



Effect of Plasma /Copper Oxide Nanoparticles on Silk Fabric Printability with Some Natural Dyes Using Ultraviolet Fixation

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Abstract

This study investigated the effect of treatment with Nano copper oxide and Cu NPs in the form of sonicated copper sulfate after O₂ plasma treatment on the printability of silk fabric. The silk fabric was treated with various concentrations (0.5-1.5 wt %) of CuO NPs using the padding technique, squeezing to 100 % pick up, and then thermal treated at 120 °C for 30 min. The treated silk was printed with some natural dyes such as coffee, deer blood, and red cabbage dyes. The printability of the treated fabric was evaluated by measuring the color strength (K/S) as well as its fastness properties. The results showed that the treatments with plasma/ CuO NPs as well as CuSO₄ improved the printability of silk fabric with the aforementioned natural dyes. A higher concentration of CuO NPs after O₂ plasma treatment resulted in higher color strength and color fastness. The use of natural dyes also resulted in a unique range of color shades and hues, which are not possible with synthetic dyes. This study highlights the potential of natural dyes for enhancing the printability of silk fabric and providing a sustainable and environmentally friendly alternative to synthetic dyes.

Keywords: silk, natural dyes, plasma, nanoparticles, copper oxide, copper sulfate.

1. Introduction

Surface treatments of textiles could be carried out with plasma causing etching and other deformation on the fabric surface. Low-pressure plasma was applied for surface modification of textiles. [1, 2] Nanotechnology has recently been used to increase the added value of textiles and improve their properties. [3, 4] Nanoparticle treatments impart antibacterial, water, or oil repellence, antistatic properties, self-cleaning, and flame retardancy as well as improving coloration properties. [5-26] The surface etching resulting from plasma treatment is suitable for introducing nanoparticles on textiles. [27-30] The

adsorption of NPs on the fiber surface increases with plasma treatments. New functional groups such as carbonyl, carboxylic, and hydroxyl produced by plasma on the fiber surface depend on the used gas (air, oxygen, nitrogen ... etc.).

Silk is a proteinic fiber and is found in the form of filaments. Silk is soft and gloss fibers having good moisture regain breathability, and excellent draping. [31, 32] Silk could be attacked by bacteria causing damage to the fiber such as degradation and/or deformation. [31, 33-37] Antibacterial reagents such as TiO₂, ZnO, Ag, and Pt NPs could be applied on textile substrates. ZnO NPs play an important role in UV protection, self-cleaning, and antibacterial

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activity. Plasma treatment could improve ZnO desorption onto silk fabric. [38, 39]

The functionalization of textiles with cupric oxide (CuONPs) gives antibacterial properties for textiles. [40] CuO is a semiconductor. Application of CuONPs on textiles could be carried out by different techniques. The in situ process could be carried out by the synthesis of NPs in the presence of the textile fibers. [41] Another methodology is the ex-situ technique that is carried out in two steps; 1st step is the formation of NPs and 2nd step is the application of NPs on textiles. [42]

This work investigates the treatment of silk fabric with CuONPs as well as sonicated CuSO₄ solution to improve its printability with some natural dyes such as coffee, red cabbage, and deer blood. Fixation of dyes was tried either thermally and /or by subjecting them to UV irradiation. The treated silk was examined by SEM, TEM, FTIR, and mechanical properties as well as antibacterial activity. As shown in part I of this work.

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.

2.1.2. Chemicals

CuO Nanoparticles are supplied by Orchid Pharmaceutical Company, Obour City, Egypt, Nonionic detergent, urea, and Ammonium persulfate (NH₄)₂S₂O₈ as thermal initiators are supplied from Merck, Germany. Bercolin metal CM as a thickener is supplied by Berssa, Turkey. Thermal curing binders and CuSO₄ 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 O₂ plasma at 17.35 Watts for 15 min followed by padding treatment with CuONPs or sonicated CuSO₄ solution then squeezed to 100 % pickup. Treated samples were dried at 120°C for 30 mins. The concentration of NPs ranged from 0.5 to 1.5 g/100g fiber.

2.2.2. Dye extraction

Coffie was extracted according to previously reported work.

2.2.3. 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 a 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 the earth.

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 the ground. The DBD was in an airtight Plexi-glass box and the used gas (oxygen) was injected from the inlet of the electrode box.

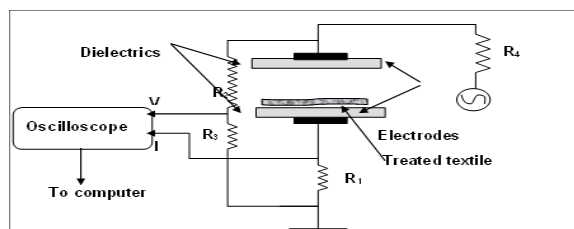


Fig 1: Schematic diagram of the discharge cell used for the treatment of the textile.

2.2.4. Preparation of Printing Paste

The composition of the printing paste was as follows: [43-46]

The printing paste recipe:	
Dye concentration	
Synthetic thickener	2 g
Binder	5-20 g
Urea	4 g
Sodium dihydrogen phosphate	0.5 g
Dyes	2 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.

Other printed samples are fixed by exposure to UV irradiation for a variety of times.

2.3. Measurements

2.3.1. Color Assessment (K/S)

The color strength of the printed samples was evaluated by Hunter Lab Ultra scan PRO. The color strength (K/S) of each printed sample was measured using a Data Color SF 600 plus Colorimeter. [47, 48]

2.3.2. Fastness Properties

The color fastness of the printed fabrics was assessed by the AATCC Test Method 16-2014 (color fastness to light), AATCC Test Method 61-2013 (color fastness to laundering), and AATCC Test Method 8-2016 (color fastness to rubbing and color fastness to perspiration). [49-51]

3. Result and Discussions

The results of untreated and treated silk fabrics were evaluated by measuring the color strength, and fastness properties.

3.1. Color Strength

The effect of plasma/CuONPs treatment on the color strength of printed silk fabric with coffee

solution, red cabbage, and deer blood dyes was investigated upon applying different concentrations of CuONPs and different methods for dye fixation either thermally or by UV irradiation. Tables 1-6 illustrate the results of color strength (K/S) for printed silk with coffee, deer blood, and red cabbage fixed thermally at 100 °C for 30 min and by UV irradiation for 48 hours.

3.1.1. Printability of silk with coffee

Table 1 shows that the color strength (K/S) of treated silk fabric with CuONPs and printed with coffee, increases gradually with increasing the concentration of CuONPs. K/S of samples treated with O₂ plasma followed by treatment with CuONPs were higher than that treated with only CuO without subjecting to plasma. All the treated printed samples fixed thermally give color strength higher than untreated ones.

Table 1 also presents the color strength of printed silk with coffee fixed via UV irradiation for 48 hours. It can be concluded that fixation of coffee-printed silk samples with UV irradiation could improve their color strength as well as improve dye fastness properties as shown later.

Table 2 shows the printability of silk with coffee upon treatment with sonicated CuSO₄ solution for 10 min after pre-treatment of O₂ plasma. A high improvement in printability is noticed. The results are approximately close to that obtained upon treatment of silk with CuONPs.

Table 1: Color strength of coffee printed silk treated* with O₂ plasma / CuONPs

Type of Sample	Plasma Power (watt)	Plasma Exposure time (min)	Conc. of CuO wt. %	K/S	
				Fixed thermally	Fixed by UV
Untreated silk	-	-	Zero	2.74	2.75
O ₂ plasma-treated silk	17.35	15	zero	3.5	3.59
CuONPs treated silk	-	-	0.5	6.76	7.22
			1	7.70	8.08
			1.5	7.89	8.44
O ₂ plasma/ CuONPs treated silk	17.35	15	0.5	9.43	10.01
			1	11.79	11.98
			1.5	11.94	11.96

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

Fixation: Thermally at 100 °C, for 30 min / Ultraviolet for 48 h.

Table 2: Effect of O₂ plasma/CuSO₄ treatment* on printability of silk with coffee.

Type of Sample	Plasma Power (watts)	Plasma Exposure time (min)	Conc. Of CuSO ₄ (wt. %)	K/S	
				Fixed thermally	Fixed by UV
Untreated silk	-	-	Zero	5.27	5.49
O ₂ plasma-treated silk	17.35	15	Zero	6.86	6.89
Treated silk with Cu SO ₄ solution	-	-	0.5	7.01	7.9
			1	8.25	8.79
			1.5	7.99	8.21
Treated silk with O ₂ plasma/CuSO ₄	17.35	15	0.5	7.44	10.2
			1	9.88	12.34
			1.5	9.11	11.99

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

Fixation: Thermally at 100 °C, for 30 min / Ultraviolet for 48 h.

3.1.2. Printability of silk with deer blood dye

Table 3 shows the color strength of silk fabric treated with O₂ plasma /CuONPs at different concentrations of NPs and printed with deer blood dye. The fixation of dye was carried out thermally at 100°C for 30 min or by subjecting it to UV irradiation for 48h. It can be observed that the enhancement in color strength (K/S) of treated silk with CuO concentration is dependent and increases gradually with increasing concentration. It is also observed that the fixation of

printed silk by UV irradiation is more effective in enhancing K/S than thermal fixation. Combined O₂ plasma/CuONPs treatments give the best color strength results of deer blood dye.

Replacement of CuONPs by sonicated CuSO₄ solution in the treatment of silk affects positively on printability of silk with deer blood dye (Table 4). The color strength (K/S) results are promising as well as fastness properties (Table 3, 4).

Table 3: Color strength of CuONPs treated* silk printed with deer blood dye.

Type of Sample	Plasma Power (watts)	Plasma Exposure time (min)	Conc. of CuO (Wt. %)	K/S	
				Fixed thermally	Fixed by UV
Untreated silk	-	-	Zero	1.76	1.84
O ₂ plasma-treated silk	17.35	15	Zero	4.04	5.05
CuONPs treated silk	-	-	0.5	8.83	9.01
			1	9.48	9.99
			1.5	9.98	10.02
O ₂ plasma/ CuONPs treated silk	17.35	15	0.5	11.63	12.98
			1	13.32	14.67
			1.5	14.0	15.55

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

Fixation: Thermally at 100 °C, for 30 min / Ultraviolet for 48 h.

Table 4: Effect of O₂ plasma/CuSO₄ treatment* on printability of silk with deer blood dye

Type of Sample	Plasma Power (watts)	Plasma Exposure time (min)	Conc. of CuSO ₄ (wt. %)	K/S	
				Fixed thermally	Fixed by UV
Untreated silk	-	-	Zero	7.9	8.93
O ₂ plasma-treated silk	17.35	15	zero	8.03	9.97
Treated silk with Cu SO ₄ solution	-	-	0.5	10.51	12.95
			1	12.36	13.38
			1.5	12.5	13.98
Treated silk with O ₂ plasma/CuSO ₄	17.35	15	0.5	12.86	15.32
			1	13.73	17.21
			1.5	13.34	17.50

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

Fixation: Thermally at 100 °C, 30 min / Ultraviolet for 48 h.

3.1.3. Printability of silk with red cabbage dye

Table 5 collects the values of color strength (K/S) of treated silk with CuONPs in the presence and absence of O₂ plasma treatments and printed with red cabbage dye. The printed silk is fixed either thermally or by subjecting it to UV irradiation. It can be seen that the K/S values of treated silk with O₂ plasma are approximately doubled compared to the untreated sample. It can be also noticed that the color strength (K/S) values increase gradually with increasing the concentration of CuONPs. The (K/S) values of printed samples fixed by UV irradiation are better than those fixed thermally. The combined O₂ plasma/ CuONPs treatment gives the best results.

3.1.4. Effect of UV exposure time on the printability of silk

Both sonicated CuSO₄ solution and O₂ plasma/CuSO₄ treatments affected markedly the color strength (K/S) of printed silk with coffee and deer blood which are fixed at different times of UV irradiation (Table 6). It was also noticed that increasing UV exposure time from 18 to 48h enhances slightly the K/S values. It could be concluded from Tables 1-6 that the printed samples with natural dyes which were fixed via UV irradiation have relatively higher color strength than their corresponding samples fixed thermally.

3.2. Fatness Properties

Tables 7-16 presented the fastness properties of treated silk with CuONPs and sonicated CuSO₄ solution either without or with O₂ plasma exposure. The washing (Alt, St), rubbing (Dry, Wet), perspiration (Acid, Alkali), and light fastness properties were examined. Tables 7-12 give the fastness properties of CuONPs treated silk printed with coffee, deer blood, and red cabbage, followed by fixation either; thermally or by UV irradiation. Tables 13-16 give the corresponding values when silk is treated with sonicated CuSO₄ solutions and printed with coffee and deer blood dyes. All fastness

properties of treated silk were found to be improved upon applying these treatments either by NPs only or combined with O₂ plasma CuONPs. Most values of washing, rubbing, and perspiration fastness are 5 or 4-5 compared to 3-4 or 2-3 for untreated ones. While the light fastness ranged between 6-7 and 7 for treated samples compared to 5-6 for untreated one. It was also observed that treatment of silk with O₂ plasma followed by treatment with Cu NPs either in the form of CuO or CuSO₄ is found to give the highest fastness values. Also, the fixation of printed samples with all applied natural dyes via UV irradiation is better than thermos-fixation.

Table 5: Printability with red cabbage of CuONPs treated* silk

Type of Sample	Plasma Power (watts)	Plasma Exposure time (min)	Conc. Of CuO (Wt. %)	K/S	
				Fixed thermally	Fixed by UV
Untreated silk	-	-	Zero	1.75	2.14
O ₂ plasma-treated silk	17.35	15	zero	3.59	4.77
CuONPs treated silk	-	-	0.5	6.49	7.33
			1	6.98	8.78
			1.5	6.89	9.09
O ₂ plasma/ CuONPs treated silk	17.35	15	0.5	7.33	9.38
			1	8.32	10.98
			1.5	9.18	11.77

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

Fixation: Thermally at 100 °C, for 30 min / Ultraviolet for 48 h.

Table 6: Printability of treated* silk with sonicated CuSO₄ at different UV exposure times

Type of Sample	Plasma Power (watts)	Plasma Exposure time (min)	CuSO ₄ conc wt.%	K/S at different UV exposure times (hours)					
				Coffee			Deer blood		
				18h	24h	48h	18h	24h	48h
Untreated silk	-	-	-	5.18	5.23	5.49	8.5	8.81	8.93
O ₂ plasma-treated silk	17.35	15	-	6.34	6.56	6.86	9.56	9.85	9.97
Treated silk with CuSO ₄	-	-	0.5	7.47	7.88	7.9	12.69	12.9	12.95
			1.0	8.36	8.68	8.79	13.35	13.43	13.38
			1.5	7.97	8.01	8.21	16.98	17.01	17.5
O ₂ plasma/ CuSO ₄ treated silk	17.35	15	0.5	9.97	9.99	10.2	14.64	15.01	15.32
			1.0	11.69	12.01	12.34	16.76	16.98	17.21
			1.5	10.95	11.3	11.99	16.98	17.01	17.5

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

Table 7: Fastness properties of CuONPs treated* silk fabrics printed with coffee dye fixed** thermally

Type of sample	Conc CuO Wt. %	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O ₂ plasma	-	17.35	15	4	4	3-4	3-4	4	4	6

Treated silk with CuONPs	0.5	-	-	4	4-5	3-4	4	4	4	6-7
Treated silk with O2 plasma/ CuONPs	0.5	17.35	15	4-5	5	4-5	4	4	4-5	6-7
Treated silk with CuONPs	1.0	-	-	4-5	4-5	5	5	4-5	4-5	6-7
Treated silk with O2 plasma/ CuONPs	1.0	17.35	15	4-5	5	5	4-5	4-5	5	7
Treated silk with CuONPs	1.5	-	-	5	5	4-5	5	4-5	5	7
Treated silk with O2 plasma/ CuONPs	1.5	17.35	15	5	5	4-5	5	4-5	4-5	7

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

**Fixation: Thermally at 100 ° C, for 30 min.

Table 8: Fastness properties of CuONPs treated* silk fabrics printed with coffee dye fixed** by UV irradiation.

Type of sample	Conc wt% CuONPs	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuONPs	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuONPs	0.5	17.35	15	4-5	5	4-5	4-5	5	4-5	6-7
Treated silk with CuONPs	1.0	-	-	4-5	5	5	5	4-5	5	7
Treated silk with O2 plasma/ CuONPs	1.0	17.35	15	5	5	5	5	4-5	5	7
Treated silk with CuONPs	1.5	-	-	5	5	4-5	5	4-5	5	6-7
Treated silk with O2 plasma/ CuONPs	1.5	17.35	15	5	4-5	5	5	5	5	7

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

**Fixation: UV for 48 h.

Table 9: Fastness properties of CuONPs treated* silk fabrics printed with deer blood dye fixed** thermally.

Type of sample	Conc wt% CuONPs	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuONPs	0.5	-	-	4	4-5	4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuONPs	0.5	17.35	15	4-5	5	5	5	4-5	5	6-7
Treated silk with CuONPs	1.0	-	-	5	4-5	5	4-5	4-5	5	7

Treated silk with O ₂ plasma/ CuONPs	1.0	17.35	15	4- 5	4- 5	4- 5	4-5	5	5	7
Treated silk with CuONPs	1.5	-	-	4- 5	4- 5	5	5	4-5	4-5	6-7
Treated silk with O ₂ plasma/ CuONPs	1.5	17.35	15	5	4- 5	4- 5	5	5	4-5	6-7

*Treatment: 100% pick up, 120 o C, 30 min.

**Fixation: Thermally at 100 o C, for 30 min.

Table 10: Fastness properties of CuONPs treated* silk fabrics printed with deer blood dye fixed** by UV.

Type of sample	Conc wt% CuONPs	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3- 4	4	2-3	3	3-4	3-4	5-6
Treated silk with O ₂ plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuONPs	0.5	-	-	4	4	3-4	4	4	4-5	6-7
Treated silk with O ₂ plasma/ CuONPs	0.5	17.35	15	4- 5	4- 5	4-5	5	5	4-5	6-7
Treated silk with CuONPs	1.0	-	-	5	5	5	5	4-5	5	7
Treated silk with O ₂ plasma/ CuONPs	1.0	17.35	15	4- 5	4- 5	4-5	5	5	5	7
Treated silk with CuONPs	1.5	-	-	4- 5	5	5	5	5	4-5	7
Treated silk with O ₂ plasma/ CuONPs	1.5	17.35	15	5	5	5	5	5	4-5	6-7

*Treatment: 100% pick up, 120 o C, 30 min.

**Fixation: UV for 48 h.

Table 11: Fastness properties of CuONPs treated* silk fabrics printed with cabbage dye fixed** thermally.

Type of sample		Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3- 4	4	2-3	3	3-4	3-4	5-6
Treated silk with O ₂ plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuONPs	0.5	-	-	4	4- 5	3-4	4	4	4-5	6-7
Treated silk with O ₂ plasma/ CuONPs	0.5	17.35	15	4- 5	5	4-5	5	4-5	5	6-7
Treated silk with CuONPs	1.0	-	-	4- 5	4- 5	4-5	4-5	5	4-5	6-7
Treated silk with O ₂ plasma/ CuONPs	1.0	17.35	15	5	5	4-5	5	5	4-5	6-7
Treated silk with CuONPs	1.5	-	-	5	4- 5	5	4-5	5	4-5	7
Treated silk with O ₂ plasma/ CuONPs	1.5	17.35	15	4- 5	4- 5	4-5	4-5	4-5	4-5	6-7

*Treatment: 100% pick up, 120 o C, 30 min.

**Fixation: Thermally at 100 o C, for 30 min.

Table 12: Fastness properties of CuONPs treated* silk fabrics printed with red cabbage dye fixed** by UV irradiation

Type of sample				Washing fastness	Rubbing fastness	Perspiration fastness	Lightfastness
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	Conc wt% of CuONPs	Plasma power (watt)	Exposure time (min)	Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O ₂ plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuONPs	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7
Treated silk with O ₂ plasma/ CuONPs		17.35	15	5	5	4-5	5	4-5	5	6-7
Treated silk with CuONPs	1.0	-	-	4-5	5	5	5	5	5	6-7
Treated silk with O ₂ plasma/ CuONPs		17.35	15	5	5	5	5	5	4-5	7
Treated silk with CuONPs	1.5	-	-	5	5	4-5	5	4-5	4-5	6-7
Treated silk with O ₂ plasma/ CuONPs		17.35	15	5	4-5	5	4-5	4-5	5	7

*Treatment: 100% pick up, 120 o C, 30 min.

**Fixation: UV for 48 h.

Table 13: Fastness properties of CuSO₄ treated* silk fabrics printed with coffee dye fixed** thermally

Type of sample	Conc wt.% of CuSO ₄	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O ₂ plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuSO ₄	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7
Treated silk with O ₂ plasma/ CuSO ₄		17.35	15	4-5	5	4-5	4	4	4	6-7
Treated silk with CuSO ₄	1.0	-	-	4-5	4-5	5	5	4-5	4-5	6-7
Treated silk with O ₂ plasma/ CuSO ₄		17.35	15	4-5	5	5	4-5	4-5	5	7
Treated silk with CuSO ₄	1.5	-	-	4-5	5	4-5	5	4-5	4-5	7
Treated silk with O ₂ plasma/ CuSO ₄		17.35	15	5	5	4-5	5	4-5	4-5	7

*Treatment: 100% pick up, 120 o C, 30 min.

**Fixation: Thermally at 100 o C, 30 min.

Table 14: Fastness properties of CuSO₄ treated* silk fabrics printed with coffee dye fixed** by UV irradiation.

Type of sample	Conc wt.% of CuSO ₄	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O ₂ plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuSO ₄	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7

Treated silk with O2 plasma/ CuSO4		17.35	15	4-5	5	4-5	4-5	5	4-5	6-7
Treated silk with CuSO4	1.0	-	-	4-5	5	5	5	4-5	5	7
Treated silk with O2 plasma/ CuSO4		17.35	15	5	5	5	5	4-5	5	7
Treated silk with CuSO4	1.5	-	-	4-5	5	4-5	5	4-5	5	7
Treated silk with O2 plasma/ CuSO4		17.35	15	5	5	5	5	5	5	7

*Treatment: 100% pick up, 120 o C, 30 min.

**Fixation: UV for 48 h.

Table 15: Fastness properties of CuSO4 treated* silk fabrics printed with deer blood dye fixed** thermally

Type of sample	Conc wt% of CuSO4	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuSO4	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	4-5	5	4-5	4	4	4	7
Treated silk with CuSO4	1.0	-	-	4-5	4-5	4-5	4-5	4-5	5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	4-5	5	5	4-5	4-5	5	7
Treated silk with CuSO4	1.5	-	-	5	4-5	4-5	4-5	4-5	5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	5	5	4-5	5	4-5	4-5	7

*Treatment: 100% pick up, 120 o C, 30 min.

**Fixation: Thermally at 100 o C, for 30 min.

Table 16: Fastness properties of CuSO4 treated silk fabrics printed with deer blood dye fixed by UV irradiation.

Type of sample	Conc wt.% of CuSO4	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuSO4	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	4-5	5	4-5	4-5	5	4-5	6-7
Treated silk with CuSO4	1.0	-	-	4-5	5	4-5	5	4-5	5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	5	5	4-5	5	4-5	5	7
Treated silk with CuSO4	1.5	-	-	5	5	4-5	5	4-5	5	7
Treated silk with O2 plasma/ CuSO4		17.35	15	5	4-5	5	5	5	5	7

*Treatment: 100% pick up, 120 o C, 30 min.

**Fixation: UV for 48 h.

4. Conclusion

The color strength of samples treated with O₂ plasma followed by treatment with CuONPs was higher than that treated with only CuO without subjecting to plasma.

The treated printed samples with coffee fixed via UV irradiation for 48 hours have higher color strength values compared to thermally fixed samples that acquired color strength higher than untreated ones.

It can be concluded that fixation of coffee-printed silk samples with UV irradiation not only improves their color strength but also improves dye fastness properties.

The enhancement in color strength (K/S) of treated silk with CuO is dependent to a great extent on its concentration and increases gradually. Combined O₂ plasma/CuONPs treatments give the best color strength results of deer blood dye.

The K/S values of treated silk with O₂ plasma and printed with red cabbage dye are approximately doubled compared to the untreated sample and it increases gradually with increasing the concentration of CuONPs.

All fastness properties of treated silk were improved upon applying these treatments either by NPs only or combined with O₂ plasma Cu NPs. Most values of washing, rubbing, and perspiration fastness are 5 or 4-5 compared to 3-4 or 2-3 for untreated ones.

Light fastness ranged between 6-7 and 7 for treated samples compared to 5-6 for untreated ones. Also, the treatment of silk with O₂ plasma followed by treatment with Cu NPs either in the form of CuO or CuSO₄ gives the highest fastness values. As well as fixation of printed samples with all applied natural dyes via UV irradiation is better than thermos-fixation.

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6. 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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