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Cu NPs Loaded Silk Fabric: Characterization and Dyeability

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Abstract

Dielectric Barrier Discharge (DBD) atmospheric O2 plasma combined with CuONPs is applied to silk fabric at a discharge power of 17.35 watts for 15 min exposure time and using various concentrations of CuONPs (0.5 –1.5 g/100 fiber). Treatment of silk with combined O2 plasma/ sonicated copper sulfate solution was also tried.

The effect of O2 plasma/ CuONPs treatment on the morphology of silk surface fabric, mechanical properties, wettability, UV protection factor, anti-bacterial activities, as well as dyeability, is investigated. Fourier-transform infrared Spectrophotometer (FTIR), Scanning Electron Microscope (SEM), Energy-Dispersive X-ray (EDX), and Transmission Electron Microscopy (TEM) analysis are also measured to determine the induced changes in silk fabric morphology and structure. These treatments result in a high UV protection factor and excellent antimicrobial activity for both G (+v) and G (-v) as well as fungi strains while keeping the silk mechanical properties, expressed as tensile strength, in good quality. The dyeability with some natural dyes such as coffee, deer blood, and red cabbage extracts was enhanced and the fastness properties were improved.

Keywords: plasma, DBD, copper oxide Nanoparticles, silk, surface treatment, natural dyes

1. Introduction

Silk is a natural protein–based fiber. Silk is highly valued for its softness and drapeability. Since silk fibers have a low ultraviolet protection factor (UPF), it is less effective in blocking harmful UV irradiation from the sun. Nanoparticles are used to enhance the UPF of silk fabric where NPs could be incorporated into the fabric to improve the blocking of UV irradiation [1-6].

Nano copper is a good reagent for blocking UV due to its ability to absorb and scatter this ray. When silk fabric is treated with CuONPs, the particles can penetrate, easily, through silk fibers and form a protective layer on the surface leading to the UPF silk increase. Various techniques could be applied to treat silk with CuONPs such as immersion, spraying, and dip-coating. Several studies prove that the UPF of silk was found to be improved by CuONP treatment. UPF values reached 50 or 70 % upon treatment with 1 or 0.5 % CuONPs respectively compared to 15 for untreated silk. These obtained UPF values are considered excellent UV protection. [7-13]

In addition, CuONP treatments could also increase durability and antibacterial properties which could be used in outdoor clothing, sportswear, and medical textiles. Overall, the treatment of silk with CuONPs is a promising method to improve its UPF and enhance its functionality. This technology could be applied to provide high protection for people.

Some studies investigated the antibacterial activity of treated silk with CuONPs. Treatment of silk with 1% CuONPs gives excellent antibacterial activity for

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both Gram-positive and Gram-negative bacteria such as Staphylococcus and E. coli. The antibacterial properties of CuONPs treated silk could be applied as medical textiles to prevent the growth of bacteria, help to increase the life of the fabric by preventing the growth of odor-causing bacteria and reduce the requirement for washing. [4, 14-16]

This work investigates the treatment of silk fabric with oxygen plasma followed by treatment with CuONPs as well as sonicated CuSO4 solution to improve its functionality as well as dyeability with some natural dyes such as coffee, red cabbage, and deer blood. The treated silk fabric was examined by SEM, TEM, FTIR, and mechanical properties as well as antibacterial activity. The wettability and UV protection factor of treated silk are also evaluated.

2. Experimental

2.1. Material

2.1.1. Fabric

Grey silk was offered by a private company. The fabric was degummed using a 15% (o. w. f) aqueous solution of Asp icon 1030 soap at a temperature of 95-100°C for 1-2 hrs. The fabric was thoroughly washed with warm water, followed by cold water, then, squeezed and air dried. [17]

2.1.2. Chemicals

CuO Nanoparticles are supplied by Orchid Pharmaceutical Company, Obour City, Egypt. Non-ionic detergent, urea, and Ammonium persulfate $(NH_4)_2S_2O_8$ as thermal initiators are supplied from Merck, Germany. Bercolin metal CM as a thickener is supplied by Berssa, Turkey. Thermal curing binders and $CuSO_4$ were laboratory-grade chemicals. Dyestuffs; Coffee, Gomphrena Glo bosa (deer blood), and red cabbage, were bought from the local market.

2.2. Methods

2.2.1. Fabric Treatments

Silk fabric was treated with O_2 plasma at 17.35 Watt for 15 min followed by padding treatment with CuONPs or sonicated $CuSO_4$ solution, then squeezed to 100 % pickup. Treated samples were dried at 120°C for 30 min. The concentration of NPs ranged from 0.5 to 1.5 g/100 g fiber.

2.2.2. Plasma Set up

The textile fabrics were exposed to low-temperature plasma generated by DBD under atmospheric pressure. [18]

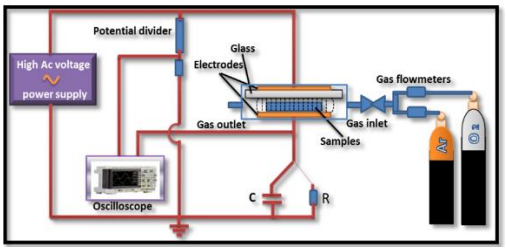

Fig 1: Schematic diagram of the discharge cell used for the treatment of the textile [19]

2.2.3. Dyeing Method

The dyeing process was carried out at a temperature of 80°C for 60 min in the Infrared Lab Dyeing Machine. The untreated and treated samples were dyed with deer blood, red cabbage, and coffee natural dyes. [20, 21]

2.3. Measurements

2.3.1. Wettability

The wettability was evaluated by measuring the wetting time according to the AATCC-39 method. [22] A drop of water is allowed to fall from a fixed height onto the surface of the silk fabric under examination. The time needed for the drop of water to disappear was measured and taken as wetting time, and the results were the average value of five readings.

2.3.2. Scanning Electron Microscope (SEM)

SEM micrographs were reported by Quanta/FEG/250 (Czech Republic) at 10-20 kV (JEOL JSM-5310) VEGA 3, TESCAN.

2.3.3. Energy-Dispersive X-ray (EDX)

SEM equipment is connected to TEAM/EDX energy dispersive X-ray analytical tool for determining the chemical composition by applying an accelerating voltage at 20 kV. The average diameters of nanoparticles were monitored using the Image J program.

2.3.4. Transmission Electron Microscopy (TEM)

Transmission electron microscopy was used to provide a direct image of nanoparticles and to measure the particle size, morphology, and size distribution. Transmission electron microscope (TEM) observation was performed on a JEOL JEM-1230 electron microscope at an accelerating voltage of 120 kV.

2.3.5. Tensile Strength

Tensile strength and elongation at a break were reported by the ASTM examination method (D 5034) using (the Grab test). [23] All reported values were the average of three readings. [24]

2.3.6. Fourier-Transform Infrared Spectro-photometer (FTIR)

FTIR spectra were recorded on a JASCO FT-IR spectrometer (ATR) was used to analyze the spectrum of the untreated and treated samples. The tester collected transmittance of the infrared in the film between 400 and 4000 cm^{-1}.

2.3.7. Antibacterial Activity

Antibacterial activity was carried out by the diffusion disc method. [11, 25-27] The silk sample was placed in a Petri dish containing solid bacteria medium (nutrient agar) or fungal medium (Doxs medium), which has been heavily seeded with the spore suspension of the tested organism. The incubation period of the tested microorganism is 24 hours. The tested microorganisms are Gram-positive (Staphylococcus aureus), and Gram-negative (Escherichia coli). The percentage reduction test was tried. [25, 26]

Specimens of the tested samples were introduced to a known concentration of bacterial suspension and the reduction in bacterial activity was measured. The % reduction of the samples was evaluated according to the following equation:

$$R = A\text{-}B/A \times 100$$

Where, R: % reduction, A: number of bacterial at zero-time, B: number of bacterial after 18 hours. An average value of duplicate tests was evaluated. [28]

2.3.8. Electro-activity Assessment

The electrical conductivity of both untreated and treated silk samples was measured by the HIOKI LCR Hi 3522- 50 testing apparatus (Japan). [29]

2.3.9. UV Protection Factor

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 good (UPF: 15–24), very good (UPF: 25–39), and excellent UV protection (UPF > 40). [8-13]

2.3.10. Color Assessment (K/S)

The color strength of the dyed samples was evaluated by Hunter Lab Ultra scan PRO. The color strength (K/S) of each dyed sample was measured using a Data Color SF 600 plus Colorimeter. [30, 31]

2.3.11. Fastness Properties

The color fastness of the dyed fabrics was assessed by the AATCC Test Method 16-2014 (color fastness to light), AATCC Test Method 61-2013 (colorfastness to laundering), and AATCC Test Method 8-2016 (color fastness to rubbing and color fastness to perspiration). [32-34]

3. Result and Discussions

The results of untreated and treated silk samples were evaluated by measuring the wettability, conductivity, tensile strength & elongation, SEM, EDX, TEM, FTIR, UPF, antibacterial activity, and color strength.

3.1. Wettability

The wetting times of untreated and treated silk with both O_2 plasma and CuONPs separate or a combination of them both; O_2 plasma / CuONPs were evaluated. The obtained results are illustrated in Table 1 and Fig 2. It could be observed that all the carried out treatments affect- to a great extent- the wetting time of the treated silk samples and lead to a noticeable decrease in their wetting time compared to the untreated sample reflecting on increasing the wettability of silk fabric. This phenomenon could be attributed to the hydrophilicity enhancement of the treated silk with either CuONPs or O_2 plasma / CuONPs which may be due to the formation of OH and COOH groups as a result of O_2 plasma treatment etching and consequently increasing the surface roughens and free energy of silk. It is, also, clear that the wetting time decreased from about 20 seconds for an untreated sample to nearly a quarter of this value (5.45 s) upon treatment with O_2 plasma / CuONPs of a concentration 1.5 g /100g fiber at plasma discharge power of 17.35 watt for an exposure time 15 min.

Table 1: Wettability of treated silk with plasma / CuONPs

Type of Sample	Plasma Power (watt)	Plasma Exposure time (min)	Conc. Of CuO wt. %	Wetting Time (s)
Untreated silk	-	-	0.0	19.98
Treated silk with O_2 plasma	17.35	15	0.0	14.03
Treated with the Cu O NPs	- - -	- - -	0.5 1 1.5	13.98 12.93 12.45
Treated silk with O_2 plasma/ CuONPs	17.35 17.35 17.35	15 15 15	0.5 1 1.5	8.72 5.57 5.45

Treatment: padding 100% pickup 120° C, 30 min.

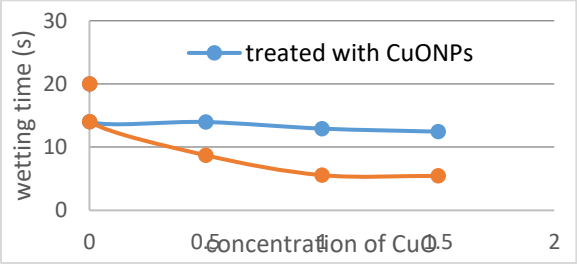

Fig 2: *Wettability of treated silk*

3.2. Conductivity of Treated Silk

The electrical conductivity of untreated and treated silk samples with O_2 plasma / CuONPs and O_2 plasma / CuSO4 is investigated and the results obtained are illustrated in Table 2. Silk fabric was treated with 1.5 g / 100 g fabric of either CuONPs or sonicated $CuSO_4$ solution to realize an increase in electrical conductivity. It can be seen from Table 2 that a significant increase in the electrical conductivity of silk is carried out due to nano deposition of Cu on the silk fabric surface regardless of the component used. [25, 26]

Table 2: Electrical conductivity of treated silk fabrics

Type of sample	Plasma power (watt)	Plasma time (min)	Electrical conductivity (ohm/m)
Untreated silk	-	-	443
Treated silk with O_2 plasma / CuONPs	17.35	15	503
Treated silk with O_2 plasma / CuSO4	17.35	15	480

Treatment: pick up 100%, 1.5 wt %, 120 ° C, 30 min

Conductive textiles have an important role in recent textile technology. Some researchers aim to add electronic devices into textile substrates to impart new features such as transmitting, tracking, and controlling movements. [35] The conductivity of textiles is improved by several methods. Both Ag and CuONPs are known as electrically conductive and are, mainly, applied on silk and wool. Although silk fabric is considered a poor conductor of electricity when it is treated with CuONPs, static charges are formed and lead to an increase in silk conductivity as shown in Table 2.

3.3. Tensile Strength

The mechanical properties of the untreated and treated silk with O_2 plasma, O_2 plasma / CuONPs, and O_2 plasma / $CuSO_4$ were evaluated in terms of its tensile strength and elongation % at break, and the obtained results are shown in Table 3. It is noticed that the tensile strength value of the untreated silk sample is 0.6317 Kg_f /mm^2 with Young's modulus of 0.0160 Kg_f/mm^2. However, after O_2 plasma treatment, a slight improvement in the tensile strength is observed, 0.6663 Kg_f /mm^2. While, after treatment with O_2 plasma/CuONPs and O_2 plasma/$CuSO_4$, a great enhancement in the results is achieved of values 2.71 and 2.883 Kg_f/mm^2 with Young's modulus 0.2071 and 0.312 Kg_f /mm^2 respectively. The reason behind such improvement can be explained by the formation

of hydrogen bonds on the silk fabric surface after O_2 plasma treatment. [29] The oxygenated species formed during O_2 plasma treatment not only attaches to the silk surface through hydrogen bonding but also they form hydrogen bonds among themselves. [36] This hydrogen-bonded assembly leads to an extraordinarily complex structure at the silk fabric surface treated with O_2 plasma / CuONPs and O_2 plasma / $CuSO_4$ and eventually, this contributes to the enhanced mechanical performance.

Table 3: Tensile strength of untreated and treated silk fabric

Type of sample	Tensile strength Kg_f /mm^2	Elongation %	Young modulus Kg_f /mm^2
Untreated silk	0.6317	8.000	0.0160
Treated silk with O_2 plasma	0.6663	8.333	0.0151
Treated silk with O_2 plasma/CuONPs	2.71	10.00	0.2071
Treated silk with O_2 plasma/CuSo4	2.883	11.33	0.312

Treatment: pick up 100%, 1.5 wt %, 120 ° C, 30 min

3.4. Morphology Analysis

The morphology of the silk surface has been observed by a scanning electron microscope (SEM). The images of SEM for untreated and treated silk are shown in Figures (1- 4). Figures (1, and 2) represent the images of untreated and O_2 plasma treated silk. On the other side, Figures (3, and 4) show the graphs of O_2 plasma / CuONPs and O_2 plasma / $CuSO_4$ treated silk respectively. These graphs show the changes formed on the silk surface and its morphology. The surface of untreated silk is observed to be smooth (Fig. 1). The etching effect which is noticed in Figure (2) is due to O_2 plasma treatment at 17.35 watts for 30 min which introduced some functional groups on the surface and forming cracks. Besides that, plasma treatment increased the silk fabric surface roughness, extending its effect to the wettability, printability, durability, and fastness properties.

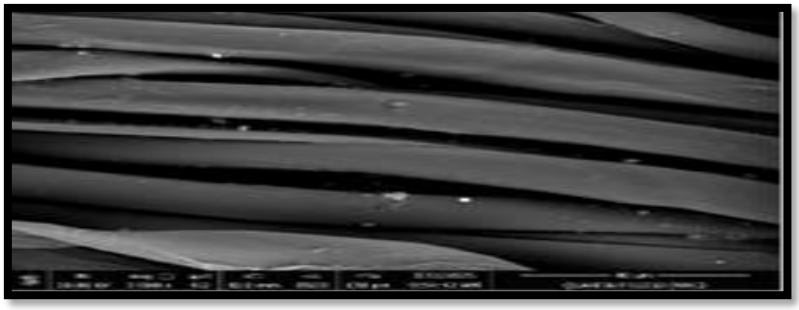

Fig 1: *SEM image of untreated silk fabric*

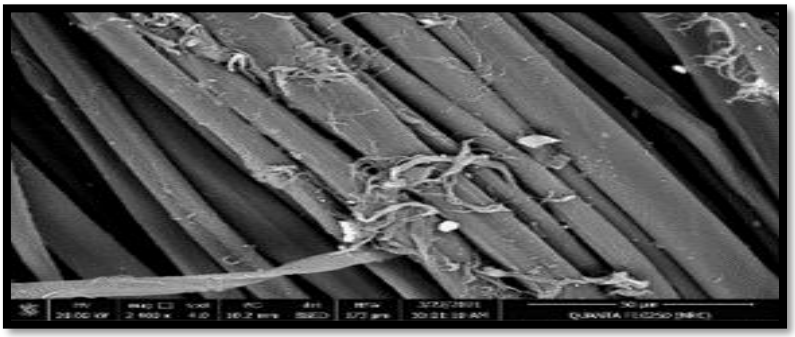

Fig 2: *SEM of treated silk fabric with O_2 plasma*

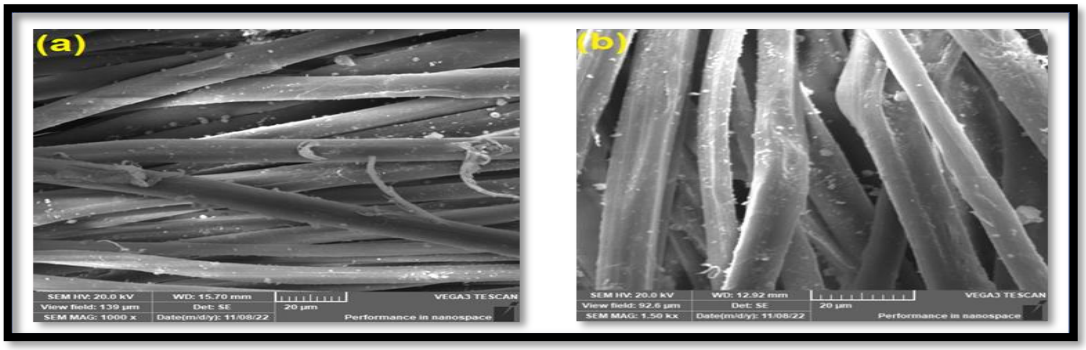

Fig 3: *SEM image of treated silk fabrics with O_2 plasma/CuONPs*

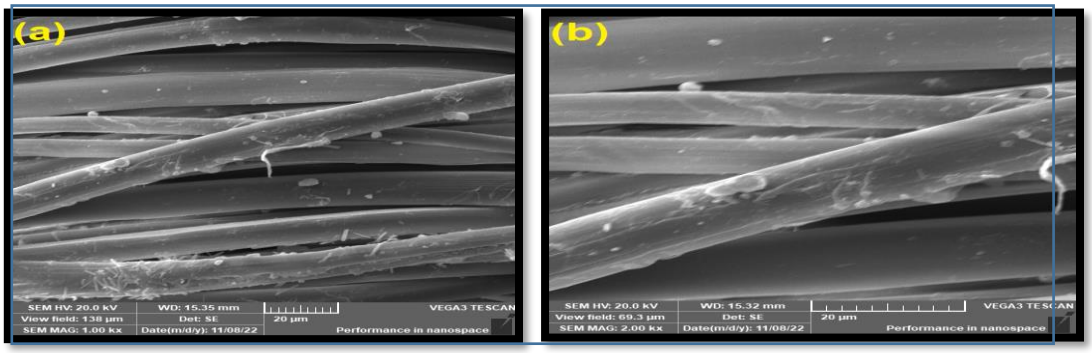

Fig 4*: SEM image of treated silk fabrics with O_2 plasma/ $CuSO_4$*

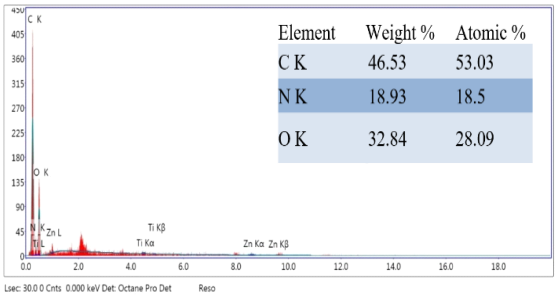

Fig 5: *EDX of untreated silk fabric*

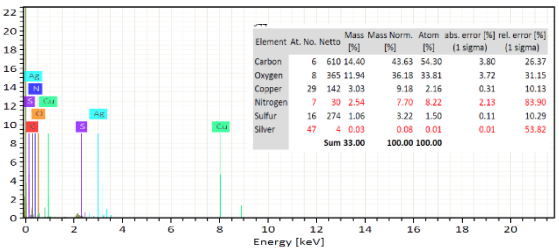

Fig 6: *EDX of CuO-treated silk fabric*

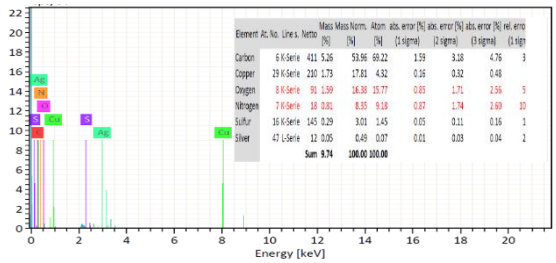

Fig 7: *EDX of $CuSO_4$ treated silk fabric*

3.5. Transmission Electron Microscopy (TEM)

The copper nanoparticles were further investigated by TEM. Figure 8 (a, b) shows the TEM image and particle size distribution of copper nanoparticles created by treatment of silk fabric with O_2 plasma/ CuO or sonicated $CuSO_4$. The average size and poly disparity determined by TEM are by the results in the TEM image. The average size of copper nanoparticles was about 4.34 nm with a narrow size distribution upper limit of 7 nm. Furthermore, the synthesized copper nanoparticle colloids showed good stability. This average size of copper nanoparticles, 4-7 agreed with the size distribution found using a particle size analyzer. Due to the small size of Nano copper particles and spherical shape, they can easily enter in between the polymer molecules and perhaps act as fillers or cross-linking agents which also contribute to the load sharing phenomenon during load application to fabrics.

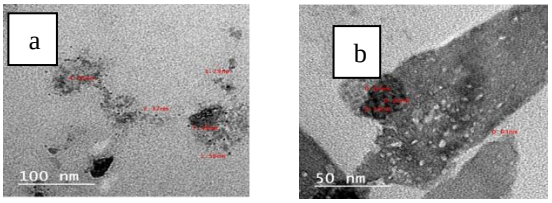

Fig 8: *TEM of treated silk with CuO (a) and $CuSO_4$ (b)*

3.6. Fourier-Transform Infrared Spectrophotometer (FTIR)

Fourier transform infrared (FTIR) is used to investigate the functional groups on the surface of the fabric samples (Figs **9, 10**). All samples clearly showed the distinctive peaks of silk and the building blocks of silk (amino acids), with some new-found peaks due to chemical treatments. Region 1700 to 1500 cm^{-1} represents the peptide backbone. Peaks at 1621, 1514, and 1226 cm^{-1} can be attributed to amide-I (crystalline β-sheet confirmation of C=O stretching), amide-II (C-N deformation of random coil conformation), and amide-III (C-N stretching vibrations), respectively [39]. The broad peaks between 3500 and 3100 cm^{-1} correspond to the overlapping of N-H stretching of the amide group and hydrogen-bonded OH stretching (3282 cm^{-1}). Peaks at 2875, 1446, and 1170 cm^{-1} can be assigned to -CH groups (alkane) from silk protein, carboxylate groups, and phenolic OH groups from amino acids, respectively [40]. Moreover, the presence of a peak at 1066 cm^{-1} represents the Gly-Ala peptide bond in the polymeric chain of silk fiber [41].

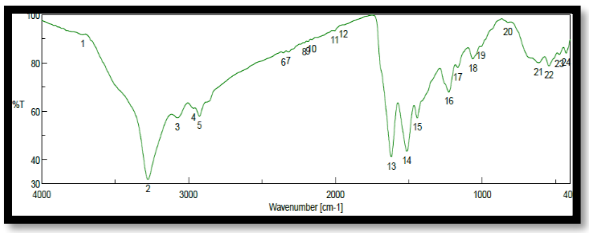

Fig 9*: FTIR of untreated silk*

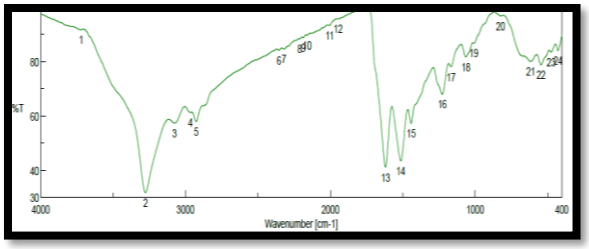

Fig 10*: FTIR of treated silk*

Due to the nature of the technique, FTIR is only a qualitative analysis for the evaluation of changes in the surface chemistry of plasma-treated polymers which can, however, provide a quick screening for the discrimination on the relevance of the effects of

plasma working parameters. As can be seen in Figures, and as is evident from the FTIR measurement, O_2 plasma-treated silk incorporates oxygen in the form of C-O and O-H (negative sites) in the fiber surface and increases electronegativity. [42-47] Figure 9 shows the FTIR spectrum of the untreated fabric, which presents the characteristic peaks of silk. The first peak at 3295 cm^{-1} is the absorption related to the stretching of hydrogen-bonded N–H groups, while the two peaks at 2932 and 2859 cm^{-1} are characteristic of the asymmetric and symmetric C–H stretching of the polymer backbone. On the other hand, in Cu-C spectra, new peaks appeared at 1041 and 907 cm^{-1} due to Cu-O-Cu stretching vibrations and Cu-C rocking vibrations in silane coupling agents [48]. The new peaks in Cu-C are attributed to the deposition of the coupling agent in silk fabric. Further peaks of high absorbance can be found at 720 cm^{-1}, where there is the presence of a shoulder due to hydrogen-bonded secondary amines, and at 680 cm^{-1} which has been assigned to the bending motion of the N–C═O group.

3.7. UV Protection Factor (UPF) of Treated Silk

The untreated silk samples give low UPF (3.8) as shown in Table 4 which is below the protection UPF value. [8-13, 49] So, treatment is required to provide skin protection against ultraviolet rays. Treatment of silk with O_2 plasma/CuONPs increases UPF up to 47.8 providing excellent protection while treatment with O_2 plasma/$CuSO_4$ increases UPF value up to about 18 (Table 4). The uniform distribution of Nanoparticles onto the silk fabric increases the UPF. UV protection of the fabric may be due to the reflection and scattering of UV rays by CuONPs.

Table 4: UPF of untreated and treated silk with CuONPs

Type of Sample	Plasma Power (watt)	Plasma Time (min)	Concentration (% wt)	UPF	
				Treated with CuONPs	Treated with $CuSO_4$
Untreated silk	-	-	-	3.8	3.8
Treated silk with O_2 plasma	17.35	15	-	6.7	6.7
Treated silk with NPs	-	-	0.5 1 1.5	7.6 9.6 13.3	13.4 14.4 15.2
Treated silk with O_2 plasma / NPs	17.35	15	0.5 1 1.5	34.7 44.9 47.8	14.9 17.4 17.9

Treatment: 100 % pick up, 120°C, 30 min

Table 5: UPF of printed silk with coffee fixed thermally

Type of Sample	Plasma Power (watt)	Plasma Time (min)	Concentration (% wt.)	UPF of Printed Silk	
				Treated with CuONPs	Treated with $CuSO_4$
Untreated silk	-	-	-	6.7	15.5
Treated silk with O_2 plasma	17.35	15	-	12.7	25.76
Treated silk with NPs	-	-	0.5 1 1.5	19.9 38.7 39.3	30.2 38.0 45.76
Treated silk with O_2 plasma/NPs	17.35	15	0.5 1 1.5	30.4 40.8 47.4	38.12 44.2 48.6

Treatment: 100% pick up, 120 ° C, 30 min, Fixation: 100° C, 30 min

Table 6: UPF of printed silk with coffee fixed by UV irradiation

Type of Sample	Plasma Power (watt)	Plasma Time (min)	Concentration (% wt.)	UPF of Printed Silk	
				Treated with CuONPs	Treated with $CuSO_4$
Untreated silk	-	-	-	5.32	11.0
Treated silk with O_2 plasma	17.35	15	-	8.34	12.03

Treated silk with NPs	-	-	0.5 1 1.5	20.4 28.9 31.45	29.7 33.2 37.9
Treated silk with O_2 plasma/NPs	17.35	15	0.5 1 1.5	22.69 31.0 39.3	30.21 38.0 47.4

Treatment: 100% pick up, 120˚ C, 30 min, UV Fixation: 48 h

Table 7: UPF of printed silk with deer blood

Type of Sample	Concentration of NPs (wt %)	UPF of Printed Silk			
		Thermo-fixed		UV fixed	
		Treated with CuO	Treated with $CuSO_4$	Treated with CuONPs	Treated with $CuSO_4$
Untreated silk	-	44.9	44.9	38.9	38.9
Treated silk with O_2 plasma	-	64.54	64.54	66.43	66.43
Treated silk with NPs	0.5 1 1.5	72.43 80.54 90.1	130.2 94.7 79.8	78.9 101.4 103.4	102.6 198.0 201.1
Treated silk with O_2 plasma/NPs	0.5 1 1.5	94.7 108.87 109,01	194 171.8 220.07	92.07 107.3 116.8	162.4 254.07 256.2

Plasma: 17.35 watt, 15 min, treatment: 100 % pick up, 120˚ C, 30 min,
Thermo fixation: 100˚ C, 30 min

Table 8: UV protection of silk fabric printed with red cabbage dye and thermo-fixed

Type of Sample	Concentration (wt %)	Plasma Power (watt)	Plasma Exposure time (min)	UPF
Untreated silk	-	-	-	20.3
Treated silk with O_2 plasma	-	17.35	15	34.5
Treated silk with CuO	0.5	-	-	39.4
Treated silk with CuO/plasma		17.35	15	49.4
Treated silk with CuO	1	-	-	50.34
Treated silk with CuO/plasma		17.35	15	62.4
Treated silk with CuO	1.5	-	-	49.89
Treated silk with CuO/plasma		17.35	15	61.02

Treatment: 100 % pick up, 120˚ C, 30 min, Thermo fixation: 100 ˚C, 30 min

Scattering increases as the diameter of NPs approaches one-tenth of the light wavelength [50]. So, the NP size affects strongly on UPF. Tables 5 and 6 represent the UPF values of printed silk with coffee, fixed thermally or by UV irradiation respectively. High UV protection values are obtained either for silk treated with CuONPs or sonicated $CuSO_4$. Also, Tables 7 and 8 illustrate the UPF values of printed silk with deer blood and red cabbage respectively. It is noticed that the untreated printed one has a satisfied UPF value which is increased to give an excellent UV protection value.

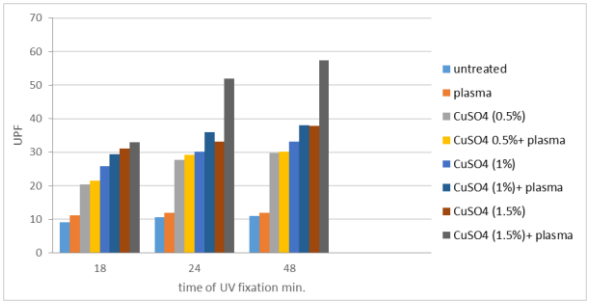

Fig 11: *UPF of untreated and treated silk printed with coffee dye*

It is also noticed from Fig 11 that UPF values of printed silk with coffee are a function of UV fixation time and increase gradually with increasing fixation time.

3.8. Antibacterial Activity

Bacteria and fungi could attack silk fabric. So, some treatments of silk fabric were carried out to enhance its antibacterial properties. Nanoparticle treatments are eco-friendly processes. Both untreated and treated silk with O_2 plasma/ CuONPs or sonicated $CuSO_4$ are subjected to antibacterial tests. The activity against Gram (+ve); Staphylococcus strain (S. aureus) and Gram (- ve); Escherichia Coli strain (E. Coli) and two kinds of fungi; Aspergillus Niger and Candida albicans are measured. The results are illustrated in Table 9.

It was observed that the aforementioned treatments with either CuONPs or sonicated $CuSO_4$ improved, markedly, the antimicrobial activity of the treated samples compared to the untreated ones. It is also noticed that CuONPs are more effective than the sonicated $CuSO_4$ against all strains except E. coli strain (G -ve) which gives a % reduction of 92.9 % and 58.4 % for samples treated with O_2 plasma/$CuSO_4$ and O_2 plasma/ CuONPs respectively.

Table 9: Antimicrobial activity of untreated and treated silk fabric

Type of sample	Reduction %			
	S. aureus (G +ve)	E. Coli (G - ve)	Aspergillus Niger	Candida albicans
Untreated sample silk	0	0	0	0
Treated with O_2 plasma/ CuONPs	88.4	58.4	86.4	88.4
Treated with O_2 plasma/ $CuSO_4$	71.2	92.9	80.8	72.1

Plasma: 17.35 watt, 15 min, treatment: 100 % pick up, 1% NPs, 120˚ C, 30 min

3.9. Dyeability with Natural Dyes

Table 10 illustrates the color strength values (K/S) of dyed silk fabric after treatment with O_2 plasma followed by treatment with CuONPs or sonicated $CuSO_4$. The used dyes are natural; red cabbage, deer blood, and coffee solution. All the treatments enhanced the dyeability of silk with all aforementioned natural dyes where oxygen plasma application increased the color strength of samples due to increasing the amounts of functional groups within the silk. [40] The CuONP applications are effective in enhancing the dyeability of silk because of its high surface reactivity, chemical stability, and thermoelectric properties. The greater the surface reactivity, the greater will be the reactive oxygen species (ROS) production, and vice versa. The relationship between the surface chemistry (capping agents) of CuONPs and the generation of ROS has been well documented. [51, 52]

Table 10: Colour strength of dyed untreated and treated silk samples

Type of Sample	Colour Strength (K/S)		
	Deer Blood	Red Cabbage	Coffee
Untreated silk	1.15	1.42	6.9
Treated with O_2 plasma	2.63	2.65	8.85
Treated with O_2 plasma/ CuONPs	3.69	2.94	9.09
Treated with O_2 plasma/ $CuSO_4$	3.88	3.0	10.6

Plasma: 17.35 watt, 15 min
NPs: pick up 100%, 1.5 % (o. w. f), 120 ˚C, 30 min.
Dyeing: 80˚ C, 60 min, Infrared Lab Dyeing Machine

The fastness properties of CuONPs treated silk dyed with the aforementioned natural dyes are shown in Table 11. It is clear that all fastness properties for washing, rubbing, respiration, and light of treated silk are found to improve significantly compared to untreated samples.

Table 11: Fastness properties of treated silk fabrics printed with natural dyes

Type of Sample	Natural Dye	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
		alt	st	dry	wet	acid	alkali	
Untreated silk	Coffee	3-4	3-4	2-3	2-3	3-4	3-4	5-6
Treated with O_2 plasma		4	4	3-4	3-4	4	4	6
Treated with O_2 plasma/CuONPs		4-5	5	4-5	4-5	5	4-5	6-7
Treated with O_2 plasma/ $CuSO_4$		4	4-5	3-4	4	4	4-5	6-7
Untreated silk	Deer Blood	3	3	2-3	3	3	3-4	5
Treated with O_2 plasma		4	4	3-4	3-4	4	4	6

Treated with O_2 plasma/CuONPs		5	5	5	5	5	4-5	6-7
Treated with O_2 plasma/ $CuSO_4$		5	5	4-5	5	4-5	4-5	7
Untreated silk	Red Cabbage	3-4	3-4	2-3	3	3-4	3-4	5-6
Treated with O_2 plasma		4	4	3-4	3-4	4	4	6
Treated with O_2 plasma/CuONPs		5	4-5	5	4-5	4-5	5	7
Treated with O_2 plasma/ $CuSO_4$		4-5	4-5	4-5	4-5	4-5	4-5	6-7

Plasma: 17.35 watt, 15 min
NPs: pick up 100%, 1.5 % (o. w. f), 120 °C, 30 min.
Dyeing: 80° C, 60 min, Infrared Lab Dyeing Machine

4. Conclusion

Silk fabric is treated with Dielectric Barrier Discharge (DBD) atmospheric O_2 plasma combined with CuONPs at a discharge power of 17.35 watts for 15 15-minute exposure time. Treatment of silk with combined O_2 plasma/ sonicated copper sulfate solution was also tried. The effect of variation concentrations of CuONPs (0.5 –1.5 g/100 fiber) in the form of copper oxide or copper sulfate on different properties of silk fabric is studied. It could be concluded that:

- The wetting time of treated silk decreased to nearly a quarter of untreated one.
- A significant increase in the electrical conductivity of silk is carried out due to Nano Cu deposition on the silk fabric surface.
- A great enhancement in the mechanical properties of treated silk is achieved.
- SEM shows the change in surface morphology of treated silk.
- Copper appears in the treated silk composition.
- The average size of copper NPs was about 4.34 - 7 nm.
- Treatment of silk with O_2 plasma/CuONPs increases UPF and provides excellent UV protection.
- Treatments with either CuONPs or sonicated $CuSO_4$ after oxygen plasma improved the antimicrobial activity of the treated samples compared to the untreated ones.
- The CuONP applications are effective in enhancing the dyeability of silk with some natural dyes.

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7. Author Declarations

The authors declare that the data supporting the findings of this study are available in the article

The authors declare that there is no conflict of interest.

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