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Layer by Layer Assembly of Nanosilver for High Performance Cotton Fabrics

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Abstract: High performance cellulosic fabrics are of increasing attention as a wearable fabric with special functions. The current report deals with preparation of multifunctional cotton fabrics by using simple and facile layer by layer technique. Firstly, silver nitrate was reacted with carboxymethyl cellulose to prepare Ag nanoparticles-carboxymethyl cellulose composite. Multi-layers of the so-obtained composite were applied on the cotton fabrics using pad-dry-cure method. Ag nanoparticles were deposited with mean size of 18.2 nm onto cotton fabrics which served as a cross linker between carboxymethyl cellulose macromolecules and cotton macromolecular blocks. Application of composite multilayers brought new properties for the finished cloths such like coloration, ultraviolet resistance, electrical resistance and biocidal action. The ultraviolet transmission radiation was significantly reduced to 7-10 % after applying ten composite layers. Valuable antibacterial textiles which are required in different medical purposes could be successfully produced, as excellent antibacterial activities were achieved by using the reported method. The developed process can be easily adapted to the existing textile machinery, making it industrially viable to produce fabric's versatility.

Keywords: AgNPs-CMC, Cotton, Color data, Transmission, UPF, Electrical conductivity, Antibacterial activities

Introduction

Basically, the inherent properties of textile fibers either from natural resources (plants and animals) or from synthetics might induce the loss performance properties of fibers by extensive using, therefore, much interest had been given to the development of functional textiles with a view to protect wearer and textile materials itself. Thus, scientists focused on creating of functionalized clothes with newly acquired properties [1-3]. A functional textile is a flexible material consisting of a network of natural or artificial fibers often referred to threads or yarns. A functional textile may be included various requirements such like antibacterial and antifungal actions [4-8], moisture management and self-cleaning [9,10], flame-retardant [11], insect repellent [12], antistatic effect and water repellant [14-18].

Silver nanoparticles (AgNPs) continue to be of great current research interest due to their intriguing prospects for the development of novel optical and electro-optical devices, catalysts and antimicrobial agents [19-24]. According to their optical properties, another interesting application for AgNPs has been recently utilized as pigment materials for fabrics and fibers [25-27]. Moreover, multifunctional properties were accomplished for fiber/fabrics by implementation of AgNPs [25,26]. The function were basically depending on the content of AgNPs within the treated materials, as very high silver content must be applied for high performance finishing.

The current work designed for coating cotton fabrics with multi layers of AgNPs in the form of composite with carboxymethyl cellulose (CMC) to impart multifunctional properties into fabrics. Cotton fabrics were coated by ten layers from AgNPs-CMC composite using layer by layer deposition technique. UV-Vis absorbance spectra were measured for coated fabrics. The topographical features of finished fabrics were examined by using scanning electron microscope (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD) and infrared spectroscopy. The change in color due to coating process was measured. UV-protection property was monitored by measuring the transmittance through coated fabrics, and the bactericidal action of multilayers treated fabrics was also evaluated.

Expermental

Materials and Chemicals

Silver nitrate (99.9 %), Carboxymethyl cellulose (CMC) (DP=350, DS=1.2), Sodium hydroxide, were all used as received. Desized, scoured and bleached plain-woven 100 % cotton fabrics (165 gm/m^2, with on average 39 and 31 threads per cm along warp and weft directions, respectively) were kindly supported by El-Nasr Company for Spinning, Weaving and Dyeing (El-Mehallah El Kobra, Egypt). The fabrics did not contain any finishing agent and were used without further treatments.

Silver Nanoparticles Synthesis

Silver nanoparticles (AgNPs) was prepared using CMC as reducing and stabilizing agent according to the method described by Hebeish *et al*. [28] with a little modification. Preparation of 500 ppm AgNPs colloidal solution is described briefly as follows: 1 g/*l* of CMC was dissolved in 0.1 N

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NaOH with stirring, temperature raised to 70 °C then 5 mmol/*l* $AgNO_3$ added one time. The mixture stirred for 30 minute to complete the preparation process.

Deposition of AgNPs Process

Layer by layer as simple technique was used to deposit AgNPs on to cotton fabrics. The process was performed for one layer deposition as follows: Cotton fabric pieces with 20 cm×20 cm dimension were immersed in 50 m*l* of AgNPs-CMC composite (containing 500 ppm AgNPs) for 5 minutes. Then, the fabrics pieces were squeezed at constant pressure using laboratory padder to get 100 % wet pick up. After padding, fabrics were dried at 70±3 °C, followed by curing at 120±5 °C for 5 minutes for AgNPs thermal fixation. Rinsing process was done with cold tap water two times for 5 minutes, followed by drying at 70± 3 °C. Three, six and ten layers were obtained by repeating the same process to get multi-layered treated fabrics. The CMC solution in absence of AgNPs was used as padding solution to get 1-10 layers by the same deposition technique for comparison.

Measurments

Absorbance of Solution

The absorption spectra of the prepared AgNPs solution was measured using a multi channel spectrophotometer (T80 UV/VIS, d=10 mm, PG Instruments Ltd., Japan). AgNPs solution was diluted 50 times and the UV-visible absorption spectra measured in wavelength range of 250 to 600 nm.

Zetasizer

A Milli Q water diluted solution of the prepared samples was exposed for dynamic light scattering by locating in a Malvern Zetasizer Nano 3600 (Malvern Instruments Ltd. from UK) conducted with a He-Ne laser lamp of 0.4 mW power and 633 nm wavelength in an isolated chamber for temperature controlling. The mean size and the size distribution of particles were measured by the intensity of scattered light when the angel between the scattered and incident beam was at 90°. Three measurements were determined for every sample at 25 °C and the average was calculated.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX)

The surface characterization of untreated and coated cotton fabrics were measured by scanning under high resolution electron microscopy. Fabric samples were placed on copper coated carbon tap and then conducted to scanning electron microscope (SEM Quanta FEG 250 with field emission gun, FEI Company-Netherlands). Energy dispersive X-ray spectroscopy (EDX) analysis unit (EDAX AMETEK analyzer) attached with the electron microscope was used to record the chemical structure of treated fabrics surface.

X-ray Diffraction (XRD)

For measuring of X-ray diffraction (XRD) patterns for cotton fabrics after AgNPs deposition, treated cotton fabric was fixed in XRD with Empyrean as diffractometer system (from PANalytical, Netherland) using Pixcel 3D Amedipixz collaboration and monochromatized Cu Ka (k=1.54060 Å) radiation. The diffraction angle (2θ) was monitored in the range of 5° to 80°.

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Nanosilver deposited cotton fabrics and the untreated fabrics were both characterized by infra red spectroscopy. ATR-FTIR spectra were measured by using a Bruker Vertex 70 Spectrometer (Bruker Analytik, GmbH, Germany) conducted with platinum ATR in the medium range of infra red. Fabric samples were subjected to ATR-FTIR spectroscopy. The instrument was adjusted to be 4000-500 cm^{-1} scanning area, 128 repetitious scans average with 2 cm^{-1} interval scanning and 4 cm^{-1} the spectra resolution. The resulted spectra were manipulated using 9 points smoothing and then normalized.

Color Measurements

The color space (L a b) from CIE lab of the coated fabrics were recorded using a spectrophotometer with pulsed xenon lamps as light source ((KONICA MINOLTA CM 3610d, Japan) 10° observer with D65 illuminant, d/8 viewing geometry and measurement area of 8 mm. L is lightness from black (0) to white (100), a^* is a red (+)/green (-) ratio and b^* is yellow (+)/blue (-) ratio [29,30]. The corresponding reflection and absorbance through cotton fabrics were performed in wavelength range of 360-800 nm. Every sample was measured at three different areas and the average was considered.

Silver Content

Silver contents in the treated cotton fabrics were measured for the extracted solution from fabrics using the method reported recently in literature [4,25,27]. Solutions were analysed with high-resolution continuum source flame atomic absorption spectrometer (HR-CS AAS, ContrAA 300, Analytic jena AG, Technology quality innovation, Jena, Germany) conducted to continuum source. Standard solution of 1000 mg/*l* silver nitrate was used to prepare calibration solutions in the range of 0-5 mg/*l*.

Transmission and Ultraviolet Radiation Blocking

The transmission through the treated cotton fabrics was measured in the ultraviolet radiation range of 280-400 nm wavelengths with 5 nm interval. To record the transmission, the fabrics were conducted to Specord 50 UV/VIS spectrophotometer instrument (analytic Jena AG, Germany) with integrating spheres [31]. Two repetitions for each sample at different area were performed and the average was calculated.

By using the transmittance data, the ultraviolet radiation blocking for treated fabrics was recorded by using AATCC Test Method 183-2004 [31]. The ultraviolet protection factor (UPF) was calculated according to equation (1). The average transmittance percent in the A- and B-ranges of ultraviolet radiation were both computed using equations (2) and (3), respectively. Consequently, the percent of ultraviolet radiation blocking in the A- and B-ranges were then calculated using equations (4) and (5).

$$UPF = \frac{\sum_{280\text{ nm}}^{400\text{ nm}} E_\lambda \times S_\lambda \times \Delta\lambda}{\sum_{280\text{ nm}}^{400\text{ nm}} E_\lambda \times S_\lambda \times T_\lambda \times \Delta\lambda} \tag{1}$$

$$T(UV-A) = \frac{\sum_{315\text{ nm}}^{400\text{ nm}} T_\lambda \times \Delta\lambda}{\sum_{315\text{ nm}}^{400\text{ nm}} \Delta\lambda} \tag{2}$$

$$T(UV-B) = \frac{\sum_{280\text{ nm}}^{315\text{ nm}} T_\lambda \times \Delta\lambda}{\sum_{280\text{ nm}}^{315\text{ nm}} \Delta\lambda} \tag{3}$$

$$UV-B = 100 - T(UV-B) \tag{4}$$

$$UV-A = 100 - T(UV-A) \tag{5}$$

where UPF is the ultraviolet protection factor through fabrics, T(UV-A) and T(UV-B) are the percent of transmittance in the A- and B-ranges of ultraviolet, respectively. E_λ is relative erythemal spectral effectiveness, S_λ is solar spectral irradiance, T_λ is average spectral transmittance of the fabrics (measured) and $\Delta\lambda$ is the interval of measured wavelength (5 nm in the current work). Values of E_λ and S_λ were obtained from the AATCC test method 183-2004. UV-A and UV-B are the ultraviolet protection factor in the A- and B-ranges of ultraviolet, respectively.

Electrical Conductivity

The electrical conductivity for treated fabrics was measured according to AATCC test method for electrical surface resistivity of fabrics [32]. The treated fabrics were situated between two parallel metal electrodes (7 KA1100, Siemens). The current adjusted at 1 mA and the voltage changed from 100 V to 500 V for more accuracy. When the electrical current passed into fabrics, the electrical resistance was changed and then recorded. All measurements were performed at conditions of 65±2 % RH & 20±2 °C. The electrical resistance was measured at three different areas for both faces of fabrics and the average was considered.

Antibacterial Activity

Antibacterial action of treated cotton fabrics was measured quantitatively against *Escherichia coli* (ATCC 2666) as gram -ve bacteria. The antibacterial test was performed by bacterial counting method using the standard test method according to the AATCC test method 100-1999 [33]. Before testing, fabrics samples were incubated at 35-37 °C. After incubation step, certain weight from all fabrics were transferred into 100 m*l* of nutrient broth (1:500) (*ca.* 1.5×10^8 colony forming units (CFU)/m*l*) and were shaken vigorously for 1 min. A 0.9 % (w/v) of normal saline solution was prepared, serially diluted and then plated onto Eosin Methylene Blue (EMB) agar plates. All plates were incubated for 24 hours at 37 °C and then the colonies were counted. The reduction percentage of bacterial colonies for fabrics was calculated by using equation (6).

$$R\ \% = \frac{B-A}{B} \times 100 \tag{6}$$

where R % is the reduction percentage of bacterial colonies, A is the number of bacterial colonies surviving on the agar plate with treated fibers, and B is the number of bacterial colonies surviving on the agar plate for control.

Results and Discussion

Characterization of AgNPs

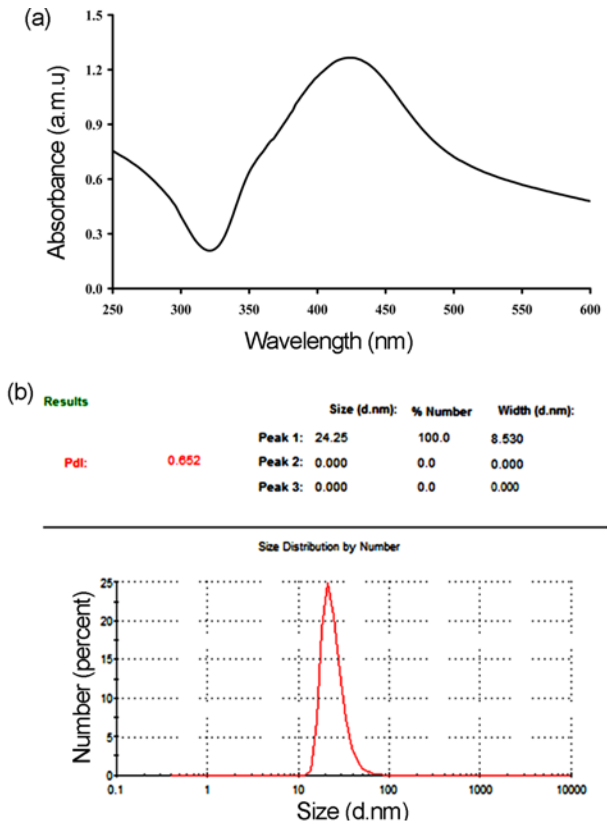
UV-Visible Spectra

Reaction mechanism for formation of silver nanoparticles (AgNPs) by carboxymethyl cellulose (CMC) macromolecules was reported in literature [28,34]. Where, CMC was concurrently used as reducing agent for silver ions (Ag^+) and stabilizer for the so obtained silver nanoparticles (Ag^0). CMC has reducing alcoholic and aldehydic groups which played the dual role for reduction and stabilization of the net produced NPs. Subsequently, the produced AgNPs were stabilized by the polymeric chains of CMC for avoiding the aggregation of smaller particles which might result in enlarged clusters.

At the end of reaction process between silver nitrate and CMC, the absorbance of solution was measured to follow the formation of AgNPs. Figure 1(a) shows the UV-Vis spectra of the prepared AgNPs colloidal solution after the required dilutions to avoid noisy peaks. It can be clarified that, the maximum absorbance peak ($\lambda_{\max}$) was formed at 420 nm with acceptable maximum intensity. According to that reported in literature with regard to AgNPs [28,35-39], the recorded band is assigned to surface plasmon resonance of spherical AgNPs. The absorbance peak of Ag ions normally appears in range of 220-250 [25,28] and this peak was not recorded here, indicating that, full reduction of Ag^+ was carried out by the CMC.

Zetasizer

The dynamic light scattering (DLS) technique was used to detect the mean particle size of AgNPs and poly- dispersibility index (PdI) of AgNPs-CMC composite in the colloidal solution. The obtained mean particle size was measured from Zetasizer analyzer (Figure 1(b)) and was 24.25 nm. However quite high content from CMC and AgNPs was



PdI: 0.652		Size (d.nm):	% Number	Width (d.nm):
	Peak 1:	24.25	100.0	8.530
	Peak 2:	0.000	0.0	0.000
	Peak 3:	0.000	0.0	0.000

Figure 1. (a) The UV-visible absorbance spectra of AgNPs-CMC colloidal solution and (b) the mean size and poly-dispersibility index of AgNPs-CMC colloidal solution.

involved in the colloidal solution, the dispersity of AgNPs was relatively high as PdI equal to 0.652, which confirmed the high homogeneity of the so-uploaded composite layers. But the concentrated colloidal solution is one of the current work's objectives, to upload multi-layers of AgNPs-CMC composite on surface of cotton fabrics.

Characterization of Coated Cotton

UV-Visible Spectra

The cotton fabrics were treated by different layers form the prepared AgNPs-CMC composite and CMC solution. The absorbance spectra were measured for AgNPs-CMC coated cotton in the range of 360-800 nm to investigate the surface plasmon resonance of AgNPs and the results are shown in Figure 2. The untreated cotton fabric did not exhibit any absorption spectra. The AgNPs-CMC coated cotton fabrics exhibited an absorption band placed in the range of 400-420 nm which could be attributed to surface plasmon absorption band of AgNPs. This agrees with the results of UV-Vis spectra for AgNPs-CMC composite solutions. The absorbance was gradually growing up by increasing number of the applied composite layers. This may account for increasing of silver content deposited on treated fabrics which increases by increment of the number of uploaded layers. These spectral results are analogy with data recently reported for in-situ incorporation of AgNPs into cotton [40].

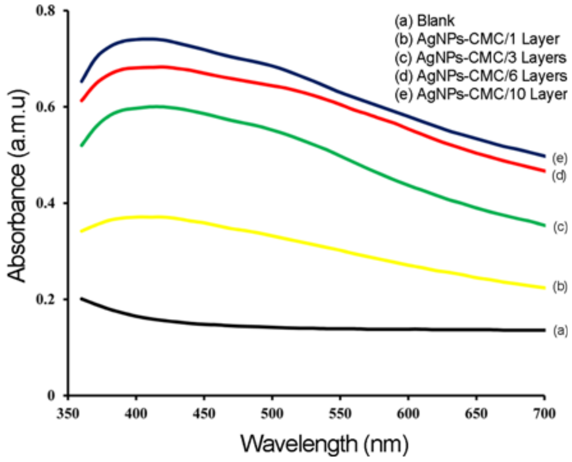


Figure 2. Absorbance spectra for AgNPs-CMC coated cotton fabrics.

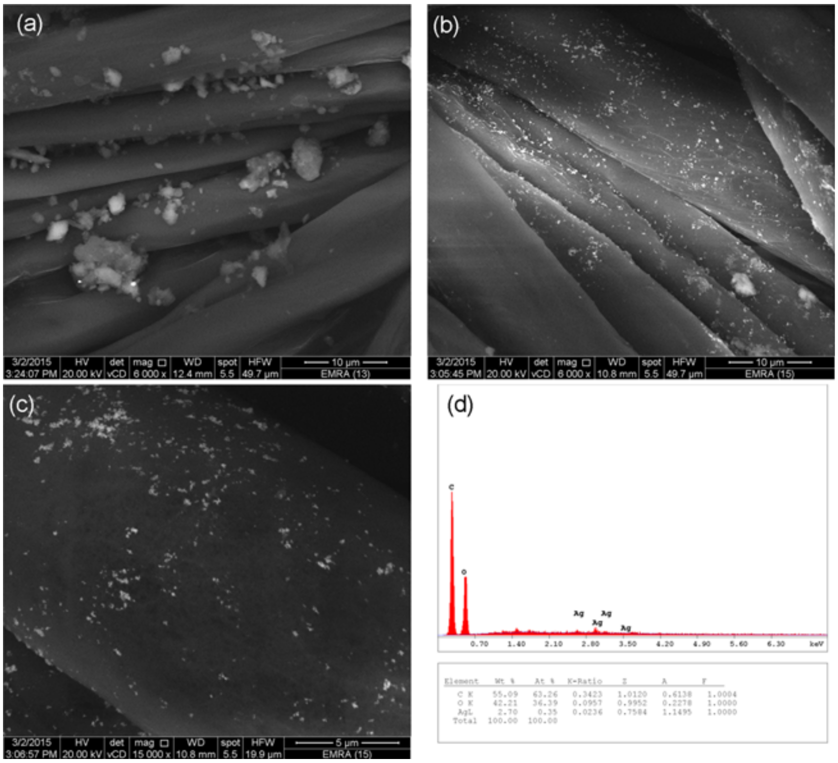
SEM and EDX

The surface topography of coated cotton fabrics were investigated by scanning electron microscope (SEM). Figure 3(a) displays the image for surface of CMC coated cotton, as polymer particles of CMC with bulked size were observed on the surface of fabrics. In Figures 3(b) and 3(c), the deposition of AgNPs on the fabric was shown at two different magnifications. At lower magnification (Figure 3(b)), CMC particles were appeared with that of AgNPs on the surface of coated fabric. Strong signals of carbon and that of oxygen were reported in EDX analysis, originated from the function groups of cellulosic cotton building units and also for CMC uploaded blocks. An optical absorption peak at 3 keV was also recorded in EDX spectra (Figure 3(d)), attributed to surface plasmon resonance of AgNPs (Figure 3(b)).

XRD Patterns

XRD patterns for the untreated and AgNPs-CMC coated cotton fabric are shown in Figure 4. In Figure 4(a), the strong diffraction peaks at 2θ=14.8 °, 16.5 °, 22.5 °, and 34.1 ° are characteristic peaks of cellulose I crystalline form [41,42]. By comparing XRD patterns shown in Figure 4(a) with that in Figure 4(b), the characteristic peaks intensity of the cellulose substrate is not changed, confirming the state of crystalline cellulose I didn't change after the uploaded layers of silver deposition.

A new peak appeared at 2θ=38.2 represent the diffraction peak with miller indices (hkl) of (111). This diffraction peak is corresponding to metallic silver with face centered cubic symmetry (FCC) [43-45]. This XRD pattern peak is in agreement with that reported in the International Center for Diffraction Data (JCPDS data number 04-0783 card). The peak intensity is tiny, indicating that the low sensitivity of



Element	Wt %	At %	K-Ratio	Z	A	F
C K	55.09	63.26	0.3423	1.0120	0.6138	1.0004
O K	42.21	36.39	0.0957	0.9952	0.2278	1.0000
AgL	2.70	0.35	0.0236	0.7584	1.1495	1.0000
Total	100.00	100.00				

Figure 3. SEM photos of the cotton fabrics (a) coated with CMC at 6000X magnification, (b) coated with AgNPs-CMC at 6000X magnification, (c) coated with AgNPs-CMC at 15000X magnification, and (d) EDX analysis for AgNPs-CMC coated cotton.

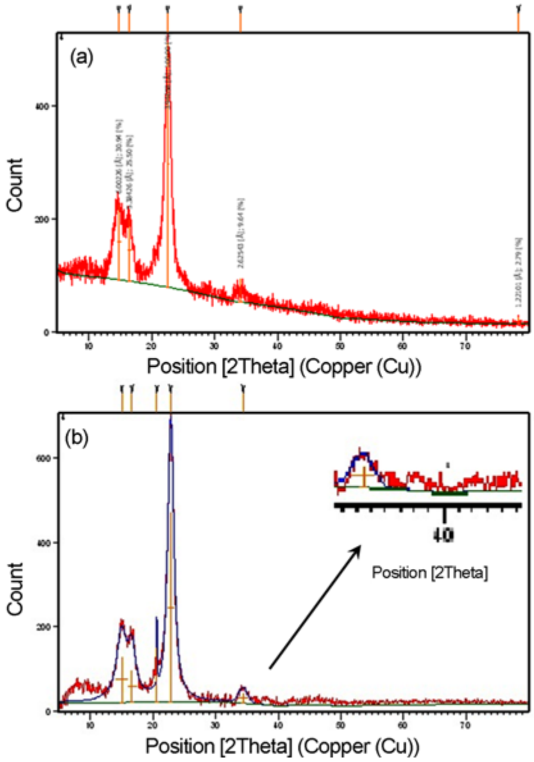


Figure 4. X-ray diffraction of (a) untreated cotton and (b) AgNPs-CMC coated cotton fabrics and insight pattern is magnifying view for Ag pattern.

XRD to detect AgNPs on fabrics compared to powder. However, the high intense peak for FCC materials is generally (111) reflection, which is observed in the sample. The diffraction peak is appeared broad which reflects that the crystallite size is small [39]. The silver oxide (AgO) phase was not detected in the XRD figure.

The crystal size of AgNPs on cotton fabric was calculated using the Scherrer formula (equation (6)). By analyzing the broadening of the (111) reflection peak, the average crystal size of AgNPs is 18.2 nm. The inconsistent result of Ag particle size between Zetasizer analyzer and XRD might be due to the difference between coherent length and particle size [42]. It may be also due to the disorderly distribution of AgNPs on the cotton surface.

$$d = k\lambda/\beta\cos\theta \tag{6}$$

$$\beta = \text{FWHM} \times 3.14/180 \tag{7}$$

where d=average particle size, k is constant (0.9), λ is the wavelength of Cu Kα in radians, β is full width at half maxima (FWHM) and θ is the Bragg angle.

ATR-FTIR

ATR-FTIR spectra of uncoated and coated cotton fabrics are presented in Figure 5. Pristine cotton exhibits three significant peaks at 1643 cm^{-1}, 2898 cm^{-1} and 3324 cm^{-1}, which are corresponding to the carbonyl group (C=O) of carboxylic, the asymmetric (C-H) stretching and hydroxyl group (O-H) stretching, respectively. The absorption bands

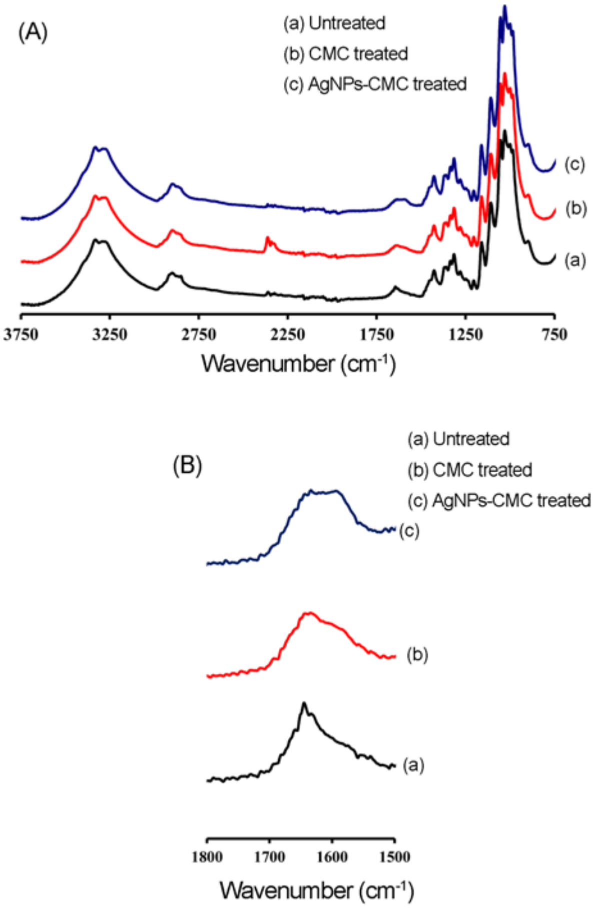


Figure 5. (A) ATR-FTIR spectra for untreated and coated cotton fabrics and (B) magnifying view for the carbonyl peaks.

between 1000 and 1200 cm^{-1} are attributed to the (-C-O-) stretching on the cellulose skeleton [46]. Absorption peaks placed in 1310-1380 cm^{-1} are related to in-plane (C-H) bending/vibration and (C-C) vibration [46]. The absorbance peak observed at 2360 cm^{-1} characterized for CO_2 from air [46].

After coating with CMC, there is no significant changing observed for all absorbance peaks of cotton except that for the carbonyl group (C=O) of carboxylic which is became a little broader and a little shoulder recorded at 1585 cm^{-1} rather than the native fabrics. Incorporation of AgNPs-CMC composite into cotton caused appearance of new peak at 1592 cm^{-1}. This peak referred to the carbonyl (C=O) of carboxymethyl groups which is assumed to be recorded at lower wave number than that of cellulose. This peak is started to be detected by deposition of CMC, but it was clearly appeared by uploading of AgNPs-CMC composite. This could be explained as a result of CMC loaded on fabrics, which is high enough in case of AgNPs-CMC composite compared to CMC alone. The high amount of CMC on cotton was achieved with using composite, reflects that AgNPs acts as a cross-linker between CMC units and cotton cellulosic chains in a coordinate complex [40,47]. While in case of CMC treated cotton fabrics, no chemical bonds were logically formed, but, CMC polymeric units were supposed to be physically deposited on the surface of cotton fabrics, which results in easy wash off for CMC polymeric blocks in rinsing bath.

Color Measurements

The colorimetric data were measured for fabrics before/after deposition of CMC and AgNPs-CMC composite and data were recorded in Table 1. All color space data (L^*, a^*, b^*) were not changed significantly after multilayered deposition of CMC even after 10 layers. Hence, deposition of CMC on cotton fabrics doesn't affect on the color of fabrics. In the contrast, the color of cotton fabrics was dramatically changed after deposition of AgNPs-CMC composite related to the color of AgNPs. It evident from the results of Table 1 that, increment of the number of uploaded layers for AgNPs-CMC composite (i.e. increasing the uploaded silver contents) resulted in gradual decrement in Lightness value L^*, as it decreased from 88.89 for the untreated cotton fabrics to 76.14 after the first uploaded layer and became 63.56 then 56.96 after third and tenth uploaded layers respectively. This enormous decrement in L^* is logically related to increment of silver contents from 0.61 g/kg to 3.31 g/kg by increasing the number of uploaded composite layers from one to ten layers.

The redness/greenness ratio (a^*) values were recorded to be -0.19, 2.61 and 6.08 for the untreated, treated cotton with one and ten uploaded layers of AgNPs-CMC composite respectively. The increment of a^* values is indication of some redness color for the treated fabrics. The yellowness/blueness ratio (b^*) value is raised from 1.24 for the untreated cotton fabrics to 6.71 after the first uploaded layer of AgNPs-CMC, then became 10.50 after tenth uploaded layers.

Reflectance spectra of the treated fabrics were represented in supplementary materials. The reflectance results are in agreement with the color space data mentioned above. The reflectance for cotton was diminished from 70 % to 25 %

Table 1. Colorimetric data from CIE lab for the cotton fabrics coated with CMC and AgNPs-CMC (light source D65)

Deposition layers		Ag content (g/kg)	*L*	a^*	b^*
Untreated fabric		0.00	88.89±0.09	-0.19±0.02	1.24±0.03
CMC	1	0.00	88.59±0.40	-0.18±0.03	2.32±0.17
	3	0.00	88.09±0.23	0.19±0.31	1.74±1.06
	6	0.00	88.93±0.21	0.29±0.09	1.14±0.50
	10	0.00	88.83±0.10	0.29±0.14	0.78±0.44
AgNPs-CMC	1	0.61±0.00	76.14±0.48	2.61±0.11	6.71±0.49
	3	1.86±0.07	63.56±0.67	5.24±0.54	9.29±1.65
	6	2.74±0.09	56.29±0.55	5.56±0.16	9.21±0.29
	10	3.31±0.08	56.96±0.26	6.08±0.04	10.50±0.05

which is related to increase of the deposited silver contents on treated fabrics by coating with ten layers of AgNPs-CMC composite.

Apparently, from colorimetric data, it could be summarized that: 1) the results of color changing for treated cotton fabrics are concurred with UV-Visible spectra data. 2) The color of fabrics was turned from white for native cotton to gray-yellow-orange for cotton treated with AgNPs-CMC composite. 3) The color of fabrics became more deeply by applying higher uploaded layers from AgNPs-CMC, related to higher silver contents embedded into fabrics. The color of cotton fabrics obtained here is comparable to that appeared for the cellulosic fibers after silver sorption manufactured in literature [48].

UV Transmission and UPF

The sun-blocking properties of textile are enhanced when a dye, pigment, delustrant, or ultraviolet absorber finish were applied, which absorb ultraviolet radiation and block its harmful and damaging effects on the skin. For persons who must work outdoors this choices were not preferable, however, well-designed clothing made from UVR-blocking textiles is symbolized as optionally better.

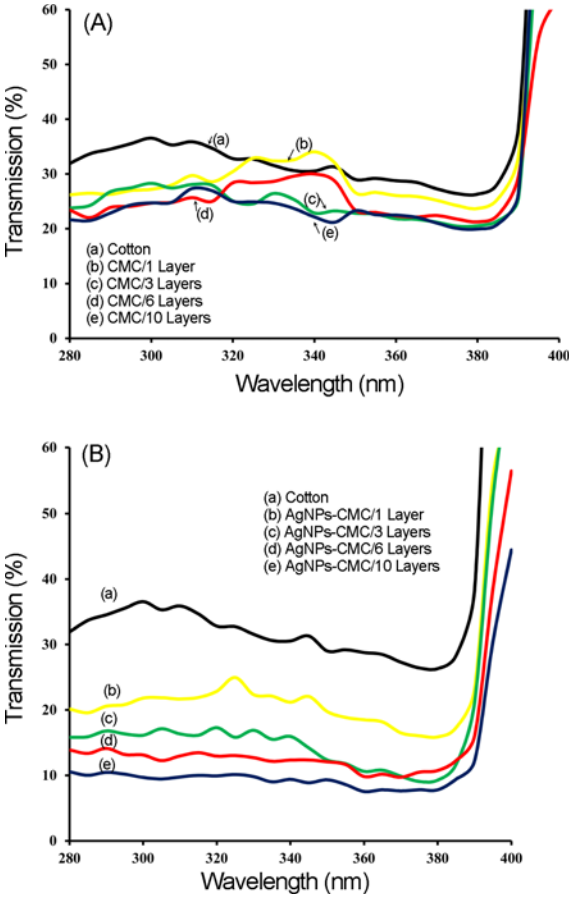


Figure 6. Transmission spectra through cotton fabrics in UV-range of wavelength (A) CMC coated cotton and (B) AgNPs-CMC coated cotton.

Results of transmission in the UV radiation range through treated cotton fabrics were presented in Figure 6. The UPF, UVA and UVB values were all calculated from the transmission results and their data were shown in Table 2. The transmission through fabrics was reduced from 30-35 % for untreated cotton to 21-26 % for CMC coated cotton regardless the number of uploaded layers. And the UPF was slightly increased from 2.85 for untreated cotton to 3.92 for CMC coated cotton. The reduction magnitude in transmission and UPF values for cotton after CMC deposition is not considered as a real result for UV absorption.

In contrary, transmission through cotton fabrics was significantly diminished to be 10-7 % after uploading of 10 layers of AgNPs-CMC composite. The transmission was observed inversely proportional with the uploaded layers of composite, as a result of the growing up of silver contents embedded into treated fabrics. The UPF values were 4.56 and 10.23 after the first and tenth uploaded layers of composite, respectively. According to their important impact on human skin, the UVA and UVB were individually calculated. UVA and UVB for cotton fabrics were raised from 59.8 and 60.3 to 86.0 and 88.8 respectively, after uploading of ten layers of AgNPs-CMC composite. Both of UVA and UVB are enhanced by 26-28.5 % after treatment with AgNPs-CMC composite. These results showed that the deposition of AgNPs-CMC composite improved UV protection property by the main effect of AgNPs embedded into cotton building blocks.

Although the UPF values obtained in the current study are still lower than the standard values required for classifying the fabrics as an excellent protector against solar UV radiation, they are similar to that reported in literature for cotton after implantation of copper gluconate complex, copper salts and nano ZnO [44,49,50] and much better after deposition of zinc salts [44]. Further enhancement in the UV protection property of cotton fabrics could be achieved by applying more layers from AgNPs-CMC composites and using more compacted fabrics.

Electrical Resistance

The electrical conductivity describes how a certain substance allows electrical current pass. The electrical conductivity through cotton fabrics was measured by determining the electrical resistance and results shown in Table 2. Results showed that, increasing number of CMC layers results in reduction of electrical resistance from 522 MΩ for untreated to 172 MΩ after application of 10 CMC layers. By using of AgNPs-CMC composite, the resistivity through fabrics was further diminished to reach 1.6 MΩ after applying 10 composite layers and with increment of silver contents up to 3.31 g/kg. Comparing to CMC, the improvement in conductivity was much higher in case of using AgNPs-CMC composite as a result of increment in silver contents and so AgNPs which were embedded into cotton fabrics. In spite of the conductivity was improved by deposition of AgNPs-CMC composite, but

Table 2. UV protection values, electric resistivity and antibacterial activities for cotton fabrics coated with CMC and AgNPs-CMC

Deposition layers		Ag content (g/kg)	UPF	UVA (%)	UVB (%)	Resistivity (MΩ)	Antibacterial action against *Escherichia colie* (%)
Untreated fabric		0.00	2.85±0.01	59.78±0.8	60.27±0.8	522.0±21.2	0.0
CMC	1	0.00	3.44±0.00	63.52±2.55	68.65±1.04	452±28.3	0.0
	3	0.00	3.65±0.25	68.40±2.01	69.43±2.06	284±14.1	0.0
	6	0.00	3.92±0.19	71.34±1.71	72.34±2.77	190.6±5.6	0.0
	10	0.00	3.88±0.00	67.42±0.30	72.26±0.54	172±7.1	0.0
AgNPs-CMC	1	0.61±0.00	4.56±0.03	73.94±0.74	75.95±0.45	113±8.0	92.5
	3	1.86±0.07	6.05±0.05	79.86±0.34	81.35±0.57	52±2.4	99.0
	6	2.74±0.09	7.75±0.07	83.12±0.02	84.81±0.40	5.3 ±0.5	100
	10	3.31±0.08	10.23±0.16	86.01±0.12	88.80±0.09	1.6±0.3	100

the electrical resistivity through fabrics was still high. Higher electrical conductivity through fabrics could be achieved by applying higher layers from AgNPs-CMC composite, resulting in increasing of silver content. Electrical conductivity in the current work is higher than that of Cu_2O deposited cotton [50] which might be a result of higher silver content. Hence, higher electrical conductive cotton could be obtained by applying much higher silver layers.

Antibacterial Activity

One of our objectives is the inclusion of certain bio-active CMC-AgNPs composite for acquiring additional antibacterial function for treated cotton fabrics. Quantitative counting method was used for the detection of antibacterial efficacy against *Escherichia coli,* as an example of gram negative bacteria and data was reported in Table 2. The data shown revealed that application of CMC multilayers did not achieve any of antibacterial activities. Regardless to the number of applied CMC-AgNPs composite layers, all the CMC-AgNPs treated samples performed excellent antibacterial activities. The higher is the number of applied composite layers, the higher silver content in fabric and hence, the greater is the imparted antibacterial activity. One composite layer was sufficient to gain excellent bactericidal action for cotton fabrics, as bacterial reduction reached 92 %. However, bacterial colonies were fully reduced (100 %) by application of 6-10 CMC-AgNPs composite layers. These antibacterial results were much better than that reported in literature for AgNPs-cotton fabrics [4-8,51].

Conclusion

AgNPs-CMC composite was prepared by interaction of silver nitrate with CMC. Layer by layer technique was used to prepare multi-functional cotton fabrics by applying multi layers from the so prepared composite. The cotton fabrics were coated with CMC a lone as reference to study the effect of deposited AgNPs. SEM showed that AgNPs and CMC were both deposited on fabrics and the size of AgNPs calculated from XRD was 18.2 nm. ATR-FTIR confirmed that CMC is physically adsorbed on the cotton surface and consequently results in ease wash off within rinsing bath. The color of fabrics was changed to gray-yellow-orange by treating with AgNPs-CMC composite and the color became more intense by growing numbers of composite layers. The UV transmission radiation was significantly reduced from 30-35 % to 7-10 % after applying ten composite layers. The UPF and electrical resistance were found to be gradually increased with the number of composite layers as a result of increasing the amount of AgNPs embedded into cotton. The multilayers of AgNPs-CMC composite imparted an excellent antibacterial property to cotton fabric and application of this method produce valuable medical and antiseptic textile goods which are required in different biomedical purposes.

The current study offers quite simple approach for production of high performance cotton by acquiring fabric coloration, improved UV protection properties and excellent antibacterial action. The promising results obtained in the current study for layer by layer technique, opening the way for evaluation of another secured functions.

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