Egypt. J. Chem. **Vol. 65**, No. 12 pp. 385 – 396 (2022)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Natural Dye Printability of Modified Silk Fabric with Plasma/Nano Particles of Metal Oxides

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Abstract

The plasma treatment is used, widely, to impact the surface characteristics and improves the coloration properties of silk fabrics. Here, the dielectric barrier discharge plasma type is implemented where, both the untreated silk and plasma treated one alone and with nanoparticles mixtures of Zinc Oxide (ZnO) and Titanium dioxide (TiO_2) with various percentages have been characterized. This investigation is characterized by wet- out time, scanning electron microscope (SEM), FTIR, color strength (K/S) and fastness properties. The investigation results using the FTIR indicates that plasma treatment has increased the hydroxyl functional group while, the wet- out time results of plasma NPs-treated silk fabrics identified to what extent the hydrophilic properties were improved and confirmed via the contact angle measurements which is too close to zero. The tensile strength measurement is also confirmed the surface properties enhancement. The printability of treated silk with natural dyes as well as antibacterial properties are improved

Keywords: plasma, printing, nanoparticles, silk fabric, antibacterial.

1. Introduction

Silk is considered the queen of textiles due to its luxury appeal, elegance, and comfort. It is produced by the silkworm as a filament fiber [1] and it is a natural polymer formed of repetitive hydrophilic and hydrophobic peptide sequences [2]. Determining wettability is crucial for characterizing liquid transport, fiber surfaces and adhesion with a polymer [3, 4] unfortunately silk has poor wetting properties [5].

Development of high-performance materials for the world market using plasma technology offers a promising future for textile industries [6] which is well- aligned with the high awareness of environmental regulations and concerns. Reduction of waste, contamination problems, and time are all advantages of plasma treatment when compared to conventional wet chemical processes [4, 7]. It is a simple procedure, well controlled, has energy and conservation benefits and is a fast solvent free technique compared to other treatments that use a huge amount of chemicals and water [8, 9]. Treatment of silk fabrics with plasma technology is a dry ecofriendly process with low degrees of penetration into the fabric, leaving the bulk properties unaffected, while affecting only the uppermost atomic surface layers of the fabric [10]. Atmospheric pressure plasma introduces polar groups onto the fiber surface, increasing the hydrophilicity thus transferring hydrophobic surface to hydrophilic, thereby changing surface functionalities [11, 12] and modifying the physicochemical properties of the fabric surface [13]. Dielectric barrier discharge (DBD) is a cold, non-equilibrium, atmospheric pressure plasma that alters the surface properties of the fabrics [14].

Nanotechnology is the futuristic approach for improvement in the performance of textiles. In order to impart anti-bacterial, water and oil repellency, soil resistance, anti-static, flame retardancy and enhanced dye-ability properties to fabrics, emphasis has been directed towards the use of nano size substances and generating nano structures during finishing and manufacturing processes [9]. ZnO nanoparticles (NPs) have remarkable properties and play a role in improving antifungal and antibacterial properties, static electricity, and UV protection. The ZnO nanoparticles change the properties of the oriented surface fibers of silk by creating new chemical bonds with molecular constituents of silk

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Receive Date: 27 December 2021, Revise Date: 16 March 2022, Accept Date: 28 March 2022

DOI: 10.21608/EJCHEM.2022.113249.5145

fibers or by insertion into the structure of molecules and etching the surface of silk fibers **[9].** TiO2 possesses unique structural, physicochemical, optical, and electrical properties, nontoxicity and low cost rendering it as one of the most attractive nanomaterials for the functionalization of textiles [15]. Using combined plasma and NPs treatments show a noticeable effect and great enhancement on the functional properties of textile materials as well as achieving high improvement results in both dyeing and printing properties depending on the types of plasma used [9]. The nanoparticles penetrate the pores, and crevices of the substrate and lock mechanically. This mechanical interlocking is an adhesion mechanism that can be attributed to the surface roughness effect. As the etching of the fibers caused by plasma leads to an increase in the surface roughness, high adhesion properties could be achieved [16].

Natural dyes are mostly obtained from plants and have been used for purposes like food coloration, in cosmetics and for functional textiles. Natural dyes are also known for their wide range of natural colorants as well as their color palettes [17]. Curcuma, known as turmeric, belongs to the Zingiberaceae family, it is used as a coloring matter besides its medical properties. Turmeric has been proven by Ghoreishian and coworkers to impart antibacterial properties to dyed silk fabric [18].

The aim of this work is broken down into, enhancing the poor wetting characteristics of silk, increasing the self-cleaning characteristics, improving color strength and fastness properties as well as imparting antibacterial, antifungal and UV protection characteristics to the fabric. These have been done through depositing a treatment with plasma/Nano mixture of ZnO/TiO_2 on the surface of silk fabric.

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 Aspicon1030 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 [19].

2.1.2 Chemicals

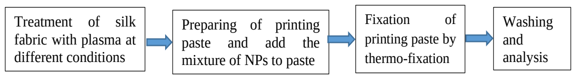
Nano particles is supplied by Orchid Pharmaceutical Company, Obour city, Egypt, Nonionic detergent, urea, Ammonium persulfate $(NH_4)_2S_2O_8$ as thermal initiator are supplied from Merck, Germany. Bercolin metal CM as thickener is supplied by Berssa, Turkey. Thermal curing binders were of laboratory grade chemicals. Dyestuffs: Curcuma tinctoria, was bought from the local market.

2.2 Methods

2.2.1 Fabric Treatments

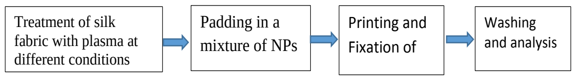
1st Technique:

In this technique silk fabric was treated with plasma followed by printing with paste containing the NPs. The untreated and treated samples were fixed by thermo-fixation.



2nd Technique:

This technique is composed of two steps; plasma treatment of the silk fabric followed by padding with Nano particles, b) printing of the untreated and treated samples followed by thermo-fixation.



2.2.2. Plasma Set up

The textile fabrics were exposed to low temperature plasma generated by DBD under atmospheric pressure. A schematic drawing of the experimental arrangement is depicted in Fig 1. The DBD cell consisted of two electrodes of stainless-steel discs; each had a diameter of 25.5 cm and thickness of 2 mm. The lower electrode was fixed to a Perspex base that was 30 cm in diameter and 2 cm in thickness and connected to earth.

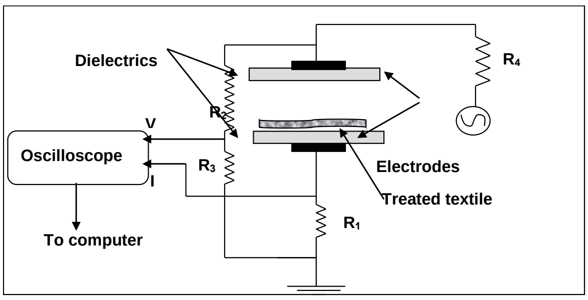


Fig 1: Schematic diagram of the discharge cell used for the treatment of the textile.

The upper electrode was connected to a high voltage AC power supply that had a 50 Hz frequency and a variable voltage of 0-20 kV. A dielectric material of glass that had a thickness of 1.7 mm was pasted to the upper electrode. The gap distance (d) between the dielectric glass and the lower electrode was 3 mm. The discharge voltage and discharge current were measured using a two-channel digital storage oscilloscope (HM-407). The discharge voltage was connected to the oscilloscope via a 2000:1 resistive potential divider. The discharge current that flowed through the DBD cell was measured as a voltage across a resistor of 1 k connected in a series to ground. The DBD was in an airtight Plexi-glass box and the used gas (air) was injected from the inlet of the electrode box.

2.2.3. Preparation of Printing Paste

The printing paste recipe:

Synthetic thickener	2 g
Binder	5-20 g
Urea	4 g
Dyes	3 g
Water	X g
	100 g

All the printed samples were fixed via thermo-fixation at 180°C for 3min and washed as follows:

- Rinsing thoroughly with cold water
- Treatment with hot water
- Treatment at 60°C with 2g/l nonionic detergent
- Washing with hot water
- Rinsing with cold water
- Finally, the samples were dried and assessed for color strength measurement.

2.3 Measurements

2.3.1. Wettability

The wettability was evaluated by measuring the wetting time according to the AATCC-39 method [20]. A drop of water is allowed to fall from a fixed height onto the surface of silk fabric under examination. The time needed for the drop of water to disappear was measured and had taken as wetting time, and the results were the average value of four readings.

2.3.2. Scanning Electron Microscope (SEM)

SEM micrographs were reported by Quanta/FEG/250 (Czech Republic) at 10-20 kV.

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 applying an accelerating voltage at 20 kV. The average diameters of nanoparticles were monitored using Image J program.

2.3.4 Tensile Strength

Tensile strength and elongation at a break were reported by ASTM examination method (D 5034) using (Grab test). All reported values were the average of three readings [21]

2.3.4. Fourier-Transform Infrared Spectrophotometer (FTIR)

FT-IR 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} are examined.

2.3.5. Antibacterial Activity

Antibacterial activity was carried out by the diffusion disc method (16). A fabric 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 aureue), Gram negative (Escherichia coli), and single cell fungi (Candida albicans). The diameter of the clear zone of inhibition surrounding the sample was taken as a measure of the fabric activity against the particular test organism. An average value of duplicate tests was evaluated [22]

2.3.6. Self-Cleaning

Evaluation of the Self-cleaning properties of the treated samples was according to the following equation:

Decomposition (%) = $[(K/S)_s - (K/S)_w] / [(K/S)_s - (K/S)_0] \times 100$

Where, $(K/S)_o$: Color strength of non- stained fabric, (K/S) s: color strength of coffee stained fabric, and $(K/S)_W$: color strength of coffee stained fabric after light irradiation. [23]

2.3.7. Color Assessment (K/S)

Color strength of the printed samples was evaluated by Hunter Lab Ultra scan PRO. The color yield (K/S) of each printed sample was measured using a Data Color SF 600 plus Colorimeter.

2.3.8. Fastness Properties

The color fastness of the printed fabrics was assessed by the AATCC Test Method 16-2001 (color fastness to light), AATCC Test Method 612001(color fastness to laundering), AATCC Test Method 82001(color fastness to rubbing and color fastness to perspiration).

3. Result and Discussion

3.1. Wettability

The effect of treatment with O2 plasma/ TiO2: ZnO NPs on the wettability of silk fabric was studied. The wetting times of untreated and treated silk samples are illustrated in Table 1.

It is shown from Table 1 that there is a noticeable decrease in wetting time of all treated silk either with O2 plasma, TiO2: ZnO NPs only or combined O2 plasma/ TiO2:ZnO NPs mixtures compared to untreated one. It is well known that as the wetting time decreases the wettability of the fabric increases. This means that all treatments lead to improve the hydrophilicity of silk which may be due to formation of polar functional groups (OH, COOH) and consequently increasing the surface free energy of treated silk. The lowest wetting time 7.54 s is observed upon treatment of silk with combined O2 plasma/ TiO2: ZnO (50:50 wt. %) mixture at the aforementioned conditions in Table 1. This holds true with the results of printability Table (7). The change in surface morphology as will be shown in SEM image (Fig 2) may be one of the reasons resulting in the increase in hydrophilicity of silk fabric.

3.2. Scanning Electron Microscope and Energy Dispersive X-ray

Figure 2 shows SEM graphs of silk fabrics; untreated, treated with O_2 plasma, treated with TiO_2: ZnO (50:50 wt. %), and treated with combined O_2 plasma/ TiO_2:ZnO (50:50 and 33:67wt%). These graphs illustrate the changes induced in the silk surface morphology. Untreated silk fabric (Fig 2a) shows smooth fabric surface. The changes in the fiber surface morphology due to O_2 plasma treatment at 17.35 watt for 15 min are represented in Fig 2b where the etching effect of plasma is very clear in the form of cracks besides introducing real groups as shown in FTIR figures and hold true with wettability results. Fig 2c shows the morphology of silk sample treated with only Nano mixture of TiO_2: ZnO (50:50 wt. %). It is clear that there is a thin film and presence of NPs aggregates on the surface. Figs 2d and 2e present the treated samples with combined O_2 plasma/TiO_2: ZnO NPs mixture with ratios of 50:50 and 33:67 (wt %) respectively.

Table 1: Wettability of Untreated and Treated Silk Fabric.

Type of Sample	Plasma Power (watts)	Plasma Exposure time (min)	Wetting Time (sec)
Untreated silk	-	-	20.45
Treated silk with O_2 plasma	17.35	15	14.03
Treated silk with TiO_2:ZnO (50:50 wt.%)	-	-	11.89
Treated silk with O_2 plasma/ TiO_2:ZnO (67: 33 wt.%)	17.35	15	9.51
Treated silk with O_2 plasma/ TiO_2:ZnO (50:50 wt.%)	17.35	15	7.54
Treated silk with O_2 plasma/ TiO_2:ZnO (33:67 wt.%)	17.35	15	8.65

The micro febrile structure and cracks occurred after plasma treatment (Fig 2b) decreased due to covering the surface with NPs Figs 2d and 2e. As shown later that the mechanical properties of treated silk slightly increased which may be probably due to the inter locking of micro fibrils on silk surface, increasing inter fiber friction, and increasing the surface roughness (Figs 2b -2e). The resulted changes in silk surface after plasma treatment enhanced the adsorption of NPs (Figs 2d and 2e).

3.3. Tensile Strength

Table 2 represent the tensile strength values for untreated and treated silk with O_2 plasma at 17.35 watt for 15 min, TiO_2/ZnO (50:50 wt. %) of total concentration 3% (o.w.f) by padding technique and combined O_2 plasma/TiO_2: ZnO NPs mixtures of different ratios.

It is clear from Table 2 that the tensile strength and elongation % of O_2 plasma treated sample is slightly increased which may be due to etching effect of plasma on the fabric surface and rougher surface as shown in SEM images (Fig 2). Regardless of treatment conditions the tensile strength is found to slightly increase or remain constant for treated silk samples compared with untreated one. Combined plasma/ TiO_2: ZnO NPs mixture treatments are most effective on enhancing the tensile strength of silk fabric than those samples treated with only plasma and /or only TiO_2: ZnO NPs mixture. This holds true with pervious work [24]. It was reported that treatment of silk with NPs enhances the tensile properties and crease recovery angle with no damage for its mechanical properties.

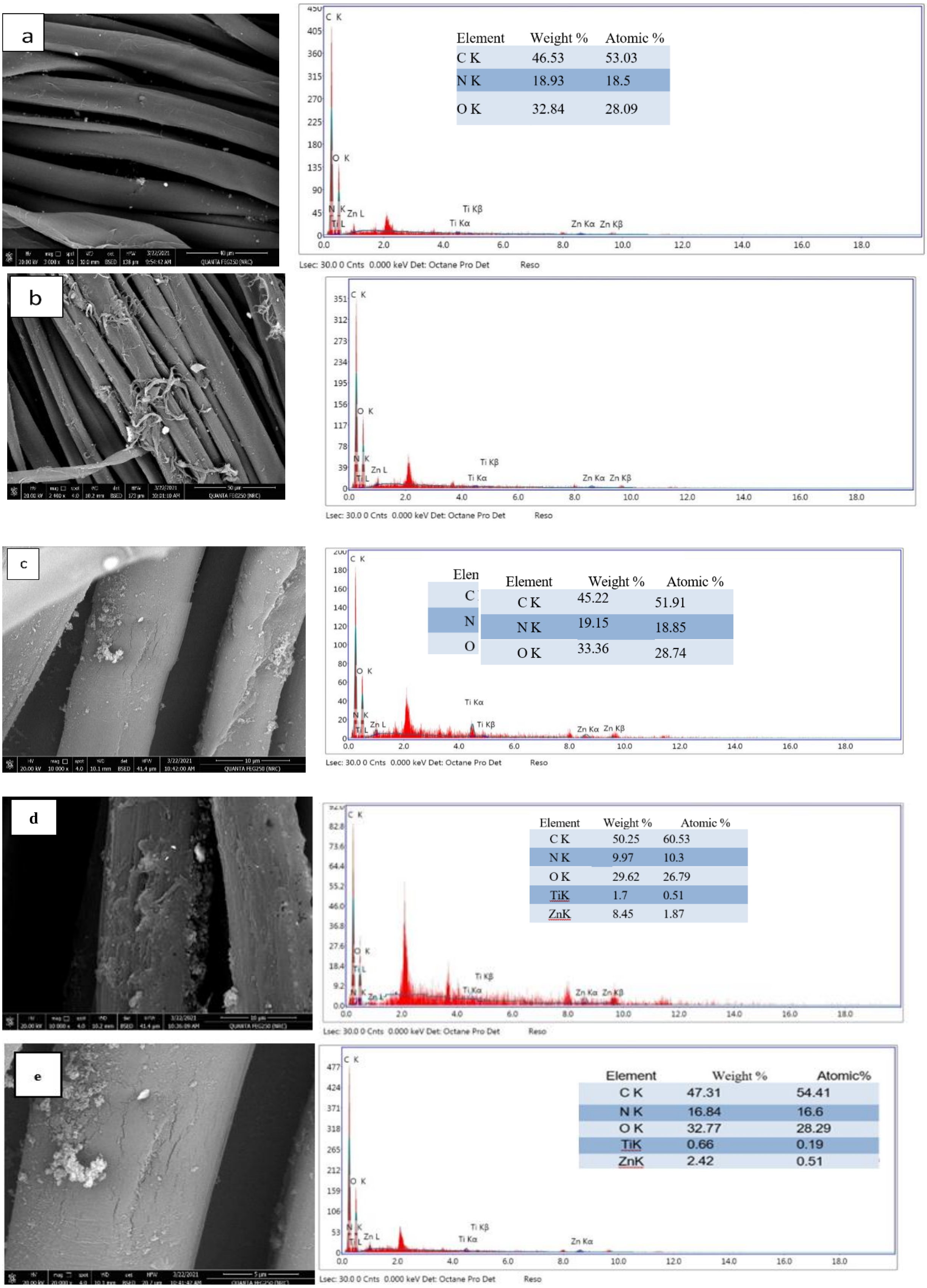


Fig. 2: SEM images of silk fabric a) untreated b) treated with O_2 plasma c) treated with TiO_2: ZnO (50:50 wt. %) d) treated with O_2 plasma /TiO_2: ZnO (50:50 wt. %) e) treated with O_2 plasma /TiO_2: ZnO (33:67 wt. %)

3.4. Fourier-Transform Infrared Spectrophotometer (FTIR)

The amide is the easiest protein group marker to be identified in protein silk fabric samples. The change in surface chemistry of silk fabric upon plasma/TiO_2: ZnO treatment was studied using attenuated total reflection FTIR spectroscopy. Fig. 3 shows the FTIR spectra of silk fabrics; untreated, treated with TiO_2: ZnO (50:50 wt. %) and treated with plasma. Figure 4 shows FTIR spectra of treated silk with plasma/TiO_2: ZnO mixtures of ratios (67:33 wt. %), (50:50 wt. %), and (33:67 wt. %).

It is well known that the appearance of peaks at different wavenumbers of 1618.95 cm^{-1}, 1514.81 cm^{-1}, and 1228.43 cm^{-1} are due to the amide I (C-O stretching vibration), amide II (C-N stretching and N-H distortion), and amide III (C-N stretching and N-H deformation vibration), respectively [25]. The bonds between C-C, C-N, C-H, and N-H stress were shown ranged from 1466.78 to 1399.69 and 1260.30 cm^{-1}. The bands in the range of 800-1200 cm^{-1} may be attributed to a specific polypeptide with respect to amino acid linkage [26]. The peak positioned at 960 $cm^{−1}$ signifies the Ala-Ala linkages in the crystalline portion of the silk [27], whereas the band at 1,048 $cm^{−1}$ appears due to the presence of the Gly-Ala peptide chain of silk fiber [28, 29]. Moreover, the appearance of the absorption bands at 3276.47 cm^{-1}, 3069.10 cm^{-1}, and 1,161 $cm^{−1}$ is caused by the free OH stretching (not hydrogen bonded) and NH stretching (hydrogen bonded) vibrations. CH_2 group frequency of alanine exhibits an absorption peak at 1,448$cm^{−1}$. The relative abundance of alanine $(Ala)_n$ indicates the existence of alpha phase.

From Fig. 4, it is apparent that after plasma treatment and coated with NPs of TiO_2: ZnO mixture slightly increased the intensity of peaks. This explained the decrease in the crystallinity which qualified to etching and partial breaking of polypeptide chains caused due to plasma treatments. Therefore, β-folding form formation, and the decrease in crystallinity helped in increasing the wettability and absorbency properties of the silk fabric. A similar result indicating increased amount of amide group formation has also been reported in the literature [30].

Table 2: 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 ZnO/TiO_2 NPs (50:50 wt. %)	0.6922	9.000	0.0150
Treated silk with O_2 plasma/TiO_2:ZnO (67:33 wt. %)	0.7436	8.666	0.0150
Treated silk with O_2 plasma/ TiO_2:ZnO (50:50 wt. %)	0.7036	8.000	0.0150
Treated silk with O_2 plasma/ TiO_2:ZnO (33:67 wt. %)	0.7042	9.333	0.0124

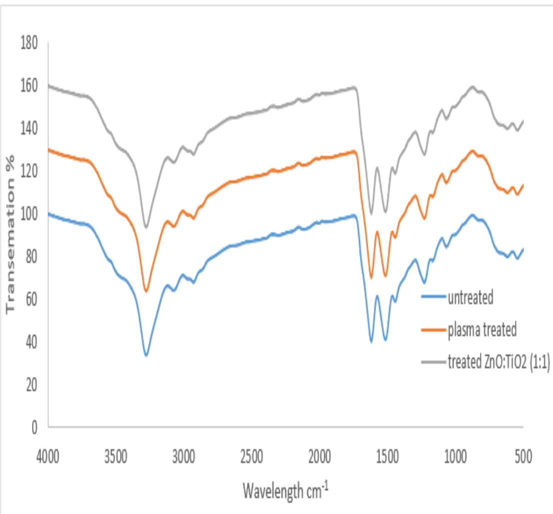


Fig. 3: The FTIR of untreated silk fabric, treated with O2 plasma and treated with Nps

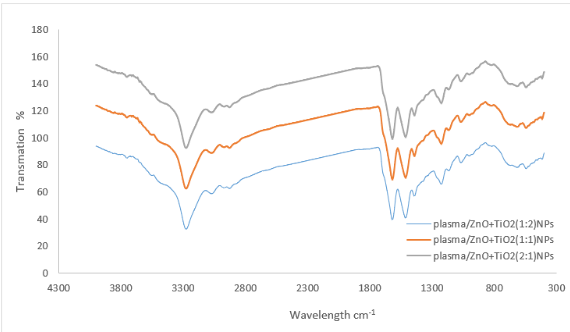


Fig. 4: The RTIR of treated silk fabric with combined O2 plasma/ NPs

3.5. Antibacterial Activity

Silk could be attacked by bacteria that caused degradation of silk. Modification of silk fabric to enhance its antibacterial activity is focused to prevent the deterioration of natural fabric caused by mildew [31]. The using of nanoparticles is among of the ecofriendly modification processes. Recently, modification of silk with Ag NPs was applied in the clinical, clothing and automotive industries [32]. The antimicrobial activity of treated and untreated silk fabric was evaluated against Gram (+ve); Staphylococcus aurecus Strain (S.aureus) [ATCC6538] and Bacillus subtilis [ATCC6633] and Gram (-ve); Escherichia coli strain (E. colli) [ATCC 2592] and single cell fungi (candida allbicans), [ATCC10231]. The diameter of the inhibition zone was estimated and illustrated in Table 3.

It was found from Table 3 that all treatment conditions either by plasma alone or combined plasma/ TiO_2: ZnO NPs mixtures affect positively on the antibacterial activity of silk fabric for Gram +ve and Gram –ve bacteria strains. The treatment with nano TiO_2: ZnO (50:50 wt%) without plasma was found to be more effective in enhancing the antibacterial activity of silk than treatment with plasma only (Table 3). It is also observed from Table 3 and Fig. 5 that the maximum inhibition zone could be attained upon treatment of silk with plasma/TiO_2:ZnO (67:33 wt. %) mixture of overall concentration 3% (o.w.f.), followed by sample treated with plasma/ TiO_2:ZnO (50:50 wt. %) while the minimum one was observed for sample treated with plasma/ TiO_2:ZnO (33:67 wt. %). It is also observed that sample treated with plasma/TiO_2: ZnO (33:67 wt. %) records +ve effect on anti-fungi (candida) which is attributed to the effect of ZnO NPs.

It has been reported [33-35] that TiO_2 and ZnO NPs can be used as antibacterial agents. The real mechanism of the antibacterial activity of TiO_2 NPs may be due to the action of TiO_2 on bacterial cell death. It was also reported that plasma has better effect on binding efficiency of TiO_2 NPs onto the fabric [33] which is hold true with the results in Table 3. It was investigated [34] that high concentration of ZnO NPs as antibacterial agent is required. So, in this study a mixture of ZnO and TiO_2 was tried. The antibacterial activity of silk treated with TiO_2: ZnO NPs mixture increases with increasing the concentration of TiO_2 while the anti-fungi increases with increasing concentration of ZnO (Table 3).

Table 3: Antibacterial activity of treated and untreated silk fabric

Type of sample	Ecolli G (-ve)	Bacillus G (+ve)	Staphyllococus aureus G (+ve)	Candida albicans
Untreated silk	Nil (-)	Nil(-)	Nil(-)	*Nil(-)
Treated silk with: -O_2 plasma	Nil(-)	Nil(-)	Nil(-)	Nil(-)
- TiO_2:ZnO (50:50 wt. %)	14 (+++)	17 (+++)	17 (+++)	Nil(-)
-Plasma/TiO_2:ZnO (33:67 wt. %)	18 (+++)	16 (+++)	15 (+++)	13 (+++)
-Plasma/TiO_2:ZnO (50:50 wt. %)	21 (++++)	20 (++++)	16 (+++)	Nil(-)
-Plasma/ TiO_2:ZnO (67:33 wt. %)	22 (++++)	21 (++++)	20 (++++)	Nil(-)

*Nil: no antimicrobial activity

- No activity, + (0-5 mm), ++ (6-9 mm), +++ (10-19mm), ++++ (20-29mm)

Figure 5: Antibacterial activity of untreated and treated silk fabrics

3.6. Self-Cleaning

Silk fabrics were treated with O_2 plasma (17.35 watt, 5 min) and then subjected to TiO_2: ZnO NPs mixtures treatments by pad-dry- cure technique. The applied NPs weight ratios of TiO_2:ZnO mixtures are 67:33, 50:50 and 33:67 wt. %. The self-cleaning activity of treated silk samples as well as untreated one (Table 4) was indicated by degradation of coffee stains under ultraviolet irradiation. The samples treated with plasma/ TiO_2:ZnO (67:33 wt. %) showed the best efficiency for removal the coffee stains, followed by samples treated with other ratios of TiO_2:ZnO mixtures; 50:50 and 33:67 wt. %. Treated silk was found to be effective in self-cleaning and suitable for production of bags, ties, and shoes [38]. TiO_2 NPs (nontoxic) coating for textile is known to remove stains, microbe, and dirt on exposure to UV rays in sunlight while keeping the fabric mechanical properties well.

Table 4 shows the self-cleaning property of treated silk fabric after treatment with O_2 plasma/ TiO_2: ZnO NPs. It is clear that the color strength a measure of self-cleaning property of coffee stains in treated silk decreases after exposure to UV for 24 compared to no decrease in untreated one. The decrease was found to be about 35% for sample treated with O_2 plasma/TiO_2: ZnO (67:33 wt. %) compared to 30% and 24% for treated samples with plasma/TiO_2: ZnO of ratios 50:50 and 33:67 wt. % respectively. After exposure to 48h UV, the color strength (K/S) of treated samples with O_2 plasma/ TiO_2: ZnO (67:33) decreases from 10.29 to 3.09 corresponding to a decrease in K/S of 70%. After washing with only water the color intensity decreases to 0.61 meaning that nearly 95% removal of stain. Modification of silk with O_2 plasma gives an increase in bonding of TiO_2 and the fiber. So, the self-cleaning is increased that may reduce water and detergent consumption. Silk fabrics containing TiO_2: ZnO NPs would be promising in wide applications of apparel, accessories and other uses of silk.

Table 4: Self-cleaning of treated and untreated silk fabric

Type of sample	K/S		% decrease in K/S
	Before exposure to UV	After exposure to UV	
Untreated silk	9.52	9.71	-
Treated silk with: O_2 plasma/ TiO_2:ZnO 67:33 wt.%	11.03	7.16	35%
O_2 plasma/ TiO_2:ZnO 50:50 wt.%	8.52	5.99	30%
O_2 plasma/ TiO_2:ZnO 33:67 wt.%	9.15	6.97	24%

UV exposure time 24 h.

3.7. Color Strength

The effect of treatment silk with plasma, nano TiO_2: ZnO and combined treatment on the color strength of printed silk fabric was studied. The treatments were carried out at different plasma powers (12.21 and 17.35 watt) for different exposure times (5-20 min). The pretreated silk samples with plasma were padded in a solution containing 3% (o.w.f) NPs mixture of TiO_2: ZnO (50:50 wt. %) then printed with natural dye (turmeric tincture). The color strength results are illustrated in Tables (5, 6).

The effect of plasma/TiO_2: ZnO NPs mixture (50:50 wt. %) treatments at different time intervals of O_2 plasma appears to increase the color intensity of silk fabrics. It is also noticed that O_2 plasma treatment at 17.35 watt is more effective than that at 12.21 watt on enhancing color strength (K/S). at both volt (12.21 and 17.35 watt) , the color strength of printed treated silk samples increases as the plasma exposure time increases up to 15 min, then it slightly decreases. The increase in color strength may be attributed to the chemical changes in silk fabrics due to the oxidation and formation of carbonyl and carboxyl groups as well as physical changes on silk fabric effect, increasing the surface roughness due to etching effect of plasma and increasing the adsorption of NPs on the surface. The decrease in the color intensity after 15 min exposure time may be due to increase of fiber crystallinity. The maximum color strength was attained upon silk samples treated with plasma/TiO_2: ZnO (50: 50 wt. %) mixture at 17.35 watt for 15 min exposure and it is nearly 6 folds the untreated one.

Treated silk fabric with O_2 plasma at the aforementioned plasma conditions were printed with the dye paste containing TiO_2: ZnO NPs mixture (50:50 wt. %) and the results of color intensity (K/S) are illustrated in Table 6. It is observed that the color intensity of treated silk increases gradually with time up to 15 min then slightly decreased.

The maximum color strength (K/S=6.86) was obtained upon applying 120 watt plasma power and 15 min exposure time and printing with dye paste TiO_2:ZnO NPs mixture (50:50 wt. %). It is also noticed from Tables 5 and 6 that treatment of silk with combined O_2 plasma/ TiO_2: ZnO (50:50 wt. %) is more effective on enhancing the printability with curcumin dye than adding NPs to the printing paste. In a separate experiment different concentration of TiO_2:ZnO mixture was used for padding treatment of O_2 plasma treated silk at 17.35 watt for 15 min and then printed. Table 7 represents the color strength results of those samples.

It was observed that the maximum color intensity (15.4) acquired to treated silk with O_2 plasma/ TiO_2: ZnO (50:50 wt. %) relative color strength ($K/S_{treated}$ / $K/S_{untreated}$ x 100) records 616% for this sample. It could be concluded that all treatment conditions affect positively on printability of silk fabric.

3.8 Fastness properties

Table 8 represents the results of washing, rubbing and respiration fastness properties for both untreated and treated silk with O_2 plasma/ TiO_2: ZnO (50:50 wt. %). The results of alt washing fastness are ranged from 4 to 5 for treated silk compared to 3-4 for untreated one, while staining washing fastness are 4-5 and 5 for treated silk compared to 4 for untreated one. Dry and wet rubbing fastness values are 2-3 and 3 for untreated sample respectively and these values increases to 5 for treated samples. Also, both perspiration and light fastness are found to be improved.

Table 5: Effect of plasma/TiO2:ZnO treatment on printability of silk

Type of sample	Plasma power (watt)	exposure time (min)	K/S
Untreated silk	-	-	2.5
Treated silk with TiO2:ZnO (50:50 wt. %)	-	-	8.32
Treated silk with O2 plasma/TiO2:ZnO (50:50 wt. %)	12.21	5 10 15 20	9.71 11.65 12.65 11.84
	17.35	5 10 15 20	10.86 14.33 15.40 11.55

Table 6: Printability of treated silk fabric by adding NPs in printing paste

Type of sample	Plasma power (watt)	Plasma exposure time (min)	K/S
Untreated silk	-	-	2.5
Plasma treated silk	12.21	5 10 15 20	3.66 4.55 6.7 6.5
	17.35	5 10 15 20	3.83 5.64 6.86 6.21

Printing: adding TiO2: ZnO (50:50 wt. %) to the paste

Table 7: Printability of silk treated with different mixtures of TiO2: ZnO NPs

Type of samples	TiO2: ZnO (wt. %)	Color strength (K/S)	Relative color strength (%)
Untreated silk	zero	2.5	100%
Plasma treated silk	zero	9.21	368.4%
Plasma/ TiO2: ZnO treated silk	67:33	14.49	579.6%
	50:50	15.4	616%
	33:67	14.19	567.6%

Treatment: plasma power 120 watt, time 15 min

Table 8: Fastness properties for untreated and treated silk fabrics

Type of sample	Plasma power	Exposure time	Washing fastness	Rubbing fastness	Perspiration fastness	Light fastness

	(watt)	(min)	Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	3-4	4	2-3	3	3-4	3-4	4
Treated silk with TiO2:ZnO (50:50 wt. %)	-	-	4	4-5	3-4	4	4	4-5	5-6
Treated silk with plasma/ TiO2:ZnO (50:50 wt. %)	12.21	5	4-5	5	4-5	4-5	4	4-5	6
		10	4-5	5	5	4-5	4-5	4-5	6-7
		15	5	4-5	4-5	5	4-5	5	6-7
		20	4-5	5	4-5	4-5	4-5	4-5	6-7
	17.37	5	4-5	4-5	4-5	4	4-5	4-5	6-7
		10	4-5	5	4-5	4-5	5	4-5	7
		15	5	4-5	5	5	5	5	7
		20	4-5	4-5	4-5	4-5	4-5	4-5	6-7

Conclusions

- The surface free energy of silk fabric treated - either with plasma alone or in presence of nanoparticles- was increased and led to improve the hydrophilicity of silk due to the formation of polar function groups.
- A decrease in crystallinity was carried out and helped in increasing the wettability and absorbency properties of treated silk fabric
- The treatment with silk with NPs enhances the tensile properties and crease recovery angle with no damage for its mechanical properties.
- The antibacterial effect of silk treated with TiO2: ZnO NPs mixture increases with increasing the concentration of TiO2 while the anti- fungi increase with the increasing concentration of ZnO.
- All the treatment conditions affect positivity and enhanced the printability of the treated silk fabrics.
- The fastness properties obtained for the treated silk fabric with O2 plasma/ TiO2: ZnO (50:50 wt. %) were improved as washing, perspiration, both dry and wet rubbing and light fastness.

Results practical recommendations

The achieved results indicated that silk fabric which is treated with plasma / nanoparticles was acquired high results of antibacterial characteristics which means that it could be used in production of women lingerie clothes as well as some special bed sheets to avoid any harsh feeling that may be happened for the sensitive bodies.

1. Conflicts of interest

In accordance with our policy on Conflict of interest please ensure that a conflicts of interest statement is included in your manuscript here. Please note that this statement is required for all submitted manuscripts. If no conflicts exist, please state that "There are no conflicts to declare".

2. Acknowledgments

Collate acknowledgements in a separate section at the end of the article before the references and do not, therefore, include them on the title page, as a footnote to the title or otherwise. List here those individuals who provided help during the research (e.g., providing language help, writing assistance or proof reading the article, etc.).

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