



Utilization of atmospheric Dielectric barrier discharge plasma for nanoparticles synthesis and immobilization on cotton fabric

Faten Hassan Hassan Abdellatif^{1*}, Usama M. Rashed² and Hend M. Ahmed¹



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¹Textile Research Division, National Research Centre, Scopus Affiliation ID 60014618 33 El Bohouth St., Dokki, Giza, Egypt

²Center of Plasma Technology, University of AlAzhar, Nasr City, Cairo, Egypt.

Abstract

In this work nanoparticles were in-situ synthesized on cotton fabric by dipping the Air/ Dielectric barrier discharge plasma pretreated fabric in the corresponding metal salts solution followed by exposure to Ar/ plasma at atmospheric pressure. The size of the synthesized nanoparticles was ranged from 7 to 30 nm with spherical shape. The immobilized nanoparticles confer the fabric with multifunctional properties such as UV blocking and antimicrobial properties. Furthermore, the nanoparticles could act as an alternative to the traditional organic dyes for dyeing cotton fabric with excellent color properties. Cotton fabric immobilized nano-particle was subsequently printed with three different reactive dyes to express the availability of their printing and obtaining different color shading.

Key words: multifunction, nanoparticles, cotton, Dielectric barrier discharge plasma, UV blocking, antimicrobial.

Introduction

The emerging of the nano-technologies in different industries has led to reasonable progress especially in textile industry due to the valuable properties of nano scale materials; 1 to 100 nm; comparing to that of bulk materials. Nano-materials can improve the existing properties of the textile materials; furthermore, new functionalities i.e. antibacterial, flame retardant, UV blocking, electric conductivity and super hydrophobicity could be induced in textile materials using different nano-scale materials. These functionalities are essential to obtain products that can fit with the user requirements with maintaining the ecology system [1-3] [4-12].

Furthermore, nano-materials have been used as an alternative to the conventional dyeing stuff of textile materials [13]. Nano-materials can color the textile substrates by their surface plasmon resonance property. This property attributed to the interaction of the light radiation with the nano-materials surface. The color resulted from the nano-materials is governed by their shape and size. Metals like Au, Ag,

Cu and alkali metals have intense color resulted from their free electrons and their plasmon resonances in the visible region [14][10]. The optical properties of the nanoparticles are also influenced by the distance between the nanoparticles, surrounding environment, their refractive index [14, 15]. Many studies have been done about the coloration of textile fabrics using several nanoparticles. The resulted colored fabric exhibited good color properties with high fade resistance [16-20].

Several methods were used for nano-materials synthesis i.e. chemical vapor condensation [21], Pyrolysis by laser [22], W/O micro emulsion [23], Sol-gel [24], microbial synthesis of nanoparticles [25] and plasma [26].

Plasma is recently used as cheap, eco-friendly, solventless and high purity technique. The state of matter changes from solid to liquid and from liquid to gas when the matter exposed to energy. By increasing the energy the gas can ionize to plasma. Plasma usually consists of free radicals, electrons, ions, atoms, molecules and excited particles. When solid

*Corresponding author e-mail: tota_nrc@yahoo.com

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surface is placed in the space of plasma, it will be modified chemically and physically without altering the bulk properties of the exposed surface.

low-temperature plasma techniques have been emerged as new synthetic tool for nano-materials synthesis. Plasma is usually applied on the metal precursor in presence of hydrogen and argon gases to produce nano-sized materials in high yield such as Ag, Cu, Fe, etc.

At atmospheric pressure, plasma can produce various chemically reactive species which responsible for textile surface processing. It considered a first choice for imparting the required functionalities onto textile fabrics. Moreover, atmospheric pressure plasma has many advantages i.e. low cost, facile to operate, high energetic efficiency, and production of high yields. These advantages open great opportunities to replace or enhance the conventional wet-chemical processing with plasma process. Dielectric barrier discharge (DBD) is a type of atmospheric pressure plasma; it is widely used for textile surfaces modifications by generation of different polar groups, i.e. carboxylic groups, hydroxyl radicals and acylamino groups. The generation of these active groups on fabric surface could improve the wettability and the fabric surface energy. The utilized gas in this type of plasma could be inert such as helium, argon and neon or chemically reactive such as air, nitrogen, oxygen and ammonia [27].

It has been reported that using H₂ in DBD plasma led to the generation of H atom and/or H radicals, which have high reducing ability. The reducing characteristic of H atom and H radicals is efficient in metal ions reduction. Conventionally, the nanoparticles are synthesized parallel to their deposition on the substrate surface. Cheng et al introduced another approach by using two step synthesis method. In this approach the metal compound of nanoparticles are deposited firstly on the substrate surface followed by their reduction to produce metal nanoparticles [28].

In this work nanoparticles were in-situ synthesized on cotton fabric using atmospheric pressure DBD plasma. The metal content of the resulted cotton samples was determined using atomic adsorption. ATR-FTIR was used to characterize cotton fabric loaded with different nanoparticles while their morphology was investigated by SEM. the size and

the shape of the nanoparticles were investigated using TEM. Furthermore, the color, UV blocking and the antimicrobial properties of the resulted cotton samples were also investigated.

2. Experimental

2.1. Materials

Cotton (100%): Mill desized, bleached, and mercerized cotton fabrics (130 g/m²) produced by Misr/Helwan for Spinning and Weaving Company, Egypt. the fabric was washed with non-ionic detergent and dried before any further treatments. Copper oxide 98%, magnesium oxide $\geq 99\%$ and zinc oxide 99.9% were purchased from Sigma Aldrich. Reactive dye namely, Tulactiv Red P-4BN, Tulactiv orange G-5BN were kindly supplied by Ciba. Reactive Blue 19 was kindly supplied by Sigma-Aldrich. Other reagents were of laboratory grades.

2.2. Method

2.2.1. In-situ deposition of metal salts on cotton pre-treated atmospheric pressure DBD plasma

Cotton fabric was subjected to air/ DBD plasma for 15 min at 150 voltage. The cotton samples were placed between two electrodes and subjected to low temperature plasma under atmospheric barometric pressure.

In round flask 1.5 g of AgNO₃ was dissolved in 50 ml H₂O. 0.1 M ammonium hydroxide solution was added drop wisely to AgNO₃ solution with magnetic stirring until the conversion of AgNO₃ solution to AgOH. The plasma activated cotton fabric was padded in the latter mixture for 30 min to ensure the deposition of AgOH onto the fabric surface leading to the changing in the fabric color from white to dark brown. The fabric sample was dried at 60 °C for 1 hour. 0.1 g of MgO, CuO and ZnO were added separately to AgNO₃ solution to deposit these metal oxides in combination of AgOH onto cotton fabric surface. The obtained samples were treated by another atmospheric pressure DBD plasma treatment for 5 min exposure time, 100 v and flow rate 2.5 mL for Ar gas using the plasma Set up shown in Figure 1.

2.2.3. Fabric Printing

Before printing, activated cotton fabric was treated with two different amount of AgNO₃ (0.3 g or 0.14 g) following the same procedure that illustrated in the former section. The colored samples were printed using three different reactive dyes namely Tulactiv Red P-4BN, Tulactiv orange G-5BN and Reactive Blue 19 using the following printing past composition:

Printing past composition	g/100 g past
Thickener	2 gm.
Binder	15-20 gm.
Initiator	0.5 gm.
Urea	4 gm.
Dyes	3gm.
Water	X -----
Total	100 gm.

All the printed samples were fixed by steaming for 15 minutes followed by washing to remove the excess chemicals

2.3. Characterization

2.3.1. Nano-particle content

Nanoparticles content of the NPs-loaded cotton samples was determined using multi-element flame atomic absorption spectrometer (A Varian Model SpectrAA 220), equipped with a conventional pneumatic nebulizer and nebulization chamber was used to determine the metal content in the treated sawdust samples. A multi-element hollow cathode lamp for determination of silver, copper, magnesium and zinc was used. The flame composition was acetylene (flow rate: $2.0 \text{ l} \times \text{min}^{-1}$) and air (flow rate: $13.5 \text{ l} \times \text{min}^{-1}$)

2.3.2. Transmission electron microscopy (TEM)

Transmission electron microscopy was used to provide direct image to nanoparticles and to measure the particle size, size distribution, and morphology. Transmission electron microscope (TEM) observation was performed on a JEOL JEM-1230 electron microscope at accelerating voltage of 120 kV. Specimens for TEM measurements were prepared by depositing a drop of colloid solution on a 400 mesh copper grid coated by an amorphous carbon film and evaporating the solvent in air at room temperature. The average diameter of the ZnO nanoparticles was determined from the diameter of 100 nanoparticles found in several chosen areas in enlarged microphotographs.

2.3.3. Fourier transforms infrared (FTIR)

FTIR spectroscopic analysis was performed on Perkin-Elmer Spectrum 1000 spectrophotometer. The standard sample cell in the FT-IR spectrometer was a Pike Miracle single-bounce attenuated total reflectance (ATR) cell equipped with a Ge crystal.

2.3.4. SEM images and EDX spectra

The morphology of the sawdust samples were studied using scanning electron microscope SEM (JEOL JSM-5310). SEM micrographs were taken at magnification of 16000.

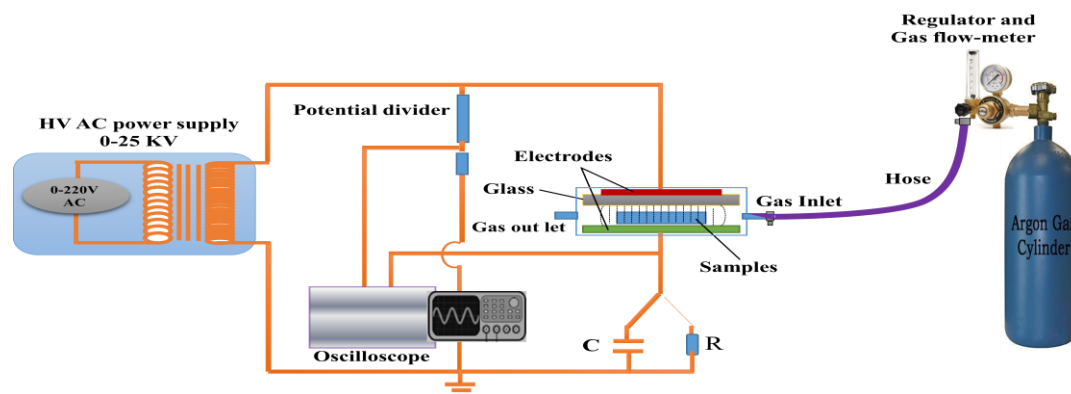


Figure 1: DBD plasma setup used for nanoparticles synthesis on cotton fabric surface

Energy dispersive X-ray technique (EDX) connected to SEM instrument was used to investigate the presence of the nanoparticles in the analyzed samples

2.3.5. UPF analysis.

The UV-protection factor (UPF) of the treated and untreated samples was determined according to the Australian/New Zealand standard (AS/NZS 4366-1996). UPF was rated as follows: providing good (UPF:15–24), very good (UPF:25–39), and excellent protection (UPF > 40) UV-Protection

2.3.6. Antimicrobial activity

Antimicrobial activity assessment against Gram positive bacteria [*Bacillus subtilis* (ATCC 6633) & *Staphylococcus aureus* (ATCC 6538)], Gram negative bacteria [*Escherichia coli* (ATCC 25922)] and pathogenic yeast [(*Candida albicans* ATCC 10231)] was evaluated qualitatively according to AATCC Test Method (147-2016) [29]. The antimicrobial activity was expressed as zone of growth inhibition (mm)

2.3.7. Coloration and color fastness screening

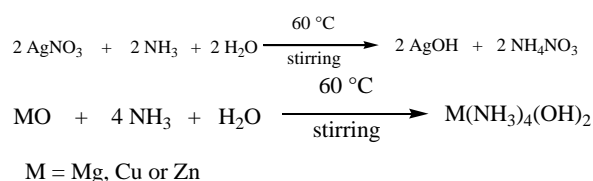
Ultra Scan PRO spectrophotometer with 10° standard viewer and D65 illuminant (Hunter Lab, USA) was

employed to investigate the color change of the tested sensor wool fabrics applying tinctorial strength (K/S) and CIE Lab. L^* is denoted as blackness (0) to whiteness (100), a^* is denoted as greenness (-) to redness (+), and b^* is denoted as blueness (-) to yellowness (+) color ratios. The colorfastness properties were recorded according to AATCC Test Method (8-2016) for rubbing [30], AATCC Test Method (61-2013) for washing [31], AATCC Test Method (15-2013) [32] for perspiration, and AATCC Test Method (16.1-2014) for light [33]. Results and discussions

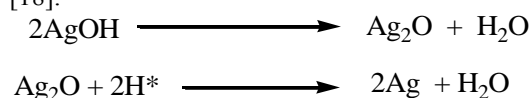
3.1. Loading of cotton fabric with different nanoparticles using DBD plasma

Cotton fabric was pretreated with air/DBD plasma for 15 min at 150 voltage. This step was essential for cleaning the fabric surface and improving its adhesion and hydrophilic properties. Moreover, the treatment of the fabric surface with air/DBD plasma can increase its surface energy that is required for creation of polar functional groups such as C=O, COOH and OH which needed for subsequent treatment of the fabric.

This step was followed by padding cotton fabric in AgNO_3 or its mixture with other three different metal oxides i.e. MgO, CuO or ZnO. The following scheme illustrates the reaction of AgNO_3 and the metal Oxide with ammonia solution.



The AgOH and/or the $\text{M}(\text{NH}_3)_4(\text{OH})_2$ particles deposited on the cotton fabric surface during their formation in the reaction mixture. After the fabric drying at 60°C , it was treated with Ar/DBD plasma. The DBD is non-thermal plasma suitable for textile treatments. The main characteristic of DBD plasma is that the temperature of the produced electron is high as (10^4 – 10^5 °C) and the electron density is in the range of (10^{18} – 10^{21} m^{-3}). These characteristic enable DBD plasma to break chemical bond with low dissociation energy [18]. Thus $\text{M}(\text{NH}_3)_4(\text{OH})_2$ could be decomposed to the related nano-metal oxides with the release of NH_3 and H_2O . The system of DBD plasma can release huge number of active species like electron and hydrogen free radicals which can play great role in reduction of AgOH to Ag nanoparticles [18].



3.2. Metal content of the treated cotton fabric

Table 1 showed the total content of Ag and other metal oxides in the treated cotton fabrics. The metal contents were determined quantitatively by the flame atomic absorption. The results exhibited the Ag content was ranged from 50 to 77 mg/g for Cotton-Ag NPs and Cotton-(Ag+ CuO) NPs, respectively. While the other metal oxides contents was 15 mg/g, 20 mg/g and 14mg/g for MgO, CuO and ZnO in their corresponding samples, respectively.

3.3. TEM

To confirm the formation of NPs, TEM analysis was carried out on the solution of the released NPs during washing of cotton fabric-loaded nanoparticles. Figure 2 reveals the different TEM images of the released NPs gave an insight about the morphology and the size of the NPs. TEM images revealed that all the nanoparticles had spherical shape and their size was ranged from 7 to 30 nm. These results prove that Ar/DBD plasma treatment is successful in synthesis of nanoparticles from their corresponding metal salts.

Table 1: the NPs content in treated cotton fabric

Sample	Mg mg/g	Cu mg/g	Zn mg/g	Ag mg/g
Cotton-Ag NPs	0	0	0	77
Cotton-Ag NPs and MgO NPs	15	0	0	67
Cotton-Ag NPs and CuO NPs	0	20	0	50
Cotton-Ag NPs and ZnO NPs	0	0	14	62

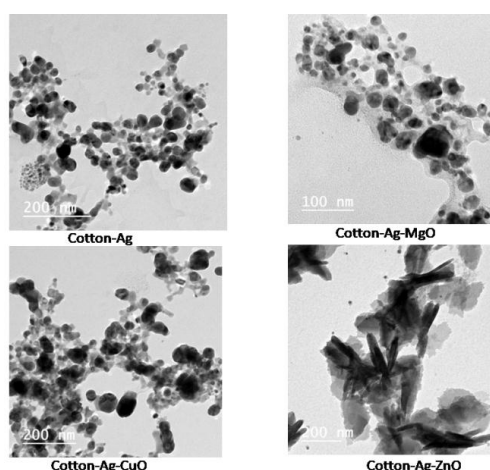


Figure 2: TEM of released NPs a) Ag NPs, b) (Ag+MgO) NPs, c) (Ag+CuO) NPs and d) (Ag+ZnO) NPs

3.4. ATR-FTIR

Figure 3 illustrates the ATR/FTIR spectroscopy of the fabrics before and after nanoparticles loading. The spectrum of the untreated cotton fabric is quite similar to the spectra of the treated samples. The characteristic peaks of cellulosic structure functional group are exhibited at 3300 cm^{-1} , 2900 cm^{-1} , 1175 cm^{-1} and 1039 cm^{-1} corresponding to (O–H, stretching), (C–H, stretching), (C–O, stretching) (C–O–C), respectively. Figure 2 exhibited that there is no significant change after loading the fabric with the different nanoparticles. Nevertheless, the intensity of some beaks, i.e. hydroxyl groups, is slightly reduced which indicate the physical interaction between the fabric and the nanoparticles [36].

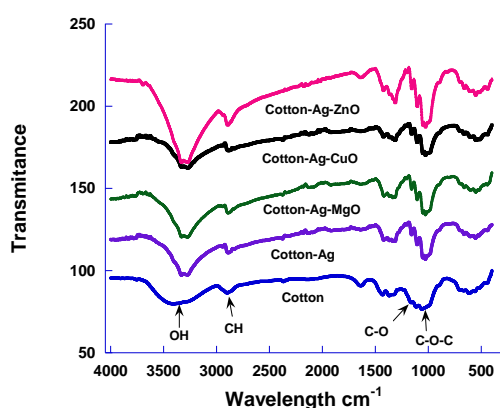


Figure 3: ATR-FTIR spectroscopy of untreated cotton fabric and cotton loaded NPs

3.5. SEM and EDX analysis

SEM was used to investigate the morphology of cotton fabric surface after the creation of the different nanoparticles by Ar/DBD plasma on the fabric surface at atmospheric pressure. Figure 4 exhibited the deposited nanoparticles on the longitudinal fibril of cotton fibers despite the presence of some aggregates of larger particles. Moreover, SEM images showed the formation of rough surface and hierarchical structure by the deposited nanoparticles. The presence of nanoparticles on the surface of fabric was confirmed using the EDX analysis by the appearance of the corresponding metal signal on the EDX spectrum in all treated samples.

3.6. UV protection

UV blocking properties of textile fabrics are usually insufficient and they can be improved by varying the thickness, type and colors of the fabric. Improving UV blocking properties of textile substrates is not important for the safety of the user only but also for the protection of the fabric and dyes from severe UV radiation [30]

UPF values of cotton and cotton loaded with the different nanoparticles are located in Table 2. These results revealed that loading cotton with nanoparticles extremely improve its UV protection functionality.

All the treated samples has excellent UPF category, nevertheless, cotton fabric loaded (Ag + ZnO) NPs exhibited the highest UPF value.

The highest UPF values of cotton fabric after loading with nanoparticles can be attributed to the large refractive index of the nanoparticles which increase their UV scattering efficiency [31].

3.7. Antimicrobial study

Cotton fabric usually creates a favorable environment for microorganism's growth. The microorganism's attachment of cotton fabric surface can degrade the fabric by bio-deterioration and causing its color fading, furthermore they can create odor problem and irritation for the user. Numerous antimicrobial agents were utilized for fabric finishing for killing or inhibiting microorganisms and protecting the user and the fabric from their fatal effects. The antimicrobial agents could be synthesized such as quaternary ammonium compounds, Polybiguanides, N-halamines, and triclosan or obtained from natural origin such as chitosan and phenolic compounds.

Recently nanoparticles have been used as inorganic antibacterial agent for finishing textile due to their destructive effect on numerous microorganisms. Nanoparticles can affect microorganisms by creation of reactive oxidative species, ions releasing or by their interaction with the cell membranes. Moreover, the nanoparticles can affect microorganisms by agglomeration on the surface and change the lipids structure, peptidoglycan, proteins, and their DNA *via* photo-catalytic process [32].

Figure 5 showed the antimicrobial activity of cotton fabric loaded different nanoparticles against four different organisms namely Gram positive bacteria [*Bacillus subtilis* (ATCC 6633)& *Staphylococcus aureus* (ATCC6538)], Gram negative bacteria [*Escherichia coli* (ATCC25922)] and pathogenic yeast [*Candida albicans* ATCC 10231]. All the samples exhibited very good antimicrobial activity against all the studied microorganisms except for cotton loaded Ag and CuO nanoparticles sample which did not exhibit any activity against *Candida albicans* (Fig. 5). The antimicrobial activity of Ag nanoparticles can be attributed to their ability to damage the structure of the cell wall, changing the permeability of the cell membrane then inhibit metabolisms of cell membrane leading to the death of microorganism, and/or via the production of reactive radical and hydrogen peroxide by the catalyze character of Ag nanoparticles. Furthermore, nano-metal oxides, such as MgO, CuO or ZnO nanoparticles have the ability of generating of very reactive species, such as H_2O_2 , super oxide anions and hydroxyl radicals. The generated reactive species can destruct the bacteria cell by the photo-catalytic properties [8, 33].

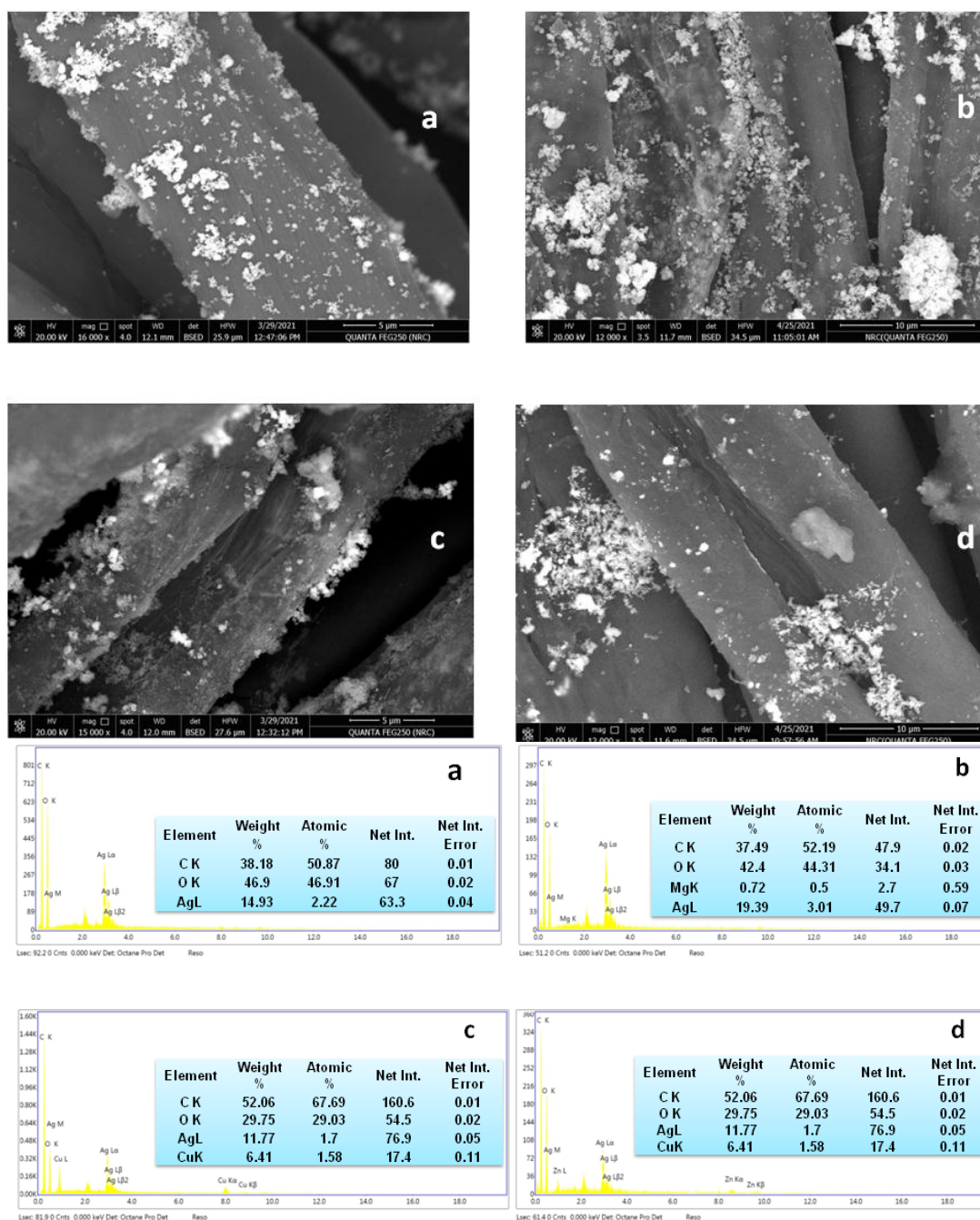


Figure 4: SEM and EDX of cotton samples loaded with a) Ag NPs, b) (Ag+MgO) NPs, c) (Ag+CuO) NPs and d) (Ag+ZnO) NPs

Table 2: UPF values for untreated cotton fabric and for cotton loaded nanoparticles

Sample	UPF	UPF category
Untreated Cotton	10	No protection
Cotton-Ag NPs	105	Excellent
Cotton-Ag NPs and MgO NPs	86	Excellent
Cotton-Ag NPs and CuO NPs	139	Excellent
Cotton-Ag NPs and ZnO NPs	227	Excellent

Table 3 showed the inhibition zone in millimeters of the studied samples against the different microorganisms.

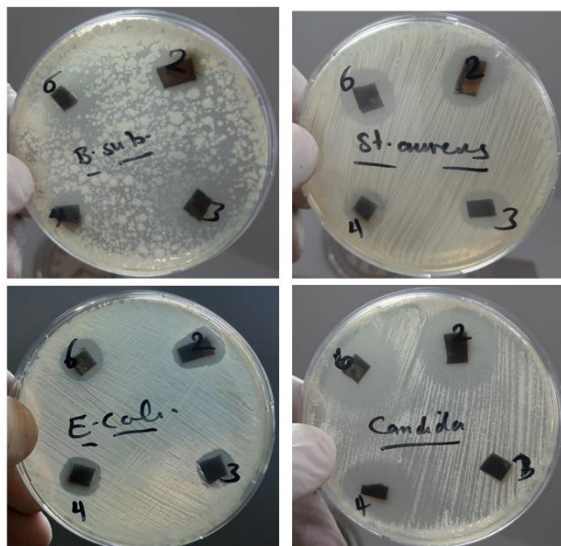


Figure 5: antimicrobial investigation of cotton loaded nanoparticles against Gram positive bacteria [*Bacillus subtilis* & *Staphylococcus aureus*], Gram negative bacteria [*Escherichia coli*] and pathogenic yeast [*Candida albicans*]. sample 2 is cotton loaded Ag and MgO NPs, sample 3 is cotton loaded Ag and CuO NPs, sample 4 is cotton loaded Ag and sample 6 is cotton loaded Ag and ZnO NPs

Table 3: Inhibition zone diameter (millimeter) of the samples

microorganism	Inhibition zone (mm)			
	cotton loaded Ag and MgO NPs	cotton loaded Ag and CuO NPs	cotton loaded Ag	cotton loaded Ag and ZnO NPs
<i>Escherichia coli</i>	15.0	14.0	16.0	15.0
<i>Bacillus subtilis</i>	15.0	13.0	12.0	16.0
<i>Staphylococcus aureus</i>	18.0	14.0	15.0	19.0
<i>Candida albicans</i>	25.0	Nil	23.0	24.0

* Nil: No antimicrobial activity recorded.

3.8. Color properties

The coloration process is essential step in textile processing, since it influences the product demand and consumer preference. Recently, coloration of cotton fabrics with different nano- particles has been emerged as novel dyestuffs which differ from the traditional dyeing approach. The decorative color obtained by in situ incorporated Ag-NPs, CuO-NPs, MgO-NPs and ZnO-NPs and its mixtures into the fabric matrix, by using Ar/DBD plasma at condition of plasma (5 min exposure time, 100 v and flow rate 2.5m/L for Ar gas) is shown in Table 4.

Table 4: Coloration screening measurements for treated cotton fabric loaded with different nanoparticles.

Cotton samples	Wavelength (nm)	K/S	L*	a*	b*
Ag-NPs	445	14.29	34.45	8.78	16.97
MgO-NPs	290	0.22	82.16	1.56	- 6.96
CuO-NPs	555	20.09	21.69	1.05	5.75
ZnO-NPs	300	0.43	73.95	3.44	6.18
Ag-NPs+MgO-NPs	390	22.52	27.70	6.63	9.06
Ag-NPs+CuO-NPs	500	25.99	21.09	2.82	4.52
Ag-NPs+ZnO-NPs	400	22.77	33.4	7.93	12.45

To investigate the effect of different deposited nanoparticles on the color of the treated fabric samples, the color strength (K/S) were evaluated. K/S value is usually reflect the amount of the dye content in the colored fabrics where, higher K/S value indicates greater color intensity and higher

amount of nanoparticles incorporated into the fabric samples.

The K/S value of cotton fabric loaded with MgO-NPs or ZnO-NPs was low as 0.22 or 0.43 respectively while the K/S value of cotton fabrics loaded with CuO-NPs or Ag-NPs was 20.09 or

14.29, respectively. These results could be attributed to that MgO-NPs are white and ZnO-NPs are yellowish while CuO-NPs or Ag-NPs are colored due to their surface plasmon resonance property. The in-cooperation of nanoparticles mixture into the fabric led to great improvement in the K/S value i.e. 22.52, 25.99 and 22.77 by loading cotton fabric with (Ag +MgO) nanoparticles, (Ag+CuO) nanoparticles or (Ag+ZnO) nanoparticles, respectively.

The CIE (L^* , a^* , b^*) system was used to investigate and evaluate the color coordinates, where L^* refers to lightness/ darkness values from 100 to 0 representing white to black, a^* is the values run from negative (green) to positive (red) and, b^* values run from negative (blue) to positive (yellow). The colorimetric data of treated cotton fabrics were provided in Table 4. Data of this table illustrated that the color of fabrics treated with MgO-NPs is white with high L^* value (82.16), low a^* value (1.56), and b^* values (-6.93) while the cotton fabric treated with ZnO NPs is yellowish with L^* (73.95), a^* (3.44) and b^* (6.18). Moreover, all the samples loaded with Ag-NPs, CuO-NPs or the nanoparticles mixtures have significantly change of (L^* , a^* , b^*) values compared to the fabric loaded with MgO-NPs or ZnO-NPs. Where, (L^*) is significantly decreased while a^* and b^* values are increased dramatically.

Table 5 showed rubbing, washing, perspiration, and light fastness for the treated fabrics. The data indicated that rubbing, washing, and perspiration fastness properties are rating from good to very good and moderate to good for light properties with

few exceptions. Generally, it could be recognized that the fabrics loaded nanoparticles showed good fastness properties due to the strong linkage between the nanoparticles and the fabric. The nanoparticles usually linked to the fabric covalently or by van der Waals bond.

3.8.1. Printing of cotton fabric loaded Ag nanoparticles

Air/DBD plasma pre-activated cotton fabric was treated with two different amount of AgNO_3 (0.3 g or 0.14 g) followed by treating with Ar/DBD plasma to create the Ag nanoparticles on the fabric surface. The resulted Ag content was 7 and 16 mg/g respectively. Decreasing the nanoparticles content was essential to facilitate the subsequent printing process by decreasing the depth of the color which strongly dependant on the nanoparticles content.

Untreated cotton fabric and cotton fabric loaded with 7 or 16 mg/g of Ag nanoparticles were printed with blue, orange or red reactive dyes. Figure 6 exhibited the role of Ag nanoparticles in color shading which depend on the Ag nanoparticles concentration. Ag nanoparticles can act as a mordant which increase the affinity of the dye. Moreover, Table 6 showed that the color strength of reactive dyes were improved with increasing the Ag nanoparticles content comparing to that of cotton printed with reactive dyes only [38].

The rubbing, washing, perspiration, and light fastness for the treated fabrics were rating from good to very good and moderate to good for light properties.

Table 5: Fastness properties for treated cotton fabric loaded different nano particles.

Cotton treated fabrics	Washing fastness		Rubbing fastness		Perspiration fastness		Light fastness
	Alt	St	dry	wet	acid	alkali	
Plasma/Ag NPs	3-4	4	2-3	3	3-4	3-4	4-5
Plasma/CuO NPs	4	4-5	3-4	3	3-4	4	5
Plasma/MgO NPs	4	4-5	3-4	4	4	4-5	5-6
plasma/ZnO NPs	3-4	3-4	4	3-4	3-4	3-4	5-6
Plasma/Ag NPs + MgO NPs	3-4	3-4	3-4	4	3	3-4	6
Plasma/Ag NPs+ZnO NPs	3-4	3-4	3-4	4	3-4	4	5-6

Plasma/ Ag NPs+ CuO NPs	3-4	4	3-4	4	3-4	4	5-6
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Table 6: Coloration screening measurements for cotton fabric dyed with Ag NPs and printed with three different reactive dyes

Cotton printing with different dyes	K/S	L*	a*	b*
Blue reactive dye untreated	10.06	42.82	18.61	36.51
Ag NPs(7 mg/g) + blue reactive dye	15.76	48.63	46.99	48.66
Ag NPs (16 mg/g)+blue reactive dye	16.98	38.07	23.48	21.83
Orange reactive dye untreated	4.45	32.33	-1.80	0.07
Ag NPs(7 mg/g) + orange reactive dye	7.38	29.71	-2.99	-7.83
Ag NPs(16 mg/g)+orange reactive dye	9.58	30.42	-3.32	-8.24
Red reactive dye untreated	9.24	34.37	23.66	13.13
Ag NPs(7 mg/g) + orange reactive dye	11.68	25.71	-4.31	1.29
Ag NPs(16 mg/g)+orange reactive dye	14.33	29.77	-12.62	-5.69



Figure 6: Images of untreated cotton fabric, dyed with Ag NPs with content of 7 mg/g or 16 mg/g and printed with three different reactive dyes

4. Conclusion

Nanoparticles i.e. Ag, MgO, CuO and ZnO were in-situ synthesized on cotton fabric using atmospheric DBD plasma. The Ag content was ranged from 50 to 77 mg/g for Cotton-Ag NPs and Cotton-(Ag+CuO) NPs, respectively. While the contents were 15 mg/g, 20 mg/g and 14mg/g for MgO, CuO and ZnO in their corresponding samples, respectively. The size of the nanoparticles was ranged from 7 to 30 nm. SEM images exhibited the deposited nanoparticles on the longitudinal fibril of cotton fibers with the presence of some aggregates of larger particles. All the treated samples showed excellent UPF, nevertheless, cotton fabric loaded (Ag + ZnO) NPs exhibited the highest UPF value. Furthermore, all the samples exhibited very good antimicrobial activity against all the studied microorganisms except for cotton sample loaded (Ag + CuO) nanoparticles which did not exhibit any activity against *Candida albicans*. The color properties of the treated cotton fabric were also investigated. The K/S value of cotton fabric loaded with MgO-NPs or ZnO-NPs was low as 0.22 or 0.43 respectively while the K/S value of cotton fabrics loaded with CuO-NPs or Ag-NPs was 20.09 or 14.29, respectively. These results could be attributed to that MgO-NPs are white and ZnO-NPs are yellowish while CuO-NPs or Ag-NPs are colored due to their surface plasmon resonance property. Generally, DBD plasma has proven to be a clean, environmental and facile approach for in-situ synthesis of nano-particle on cotton fabric.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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