly when the initial concentration of HAuCl₄ increased from 0.05 mM to 0.2 mM, which implies that the morphologies and amount of gold nanoparticles varied scarcely even though the gold ion concentration were different. Color strength (K/S) curves were measured to analyze the color properties of fabrics before and after treatment. No visible peaks were found in the K/S curve of pristine Nylon fabrics, due to the white color. The treated fabric presented a peak at 540 nm in the K/S curve, which resulted from the generation of gold nanoparticles. The peaks at 540 nm is assigned to the LSPR band of gold nanoparticles. The results indicate that gold nanoparticles could be formed from reduction of gold ions in the presence of Nylon without additional reducing agents. However, it was referred from colors that some gold ions were not reduced for high concentration of HAuCl₄, which may be due to limited reducibility of Nylon.

![Figure 1. Optical image of Nylon fabrics treated by different concentrations of HAuCl₄ and K/S curves of pristine fabric (Ny-0) and gold nanoparticle treated fabric (Ny-Au-4).](image)

In order to improve the in situ synthesis of gold nanoparticles on Nylon fabrics, trisodium citrate, one of common reducing agents, was added into the initial reaction system. It can be seen that the colors of fabrics became brilliant after the heat treatment in the presence of gold ions and citrate, which reveals that a large amount gold nanoparticles were in situ synthesized on the surface of Nylon fabrics with assistance of citrate. The color of fabric changed lighter as the concentration of citrate increased. K/S curves of the treated fabrics were measured corresponding to different concentrations of citrate. All the peaks of K/S curves were located around 540 nm. However, the intensity of maximum K/S decreased with an increase in citrate concentration, indicating that high concentration of citrate did not favor the produce of bright colors on fabrics. The narrowing of K/S peak may generated from improvement of size distribution of gold nanoparticles. It was found that the optimal citrate concentrations were 0.8 and 1.0 mM for 0.2 mM of HAuCl₄.

SEM characterization was carried out to observe the surface morphologies of difference samples. The pristine Nylon fibers displayed relative smooth surface (Figure 3a and b). After treatment, plenty of nanoparticles were seen on the surface of Nylon fibers (Ny-Au-6) (Figure 3c), demonstrating the in
in situ synthesis of gold nanoparticles on Nylon. The gold nanoparticles distributed evenly on the fiber surface though there were a few aggregates in the SEM images (Figure 3d). SEM results reveal that gold nanoparticles were synthesized effectively and coated on Nylon fibers.

Figure 2. Optical images and K/S curves of the Nylon with gold nanoparticles synthesized with assistance of different concentrations of citrate: 0.4 mM (Ny-Au-5), 0.8 mM (Ny-Au-6), 1.0 mM (Ny-Au-7) and 1.4 mM (Ny-Au-8), respectively.

Figure 3. SEM images of pristine Nylon fabric and the gold nanoparticle treated Nylon fabric (Ny-Au-6).

Figure 4. Optical images of the Nylon fabrics after treatment in the presence of HAuCl₄ (0.2 mM) and citrate (0.8 mM) at different pH values.

The influence of pH value on the coloration of Nylon was analyzed. The pH value of HAuCl₄ solution for different concentrations was in the range of 5.0–6.5. The bright red color in Nylon fabrics was produced when the pH value of reaction system with citrate was 5.5 (Figure 4). The purple red Nylon fabrics were obtained if pH value of the reaction solution was adjusted to 3 (Figure 4). While, no visible colors were seen on the Nylon fabrics when the pH value was increased to 8 (Figure 4), implying no gold nanoparticles were synthesized under basic condition. The results indicate that acidic condition facilitated the in situ synthesis of gold nanoparticles on Nylon fabrics.

Color fastness of dyed fabrics is important in practical applications. The color fastness to washing of the gold nanoparticle colorated Nylon fabric was rated as 5 for color change and 4-5 for staining. The testing results indicate that the Nylon fabrics colored by in situ synthesized gold nanoparticles showed excellent washing fastness. Fabrics are often rubbed against other surfaces. In the present study, the color fastness to rubbing of the colored fabrics was tested. The dry rubbing color fastness of
the gold nanoparticle treated Nylon fabrics was rated as 5. And the rating of the wet color fastness of the Nylon fabrics with gold nanoparticles was also 5. The staining of the cotton cloths used for rubbing was assessed to be 4-5 under wet and dry conditions. The results demonstrate that the Nylon fabrics colored with gold nanoparticles exhibited good color fastness to rubbing (dry or wet).

Furthermore, coloration of gold nanoparticles imparted Nylon fabrics with additional functions. The UV-blocking property of the Nylon fabrics with gold nanoparticles was tested. Table 1 shows the transmittance values of UV light and UV protection factor (UPF) values of the pristine Nylon fabric and the gold nanoparticle treated fabrics. The average transmittance values of the Nylon fabrics in UVA (315–400 nm) and UVB (280–315 nm) regions decreased obviously after gold nanoparticles were in situ synthesized on fabrics, which indicates that the gold nanoparticles improved remarkably the ability of UV-blocking of Nylon fabrics. UPF presents the ability of the fabric to block UV from passing through and reaching the skin. UPF value of pristine Nylon fabrics was 81.4 (Table 1). In-situ coloration with gold nanoparticles increased the UPF value of fabrics to 170.1 (Ny-Au-4). The results demonstrate that the treatment with gold nanoparticles improved the UV protection ability of Nylon fabrics.

| Sample ID | Ny-0 | Ny-Au-4 | Ny-Au-5 | Ny-Au-6 | Ny-Au-7 | Ny-Au-4 |
|-----------|------|---------|---------|---------|---------|---------|
| UPF       | 81.4 | 170.1   | 161.1   | 154.3   | 214.9   | 127.0   |
| T(UVA)    | 2.23%| 0.93%   | 1.06%   | 1.10%   | 0.90%   | 1.43%   |
| T(UVB)    | 0.94%| 0.45%   | 0.48%   | 0.49%   | 0.34%   | 0.60%   |
| T(UVR)    | 1.86%| 0.79%   | 0.89%   | 0.92%   | 0.74%   | 1.19%   |

4. Conclusion
Gold nanoparticles were in situ synthesized on Nylon fabrics through heating. Addition of citrate and acid condition favored the synthesis of gold nanoparticles on fabrics. The synthesis of gold nanoparticle imparted bright colors to Nylon fabrics, because of localized surface plasmon resonance (LSPR) of metal nanoparticles. The color properties of the Nylon fabrics treated with gold nanoparticles were analyzed. The gold nanoparticle treated Nylon fabrics had remarkable color fastness to washing and rubbing. Moreover, the coloration by gold nanoparticles improved noticeably the UV-blocking property of Nylon fabrics.

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