Structural coloration of chitosan-cationized cotton fabric using photonic crystals

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Abstract. In this work, poly (styrene-methyl methacrylate-acrylic acid) P(St-MMA-AA) composite nanospheres were deposited onto chitosan-cationized woven cotton fabrics followed by a second layer of chitosan. The deposited photonic crystals (PCs) on the fabrics were evaluated for coating efficiency and resistance, chemical analysis and color variation by optical and SEM microscopy, ATR-FTIR, diffuse reflectance spectroscopy and washing fastness. Chitosan deposition on cotton fabric provided cationic groups on the fiber surface promoting electrostatic interaction with photonic crystals. SEM images of the washed samples indicate that the PCs are firmly coated on the cotton surface only in the chitosan treated sample. The photonic nanospheres show an average diameter of 280 nm and display a face-centered cubic close-packing structure with an average thickness of 10 µm. A further chitosan post-treatment enhances color yield of the samples due to the chitosan transparent covering layer that induce bright reflections where the angles of incidence and reflection are the same. After washing, no photonic crystal can be detected on control fabric surface. However, the sample that received a chitosan post-treatment showed a good washing fastness maintaining a reasonable degree of iridescence. Chitosan fills the spaces between the polymer spheres in the matrix stabilizing the photonic structure. Sizeable variations in lattice spacing will allow color variations using more flexible non-close-packed photonic crystal arrays in chitosan hydrogels matrices.

1. Introduction

Textile coloration is traditionally obtained by means of using chemical colorants such as dyes and pigments. However, in nature brilliant, vivid and iridescent colors that arise from the physical interaction of light with biological nanostructures can be often observed [1]. These structural colors are not produced by chemical pigments but they are originated from light interference, diffraction or scattering phenomena at submicron range and can generate color effects considerably brighter than those of pigments as well as completely transparent materials [2]. Structural colors are not subject to photobleaching and are very efficient in using light. They can be found in creatures living in low-light environments and display color effects not achievable by pigmentation [3]. Structural colors can be generated from basic optical processes represented by thin film interference, diffraction grating effect, multilayer film interference, light scattering or photonic crystals. Photonic crystals (PCs) can be sources of exceptionally bright and brilliant reflected colors arising from coherent Bragg optical diffraction [4]. PCs are periodic optical materials or structures designed to affect the motion of photons in a similar way...
that periodicity of semiconductor crystals affect the motion of electrons [5]. It is known that monodisperse highly charged colloid methods spontaneously self-assemble into face-centered cubic or body-centered cubic crystalline colloidal arrays in low ionic strength aqueous solutions [6]. These arrays are the simplest form of PCs and are of particular interest because of their photonic band gaps and strong interaction with light [7]. Colloidal particles have long been used as the major components of industrial products such as foods, inks, paints, coatings, papers, cosmetics, photographic films, and rheological fluids [8]. Colloidal photonic structures can be fabricated using different methods such as colloidal self-assembly [9], block copolymer self-assembly [10], auto-cloning process and holographic lithography [11]. Few literature can be found about the application of electrostatic self-assembly on textile fibers and structures [12]. Textiles display irregular rough surfaces and different woven or knitted structures difficulting the self-assembly of PCs on the fabrics [13]. Most of the studies have focused on silk and polyester fabrics disregarding the application in cotton and other cellulosic substrates [14-16]. An effective adhesion of the PCs arrays coating is essential to allow the fabric to function as expected [17]. Since cotton fibers are negatively charged due to the presence of carboxyl and hydroxyl groups is often necessary to functionalize its surface with cationic charges [18]. Chitosan (CH) is the deacetylated derivative of chitin and represents an interesting alternative to commonly used compounds to functionalize cotton because of its protonated amino groups [19]. Moreover, CH films can act as reflectors and mimic structures found in the exoskeletons of insects [20]. The main objective of this study is to develop structural color onto cotton fabrics. Colloidal PCs based on P(St-MMA-AA) composite nanospheres were deposited onto a CH-cationized woven cotton fabric followed by a second CH layer on the top of the PCs as protective and color enhancing coating. Coated fabrics were evaluated for coating efficiency and resistance, chemical properties and color variation by optical and SEM microscopy, ATR-FTIR, and washing fastness.

2. Materials and Methods

2.1. Materials
Commercial black dyed cotton fabric with a warp density of 34 threads cm⁻¹, a weft density of 30 threads cm⁻¹ and weight per unit area of 140 g m⁻² was pre-washed with a 1 g L⁻¹ of non-ionic detergent solution at 30 °C for 30 min and rinsed. Chitosan (DD 85%, ChitoClear hq95-43000, Mw = 350 kDa) was purchased from Primex (Iceland). Styrene (St), methyl methacrylate (MMA), and acrylic acid (AA) were distilled before use. All the other reagents were analytical grade purchased from Sigma–Aldrich, St. Louis, MO, USA.

2.2. Preparation of Monodispersed P(St-MMA-AA) Composite Nanospheres
Monodisperse composite latex spheres of poly (styrene-methyl methacrylate-acrylic acid) (P(St-MMA-AA)) were synthesized by a modified soap-free emulsion polymerization method as described by Cong and Cao 2003 [21]. Briefly, 120 mL of aqueous solution (A), containing 0.4 g of Na₂S₂O₇ and 0.8 g of NaHCO₃ in a funnel, and 25 mL of monomer mixture (B), consisting of St/MMA/AA (90:5:5 v/v/v) in another funnel, were added at the same time into a 250 mL three-necked flask. The mixture was stirred at 70 °C in N₂ atmosphere for 5 h.

2.3. Cationization Process
Cationic cotton fabric (7x7 cm) was prepared by using 1 wt% CH dissolved in 1% acetic acid aqueous solution. The CH solutions were dissolved at 300 rpm for 30 min at 70 °C. The samples were padded in a mini-foulard through the CH solution at 1.5 bar of pressure and 4 rpm. The excess coating was then removed by rinsing with distilled water and dried for 12 hours at 50 °C.

2.4. Coating of Cotton Fabrics with Photonic Crystals
Three types of samples were tested: (1) Cotton sample was dipped in a 8% photonic colloid solution for 5 minutes and then dried at 60 °C; (2) A cationized cotton sample obtained impregnating the fabric into
a 1% CH using a padding machine (1.5 bar, 4 rpm, 80% pick-up) and then treated as sample 1; (3) Sample 2 followed by a second impregnation in 1% CH solution and dried again at 60 °C.

2.5. Fourier transform infrared spectroscopy (FTIR)
A Nicolet Shimadzu FTIR spectrophotometer (Madison, USA) with an attenuated total reflectance accessory (ATR) was used to record the FTIR spectra of the fabric samples. Spectra were collected in the region of 4000–400 cm⁻¹ and at a resolution of 4 cm⁻¹ with 45 scans at room temperature. A background scan with no samples and no pressure was acquired before the spectra collection.

2.6. Scanning electron microscopy (SEM)
SEM analyses of the samples were carried out with an ultra-high resolution Field Emission Gun Scanning Electron Microscope (FEG-SEM), NOVA 2000 Nano, SEM, FEI Company. Secondary electron images were performed with an acceleration voltage between 5 and 10 kV. Backscattering Electron Images were made with an acceleration voltage of 15 kV. Samples were covered with a film of Au–Pd (80-20 wt%).

2.7. Photographs
Optical photos of the fabrics coated with PCs were taken with a Nikon CoolPix4300 digital camera. The pictures were acquired under natural light, at the same time, environmental conditions, perpendicularly to the fabrics and at the distance of 15 cm.

2.8. Washing fastness
The washing fastness was evaluated according to the standard ISO 105 C06, A1S method at a temperature of 40 °C.

2.9. Spectrophotometric measurements
The color of the fabrics was evaluated using a Spectraflash 600 (Datacolor) diffuse reflectance spectrophotometer at standard illuminant D65 (LAV/Spec. Incl., d/8, D65/10°). The responses analyzed were the color characteristics: K/S is the color strength calculated using Kubelka-Munk's equation (K/S= (1-R)²/2R, where R is the reflectance). L*, a*, and b* are the coordinates of the color in the cylindrical color space by black-white (L*, lightness), red-green (a*), and yellow-blue (b*) sensations. The results were also summarized by the overall color difference (ΔE*) value.

3. Results and Discussion
Monodispersed composite latex spheres of P(St-MMA-AA) were successfully synthesized by soap-free emulsion polymerization. Figure 1-a shows the SEM micrographs of the deposited PCs. P(St-MMA-AA) nanospheres were uniform in shape with a mean sizes of 280 ± 20 nm. The coating display good adhesive property to the cotton substrate with most of the layered region exhibiting a face-centered cubic close-packing structure of P(St-MMA-AA) nanospheres. However, some gaps, cracks and random configurations are also present in the coated surfaces especially near to the edges of the inter-fiber spaces (Figure 1-b). Nanospheres seem to be densely loaded on the cotton fiber surfaces without large gaps in the cross section. The thickness of P(St-MMA-AA) layer ranging between 5 and 15 μm with an average thickness of 10 ± 5 μm. Figure 1-c, 1-e and 1-g show the SEM images of the deposited PCs in the untreated, CH pre-treated and CH bi-layer cotton fabrics, respectively. As expected, the morphology of the fabric surfaces coated with CH are smoother than untreated sample [22]. The PCs coatings completely cover the fiber and only few micro-wrinkled stripes and fibril structures protruded out from the fabric surface. It is interesting note that CH is well dispersed in the PCs matrix without aggregations. After washing, the untreated and the CH pre-treated samples show the typical longitudinal fibril structures of the cotton fibers. The washed untreated control does not exhibit any PCs onto the cotton fibers (Figure 1-d) and in the washed CH pre-treated sample they are faintly visible as some isolate crystal (Figure 1-f). However, the washed sample with the top CH layer display regions with uniform
PCs distribution with few cracks on the surface (Figure 1-h). The sandwich-like coating of the PCs between CH layers is able to ensure washing durability.

![Figure 1](image_url1)

**Figure 1.** SEM micrographs (x2000) of deposited photonics P(St-MMA-AA) composite nanospheres (a, b) and coated fabrics of sample 1 (c, d), 2 (e, f) and 3 (g, h) before and after washing, respectively.

As previously observed, PCs coated on untreated cotton (Figure 2-a) shows a chalky white appearance with weak structural color expression [23]. However, after the addition of CH onto the cotton surface the visual appearance significantly changes from almost monochromatic to iridescent colors (Figure 2-c). It seems that CH addition allows a more homogeneous distribution of PCs onto the cotton fibers and displays a different mechanism in the absorbance of scattered light probably due to differences in refractive index of CH and P(St-MMA-AA) as well as by variations of the periodical scale [24]. After washing both the samples (Figure 2-b and 2-d) the fabric did not retain any PCs exposing the black dyed cotton surface and losing iridescence. Figure 2-e and 2-f show the PCs deposited on the pre-treated CH cotton with a second CH impregnation on the top of the nanospheres before and after washing, respectively. The introduction of the CH top layer into the lattice structure drastically change the color appearance of the fabric due to the differences in light adsorption between P(St-MMA-AA) and CH films [25]. CH is able to absorb scattering light and increase the color saturation producing brighter structural colors [26]. After washing, the second CH treatment is able to retain some structural color but large gaps of black cotton are visible.

![Figure 2](image_url2)

**Figure 2.** Photographs of samples 1 (a, b), 2 (c, d) and 3 (e, f) before and after washing, respectively.

The ATR-FTIR (Figure 3) of the control cotton fabric (CO) display the very intense bands at 1160, 1100 and 1020 cm\(^{-1}\) assigned to the vibrations of the C-O-C bond of the glycosidic bridges of the cellulose structure [27]. The peaks at 2900, 2850, 3334 and 3282 cm\(^{-1}\) may be attributed to the aliphatic CH\(_2\) and OH groups of the cellulose structure [28, 29]. The absorption band at 1640 cm\(^{-1}\), often referred to as amide I band, may be assigned to the amide carbonyl C=O stretching vibrations of the azo dye present in the fibers [30]. After CH deposition (CO+CH) no significant differences can be observed compared to the control. The PCs layer deposited on the untreated sample (CO+PH) efficiently covers the cotton and black dye infrared bands. The bands at 3027 cm\(^{-1}\), 2922 cm\(^{-1}\) and 1541 cm\(^{-1}\), are assigned to CH stretching and to the bending of CH\(_2\) groups of the nanosphere. Moreover, the band observed at 750 cm\(^{-1}\) can be merely attributed to the out-of-plane C-H deformation of the monosubstituted or 1,2
disubstituted aromatic rings of P(St-MMA-AA) nanospheres [31]. The addition of PCs on the CH pre-treated sample (CO+CH+PH) shows a broad band at 3334 cm\(^{-1}\) attributed to the O-H stretching vibration of the water absorbed on CH [32]. The typical bands of amide I and amide II of CH structure are observed at 1648 cm\(^{-1}\) and 1451 cm\(^{-1}\), respectively. The peak at 750 cm\(^{-1}\) previously solely attributed to nanospheres become more intense due to the additive presence of the in-plane NH deformation vibration of CH [33]. The presence of the second layer of CH (CO+CH+PH+CH) does not significantly change the infrared spectrum compared to the CH pre-treated sample (CO+CH+PH). After washing, all the control samples show the characteristic spectrum of the untreated black cotton. The CO+CH+PH also shows an increase of the bands assigned to the cellulose structure and a decrease of nanosphere peak. On the contrary, the sample CO+CH+PH+CH did not show significant changes before and after washing. It was only observed a small reduction on the peaks attribute to the CH due to the erosion of the CH top layer. The peak attributed to the P(St-MMA-AA) remain intense confirming that a high number of nanospheres is still on the fabric surface.

![Figure 3. FTIR-ATR spectra of fabrics before (left) and after (right) washing.](image)

K/S value of black cotton control sample is significantly higher when compared with the PCs coated fabric (Table 1). All the unwashed samples show a noteworthy increase in the overall color differences (\(\Delta E^*\)) and in lightness (L\(^*\)). However, only the samples containing PCs display a decrease in K/S values in the range of one order of magnitude. The red-green (a\(^*\)) and yellow-blue (b\(^*\)) color coordinates show differences in function of the CH content. The samples pre-treated with CH show a high b\(^*\) component and a slight increase in the a\(^*\) component while the sample with the top layer of CH is less a\(^*\) and the value of b\(^*\) is half of the only pre-treated samples. This confirms the different color appearance of the fabric due to the scattering light adsorption of CH previously observed. After washing the CO+CH, CO+PH and CO+CH+PH samples display the same lightness and K/S of control dyed cotton. In terms of color coordinates the samples with CH maintain some b\(^*\) color. However, the sample with the CH top layer (CO+CH+PH+CH) is able to maintain a high degree of lightness and a low value of K/S but shows different color coordinates with prevalence of a\(^*\) color component.

**Table 1.** Overall color difference (\(\Delta E^*\)), color strength (K/S) and color coordinates: lightness (L\(^*\)), red-green (a\(^*\)), and yellow-blue (b\(^*\)) of the fabrics before and after washing. CO control K/S = 590.1.

| Sample* | \(\Delta E^*\) | K/S | L\(^*\) | a\(^*\) | b\(^*\) |
|---------|----------------|-----|---------|--------|--------|
|         | U   | W   | U   | W   | U   | W   | U   | W   | U   | W   |
| CO+CH   | 30.3 | 2.6 | 584.5 | 583.2 | 0.3  | -0.1 | 0.4  | 0.4  | 3.3  | 2.6  |
| CO+PH   | 23.6 | 0.7 | 107.0 | 581.8 | 23.5 | -0.3 | 0.5  | -0.4 | 1.9  | -0.6 |
| CO+CH+PH| 30.3 | 3.4 | 75.0  | 616.9 | 30.0 | -0.2 | 0.8  | 0.3  | 3.9  | 3.3  |
| CO+CH+PH+CH | 29.5 | 23.4 | 75.4  | 104.5 | 29.5 | 23.4 | -12.1 | 1.1  | 1.5  | -0.9 |

*CO: Cotton; CH: Chitosan; PH: Photonic; (U): Unwashed; (W): washed; (S.D.<1%) 

4. Conclusion
In this study, PCs fabricated by soap-free emulsion polymerization were applied with and without CH treatment to a cotton fabric to produce structural color. CH addition provides a more uniform coating of the PCs onto the cotton fabrics and the additional CH transparent covering layer enhances color
saturation producing brighter structural colors. Moreover, the CH post-treatment maintains a reasonable degree of iridescence onto the fabric after washing. Overall, considering the fact that no harmful binder or crosslinking agents were used, the CH-assisted deposition of PCs revealed to be a promising environmental safe and low cost coating technology for producing structural color on textiles with a good degree of washing fastness.

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