Smart Cotton Functionalized With Self-Implanted Palladium Nanopanicles: Full Ultraviolet Shielding Potency

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Abstract

Unique technique is currently demonstrated for preparation of ultraviolet protective cotton fabrics with full shielding effect, via self-implantation of palladium nanopanciles. Palladium (Pd) nanopanciles were in-situ immobilized within native & cationized cotton using two different concentrations of palladium precursor (20 & 60 mM) under strong acidic (pH 2) and basic (pH 11.5) media. Cationization (50% and 100%) of cotton fabrics was performed in order to increase the accessibility of fabric for controllable implantation of palladium nanopanciles. Size distribution of palladium nanopanciles in supernatant solution was estimated via Transmission electron microscopy to be 3.2 nm. The estimated data showed that the sample prepared with the highest cationization percent and highest concentration of palladium precursor in strong alkaline medium exhibited the highest yellowness index, color strength and excellent ultraviolet shielding effects. The yellowness index was significantly increased from 15.67 for cationized cotton to 74.99 for the sample prepared with the highest cationization percent and highest concentration of Pd^{+2} in alkaline medium (Pd-CC (100)4). Tensile strength was insignificantly decreased from 93.2 MPa for cationized cotton to 84.5 MPa for Pd-CC (100)4. Ultraviolet shielding effect was superiorly enhanced with implantation of palladium nanopanciles. The UV protection factor (UPF) was also excellency increased from 1.3 (insufficient) for native cotton to 256.6 (excellent) for Pd-CC (100)4.

Highlights

- Palladium nanopanciles was in-situ implanted within pristine and cationized cotton.
- Cationization increased the accessibility for implantation of palladium nanopanciles.
- Size of palladium nanopanciles in supernatant solution was 3.2.
- Tensile strength was insignificantly affected by implantation of palladium nanopanciles.
- UV-protective Fabric with full shielding effects was successfully obtained.

Introduction

Increment for the consideration over damaging resulted from the exposure to microbial organisms, chemical reagents, insecticides, ultraviolet irradiation and pollutants in the last decade, has heightened the requirement for protective clothing materials. Garments today is required to be waterproofing, flame resistant, self-cleaning, pest repellent and microbicidal to protect human body from the infections, ultraviolet irradiation, chemical and biological reagents, be warmer in cold weather and comfortable in summer. Conventional methodologies of finishing application, such as pad-dry-cure or coating that are recently being applied to make the fabrics acquired the microbicidal, ultraviolet shielding, self-cleaning and fire-retardant finishing reagents, are usually combined with increment in fiber thickness, loss of smoothness and drape, lowering the washing fastness, poor of mechanical properties and most importantly reduced the comfortability to the wearers (Mehta 2008; Rao et al. 2015; Simončič and Klemenčič 2016; Durán et al. 2007; Vigneshwaran et al. 2006; Fei et al. 2006).

Mostly, the protective clothes were actually ascribed to impair user potentiality. Moreover, there are vital safety issues correlating to the application as well as the disposal of chemical reagents used in contemporary finishing. Therefore, the researchers considered with the field of textile industry were continued to look for alternative finishing reagents and technologies that must be environment friendly, with high fastness, costless and do not disadvantageously affect the comfortability of clothes while providing efficiency and optimum protection (Hassabo et al. 2019; Zhang et al. 2018; Baglioni et al. 2005; Subash et al. 2012; Wong et al. 2006). Cotton fabrics were exploited in different applications and purposes owing to their outstanding properties like biodegradability, absorbability, softness, and breathability, but disadvantageous with prone to be attacked with microbes especially bacterial strains, poor ultraviolet shielding, and high flammability (Goncalves et al. 2009; Li et al. 2007a; Li et al. 2007b).

Numerous approaches were considered with investigation of different techniques for acquirement different textile materials number of additional functions, like coloration (Emam and Abdelhameed 2017; Ahmed et al. 2018), self-cleaning (Rehan et al. 2013; Emam et al. 2020a; Emam et al. 2018), optical activity (Emam et al. 2018), insect repellency (Abdel-Mohdy et al. 2008; Abdelhameed et al. 2017), microbicidal activities (Emam et al. 2020b; Ahmed et al. 2017), and ultraviolet shielding (Khan et al. 2015; Nazari et al. 2013; Ates and Unalan 2012; Emam et al. 2020b). In addition to, the protective masking and air-filtering textiles have been prepared for protection from the chemical warfare gases and produced via the immobilization of different functionalizing reagents, like lipophilic activated carbon with efficient adsorption action (Li et al. 2011).

For acquirement of any additional functions to the textile materials, numerous reports were considered with the exploitation of some organic reagents, like triclosan for antibacterial potency, benzophenones for ultraviolet shielding, dimethylol dihydroxy ethylene urea for anti-crease performance, fluorocarbons for lipophilic characters, long-chain hydrocarbons and polydimethylsiloxanes for flexibility and softening (Almeida 2006; Hewson 1994). Butane tetra-carboxylic acid, citric acid and maleic acid (Yang et al. 1998; Welch 1988; Yang et al. 2010) were also exfoliated for acquiring cotton fabrics with anti-crease action.

Different types of metallic based nanomaterials were reported to efficiently applicable in various fields, especially sewage treatment, chemical synthesis, hydrogen storage, exhaust gas treatment, and oil refinement (Moon et al. 2014; Zaluski et al. 1995; Lee et al. 2010; Hughes et al. 1995; Meyer et al. 2015; Adams and Chen 2011; Mackus et al. 2015). The priority of nanosized materials is attributed to their high surface area per volume ratio, highly organized composition, high density of coordinative sites, high oxidation activity, and superior mechanical and thermal stabilities (Cano et al. 2017). Numerous studies demonstrated the functionalization of different textile materials via immobilization of various noble-metal nanostructures such as silver (Rao et al. 2015; Simončič and Klemenčič 2016; Emam et al. 2016; Ahmed et al. 2018), gold (Emam et al. 2017; Ahmed et al. 2017), titanium dioxide (Durán et al. 2007; Vigneshwaran et al. 2006; Fei et al. 2006) and zinc oxide (Hassabo et al. 2019; Zhang et al. 2018; Baglioni et al. 2005). However, palladium (Pd) nanostructures were reported to be efficiently applicable in catalysis (Lim et al. 2010; Emam et al. 2020d; Emam and Ahmed 2019; Abdelhameed et al. 2020; Emam et al. 2020c). Palladium was successfully applied as catalyst for facilitating the hydrogen absorptivity and detection owing to its high affinities in absorption of hydrogen (Moon et al. 2014; Zaluski et al. 1995; Lee et al. 2010; Adams and Chen 2011; Rikkinen et al. 2011). Moreover, palladium nanostructures were found to be more efficient in removal of dyes from the aqueous media via the heterogenous catalysis than many typically applied methodologies, like filtration, biological treatment, chemical precipitation, adsorption and techniques. According to our knowledge, no researching studies were considered with exploitation of palladium nanostructures in textile functionalization.

Herein, a novel/investigative approach for preparation of excellent ultraviolet protective cotton fabric is uniquely proposed via self-implantation of palladium nanopanciles. Whereas, for the first time, the immobilized palladium nanopanciles were functionalized in acquirement of the treated fabrics excellent ultraviolet shielding potency. The particle size of the dispersed palladium nanopanciles in supernatant solution was estimated from transmission electron microscopic images. Regulative implantation of palladium nanopanciles was proceeded via immobilization within the polymeric matrix of both native and cationized cotton fabrics. Afterward, the modified fabrics were characterized via infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), colorimetric measurements (color coordinates and color strength), mechanical properties (tensile strength and elongation percentage), and UV-protective action (transmittance percent, ultraviolet protection factor UPF and ultraviolet protection rating).

Experimental Work

Materials and chemicals

Palladium chloride ($PdCl_2$, 99%, from Sigma-Aldrich – USA), Sodium hydroxide (99%, from Merck, Darmstadt–Germany), acetic acid and sodium carbonate were of laboratory grade chemicals. 3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (69%) of technical grade chemicals (known as Quatt-188) was purchased under the commercial name CR-2000 from Aldrich. All the chemicals were used as supplied without any further purification. Mill de-sized, scoured and bleached cotton fabric, plain weave, supplied by El-Nasr Company for spinning weaving and Dyeing El-Mahallah El-Kubra, Egypt. The fabric was further purified in the laboratory by washing at 100^{o}C for 60 min using a solution containing 2 g/L, Na_2CO_3 and 1 g/L, non-ionic surfactant. The fabric was then washed several times with boiling water then with cold water and finally dried at ambient conditions.

Procedure

Cationization of cotton fabrics

Chemical modification of the cotton gauze through cationization was carried out as per the pad-dry-cure method (Hashem et al. 2009; Hashem et al. 2005). The experimental procedures adopted were as follows: 3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (Quat-188) was mixed with sodium hydroxide solution at a NaOH/Quat-188 molar ratio of 2:1. The cotton gauze was padded in this mixture in two dips and two nips, and then squeezed to a wet pick-up of about 100%. The cotton gauze was dried at 40 ^{o}C for 10 min and cured at 120 ^{o}C for 3 min. Thus, treated cotton gauze was washed with cold water and 1% acetic acid, followed by several washing cycles and finally dried under the normal laboratory conditions.

Self-implantation of palladium Nanopanicles

The palladium Nanopanicles were self-implanted in to the native and cationized cotton fabrics by dipping method. In this procedure, pieces of cotton fabrics (0.25 g) were impregnated in distilled water and stirred till temperature reached 90 ^{o}C then palladium salt solution with specific concentration (20 and 60 mM) was added with liquor ratio of 2:50 at two different pH (2 & 11.5) and left for continuous stirring at 90 ^{o}C for 30 minutes. Afterward, the fabric pieces were air dried before they were instrumentally analyzed. Table 1 represented the samples that were prepared in the current approach under different experimental conditions.

Table 1
Description of the Pd-modified cotton fabrics.

Samples	Fabric	$PdCl_2$ (mM)	pH
Pd-C1	Cotton	20	2.0
Pd-C2	Cotton	60	2.0
Pd-C3	Cotton	20	11.5
Pd-C4	Cotton	60	11.5
Pd-CC (50)1	Cationic (50) Cotton	20	2.0
Pd-CC (50)2	Cationic (50) Cotton	60	2.0
Pd-CC (50)3	Cationic (50) Cotton	20	11.5
Pd-CC (50)4	Cationic (50) Cotton	60	11.5
Pd-CC (100)1	Cationic (100) Cotton	20	2.0
Pd-CC (100)2	Cationic (100) Cotton	60	2.0
Pd-CC (100)3	Cationic (100) Cotton	20	11.5
Pd-CC (100)4	Cationic (100) Cotton	60	11.5

Temperature = 90 ± 3°C, Time = 30 min.

Characterization and instrumental analysis

Geometrical shape and size distribution of the self-implanted palladium nanopanciles were estimated by using a high-resolution transmission electron microscope (JEOL-JEM-1200; Japan). Size distribution of palladium nanopanciles was evaluated with 4 pi analysis software (from USA) for at least 50 particles. The treated fabrics were characterized via the high-resolution scanning electron microscope (HRSEM Quanta FEG 250 with a field emission gun, FEI Company, Netherlands). Elemental analysis was also estimated using an energy dispersive X-ray analyzer (EDAX AME-TEK analyzer). The infrared spectra of the treated fabrics were obtained by using a Jasco FT/IR 6100 spectrometer. Their spectral mapping was ranged from 4000 cm^{-1} to 400 cm^{-1} and were determined with 4 cm^{-1} resolution and 64-time scanning with a rate of 2 mm/sec. Additionally, the prepared fabrics were characterized by powder X-ray diffraction using X'Pert MPD diffractometer system from Philips, at room temperature. Diffraction patterns were estimated in the diffraction angle (2θ) range of 3.5 – 50° using monochromatized (Cu Kα X-radiation at 40 kV, 50 mA and λ = 1.5406 Å).

The colorimetric data (L, a*, b*, absorbance, color strength [K/S], whiteness index E313 [D65/10] and yellowness index E313 [D65/10] of the treated fabrics were estimated using a spectrophotometer attached with a pulsed xenon lamp (UltraScan Pro, Hunter Lab, USA). The color coordinate parameters of L*, a*, and b* corresponded to the lightness (black/white, 0/100), red/green ratio (+/−), and yellow/blue ratio (+/−), respectively (Ahmed et al. 2017; Ahmed et al. 2018). The estimation was performed three times the average values. The mechanical properties of the treated fabrics were investigated, while, tensile strength (MPa) and elongation at break (%) for the fabrics were estimated related to ASTM method D2256−66T by using the strip test methodology on the tester instrument (Asano machine MFG. Co. Ltd., Japan). Transmission spectral results (T%) for ultraviolet irradiation (UVR) over pristine and cationized cotton before and after the successive implantation of palladium nanopanciles were estimated using JASCO V-750 spectrophotometer (Japan) in the range of 280–400 nm with two nanometers interval. Additionally, ultraviolet protection factor (UPF), resistance in UV-A (315–400) region (UVA) and in UV–B (280–315) region (UVB) were predicted using the AATCC test method 183–2010.44. For each sample, estimation was estimation two different times, and the average was calculated.

Results And Discussion

Synthesis of palladium nanopanciles

In spite of that, immobilization of various metallic nanoobjects for textile finishing was extensively studied (Gulrajani et al. 2008; Maneerung et al. 2008; Perelshtein et al. 2008; Saengkiettiyut et al. 2008; Ko et al. 2007; Gorenšek and Recelj 2009; Baban et al. 2010; Wu et al. 2010), but there were no researching approaches on the synergism between palladium nano-objects within cotton textiles finishing. Additionally, no researching reports were studied the direct implantation of palladium nanopanciles. Therefore, the leverage effects of direct implantation for palladium nanopanciles before and after fabric cationization on coloration, mechanical properties and UV-protection efficiency for cotton fabrics was the focus of this study.

In accordance to literature [], self-implantation of palladium nanopanciles within cotton fabrics could be hypothesized as the cellulosic building blocks of cotton fabrics with the terminal/alcoholic groups might assist in reduction of palladium ions for ingraining of palladium nanopanciles that could be highly stabilized within the intermolecular spaces of cotton polymeric matrix. Moreover, fabric cationization was performed for cotton before self-implantation of palladium nanopanciles in order to achieve the fulfill goal. Fabric cationization is supposed to enhance the implantation and stabilization of palladium nanopanciles within fabric matrix, while, such chemical modification acquired the fabric more accessible reducing groups to act more actively for ingrowth and stabilization of the requisite nanostructure (Figure 1).

TEM and size distribution

The geometrical features and topography of the implanted palladium nanopanciles that were stably dispersed within the supernatant solution containing the treated fabrics were shown in transmission electron microscopic images from which the size distribution was estimated (**Figure 2**). The microscopic images displayed the successful implantation of palladium nanopanciles with size distribution of 41.3 ±10.1 nm in alkaline medium (pH of 11.5) in the supernatant solution of native cotton treated with 20 mM of palladium chloride. Quite smaller sized palladium nanopanciles (3.2 ± 0.6 nm) were ingrained and well dispersed within the supernatant solution of cationized fabric treated with palladium precursor under the same experimental conditions, reflecting the pre-eminent effect of cationization in enhancement the accessibility of fabric/cellulosic backbone in the ingrowth of palladium nanopanciles. While, duplication of the percentage of quaternary ammonium salt exploited for cationization from 50–100% is insignificantly affected on particle size (4.6±1.7 nm).

SEM

The topography of the surface of the pristine and cationized fabrics before and after implantation of palladium nanopanciles. In order to show the effects of palladium precursor concentration and cationization on the successive implantation of palladium nanopanciles, Scanning electron microscopic images (SEM images), energy dispersive x-ray (EDX signals), and the elemental analysis of cationized cotton, Pd-C4, Pd-CC(50)4, Pd-CC(100)3 and Pd-CC(100)4 were plotted in **Figure 3**. Before successive implantation of palladium nanopanciles, the surface of the cationized fabric seemed to be smoothy, and the specialized signals of carbon, oxygen, nitrogen and chlorine were obviously detected (Figure 3a). After implantation of palladium nanopanciles, the nanopanciles were clearly dispersed on the surface of the modified fabrics. Whereas, from EDX data, the characteristic peaks of carbon, oxygen, nitrogen, chlorine, and palladium were significantly presented, that affirmed the successive implantation of nanopanciles within the fabrics (Figure 3b). Moreover, cationization were shown to extensively enhance the implantation of palladium nanopanciles to be regulatory uploaded on the fabric surface as shown in Fig. 3b&c, while, duplication of the cationization percent from 50% (Fig. 3c) up to 100% (Fig. 3e) resulted in more accessibility for implanting of more condensed nanopanciles, which could confirm the postulated mechanism of palladium nanopanciles implantation. By comparing between the microscopic images of the modified fabrics after implantation of palladium nanopanciles (Fig. 3d &3e), increment of the concentration of palladium precursor resulted in more dense masses of nanopanciles were obviously shown on the surface of the fabric.

FTIR

The chemical composition of quaternary ammonium salt, pristine cotton, cationized cotton and fabrics immobilized with palladium nanopanciles was investigated via FTIR (Figure 4). From the spectral data it could be depicted that the quaternary ammonium salt, pristine and cationized cotton were characterized with absorption signals of O–H (3330–3289 cm^{-1}) and aliphatic C–H (2888 cm^{-1}) and weak bands of C=O (1620 cm^{-1}), asymmetric C–O–C (1472 cm^{-1}), and C–C (1072 cm^{-1}) (Emam and Abdelhameed 2017; Emam and Bechtold 2015). After implantation of palladium nanopanciles, all of the absorbance bands were retained and new band of O-Pd (833 cm^{-1}) is obviously detected. Additionally, the absorption bands of C=O (1620 cm^{-1}), H–C–H, and asymmetric C–O–C became more intense.

XRD

These interpretations affirmed the successful implantation of palladium nanopanciles within the fabric matrix through chemical bonding. Figure 5 is plotted for XRD data of cotton and cationized cotton before and after implantation of palladium nanopanciles, and from the represented data it could be declared that, cotton was detected with three characteristic bands at 2θ = 14.9°, 16.7° and 21.5° corresponding for crystalline cellulose. While, after immobilization of palladium nanopanciles, two characteristic peaks for palladium Pd (111) and Pd (200) were detected at 2θ = 31.8° and 45.4°, respectively of face centered crystalline Pd (JCPDS data number 89-4897 card) (Liu et al. 2016b; Liu et al. 2016a; Emam et al. 2020d; Emam and Ahmed 2019). Moreover, for cationized cotton modified with palladium nanopanciles, an additional peak for Pd (202) at 2θ = 75.4° was appeared, to affirm the effect of cationization in increment the accessibility of fabric for regulative implantation for higher amounts of palladium nanopanciles.

Colorimetric data and mechanical properties

From the visual observation of the samples imaged in Figure 6 it could be noted that, treatment of fabrics with the demonstrated technique resulted in fabric coloration, while, the color is changed from white for native cotton to creamy white with cationization, and under different experimental conditions, the fabric color was developed to yellowish, brownish and lastly to dark black color. The color data of the pristine cotton and cationized cotton after implantation of palladium nanopanciles are presented in Table 2 and **Figure 7**. From the plotted data in Table 2, Yellowness index (YI) of the cationized cotton was extremely higher than that of pristine cotton fabrics. For fabrics prepared under alkaline condition, with increment of the concentration of palladium precursor and with duplication of the cationization percentage up to 100%, the lightness (L*) and whiteness index (WI) were significantly decreased, while, color strength (K/S), darkness (b*) and yellowness index are significantly increased.

Table 2
Colorimetric data for the Pd-modified cotton fabrics.

Fabric samples	L*	a*	b*	WI E313 [D65/10]	YI E313 [D65/10]
Cotton	86.49 ± 0.98	1.02 ± 0.12	-2.65 ± 0.21	81.28 ± 2.23	-4.81 ± 0.43
Pd-C1	75.78 ± 0.74	1.18 ± 0.23	6.08 ± 0.78	16.31 ± 2.01	14.76 ± 1.73
Pd-C2	71.39 ± 0.96	1.72 ± 0.42	7.76 ± 1.10	-1.75 ± 0.49	19.83 ± 1.88
Pd-C3	67.46 ± 1.45	3.16 ± 0.76	11.41 ± 1.15	-27.86 ± 2.17	31.35 ± 2.16
Pd-C4	63.54 ± 1.24	4.59 ± 0.54	15.06 ± 1.92	-53.97 ± 4.48	42.88 ± 2.60
Cationized (50) Cotton	84.05 ± 0.30	0.43 ± 0.08	2.59 ± 1.01	52.39 ± 4.08	5.83 ± 1.51
Pd-CC (50)1	60.30 ± 0.66	5.12 ± 0.53	15.59 ± 1.82	-72.05 ± 5.58	45.06 ± 2.52
Pd-CC (50)2	57.41 ± 0.45	6.20 ± 0.86	19.54 ± 1.56	-89.11 ± 5.14	56.93 ± 3.35
Pd-CC (50)3	45.18 ± 0.72	7.05 ± 1.02	20.39 ± 2.21	-101.00 ± 6.28	63.76 ± 3.15
Pd-CC (50)4	41.99 ± 0.83	7.76 ± 1.00	21.61 ± 2.04	-109.01 ± 6.84	65.04 ± 3.06
Cationized (100) Cotton	83.13 ± 0.40	0.10 ± 0.10	7.53 ± 1.21	24.14 ± 1.82	15.67 ± 1.52
Pd-CC (100)1	54.96 ± 0.83	5.22 ± 0.59	17.21 ± 1.44	-91.36 ± 3.86	51.47 ± 2.26
Pd-CC (100)2	45.19 ± 0.37	6.44 ± 0.88	18.97 ± 1.72	-101.00 ± 4.25	59.75 ± 2.77
Pd-CC (100)3	41.99 ± 0.44	7.58 ± 0.40	21.05 ± 1.92	-119.79 ± 5.66	70.04 ± 3.31
Pd-CC (100)4	39.70 ± 0.52	8.22 ± 0.72	24.03 ± 2.20	-124.25 ± 4.83	74.99 ± 2.80

YI was estimated to be 42.88 ± 2.60, 65.04 ± 3.06 and 74.99 ± 2.80, whereas, WI was calculated to be -53.97 ± 4.48, -109.01 ± 6.84 and -124.25 ± 4.83, for Pd-C4, Pd-CC (50)4 and Pd-CC (100)4, respectively. From the plotted results in Figure 6, it could be observably shown that, cationized fabrics were shown with higher absorbance and color strength values. Additionally, absorbance and color strength were extensively higher for fabrics prepared under alkaline conditions rather than that prepared under acidic pH with increment of palladium salt concentration and duplication of cationization percentage from 50% up to 100%. The color strength was evaluated to be 8.9, 9.2, 9.2, 11.8, 11.2 and 15.3, for Pd-C3, Pd-C4, Pd-CC (50)3, Pd-CC (50)4, Pd-CC (100)3 and Pd-CC (100)4, respectively. So, it could be summarized that, yellowness degree, absorbance and color strength could be ordered as follows: Pd-CC (100)4 > Pd-CC (100)3 >> Pd-CC (50)4 > Pd-CC (50)3 ≥ Pd-C4 > Pd-C3 >> cationized cotton > cotton.

Table 3
Mechanical properties of the Pd-modified cotton fabrics.

Samples	Tensile strength (MPa)	Elongation (%)
Cotton	107.9	17
Pd-C1	104.1	16
Pd-C2	109.2	16
Pd-C3	106.5	15
Pd-C4	103.7	13
Cationized (50) Cotton	99.1	15
Pd-CC (50)1	97.7	15
Pd-CC (50)2	95.4	16
Pd-CC (50)3	96.0	14
Pd-CC (50)4	93.6	14
Cationized (100) Cotton	93.2	13
Pd-CC (100)1	94.4	14
Pd-CC (100)2	90.3	13
Pd-CC (100)3	87.0	12
Pd-CC (100)4	84.5	12

The effects for implantation of palladium nanopanciles within the polymeric matrix of both pristine and cationized cotton on the mechanical properties were monitored via estimation of tensile strength and elongation percentage and the results were tabulated in Table 3. Cationization of fabrics and immobilization of palladium nanopanciles were resulted in decrement in the tensile strength and elongation percentage, as the pristine cotton was exhibited by tensile strength and elongation percentage of 107.9 MPa & 17 %, respectively, while, Pd-CC (100)4 was estimated with tensile strength and elongation % of 84.5 MPa & 12 %, respectively. Duplication of cationization percentage from 50 % (Pd-CC (50)4, tensile strength 93.6 and elongation percent 14 %) up to 100% (Pd-CC (100)4, tensile strength 84.5 and elongation percent 12 %) were shown with slightly lower tensile strength and no changing in elongation percentage. Cationized fabrics immobilized with palladium nanopanciles under alkaline conditions (Pd-CC (100)4, tensile strength 84.5 and elongation percent 12 %) were shown to be characterized with lower tensile strength and elongation percentage rather than that prepared under acidic conditions (Pd-CC (100)2, tensile strength 90.3 and elongation percent 13%). Increment of palladium precursor concentration from 20 (Pd-CC (100)3, tensile strength 87.0 and elongation percent 12%) up to 60 mM (Pd-CC (100)4, tensile strength 84.5 and elongation percent 12 %), resulted in nonsignificant decrement in tensile strength and no changing in elongation percentage. This could be logically attributed to that, the chemical medication and immobilization of palladium nanopanciles within the intermolecular spaces of polymeric matrix for the treated fabrics, which could result in bond breaking within the polymeric chains. However, the decrement in tensile strength for the fabrics after implantation of palladium nanopanciles could be ascribed as acceptable for application as clothing materials.

UV protection

Cotton based textile materials were widely applicable in various purposes owing to their outstanding characters like biodegradability, softness, and breathability, but they are disadvantageous with prone to microbial attacking, low capability in protection from ultraviolet irradiation, and high flammability (Goncalves et al. 2009; Li et al. 2007a; Li et al. 2007b). It was recently reported that special metallic oxides like, titanium dioxide, silicon dioxide, zirconium dioxide, magnesium dioxide and zinc oxide, in addition to some of polymeric materials were successfully applicable for coating of cotton fabrics to acquire the treated fabrics characteristic functional properties (Hojjati et al. 2007; Gandhi et al. 2010; Charpentier et al. 2012).

Ultraviolet protection factor (UPF, Table 4) and transmission percent (T%, **Figure 8**) could be ascribed as key factors for evaluation of the ultraviolet protection action for all the prepared samples in the current study. The ultraviolet shielding property was analyzed within wavelength range of 280−400 nm, as shown in Fig. 7, for all the samples prepared from native and cationized cotton immobilized with palladium nanopanciles. Transmittance percent of cotton fabric is ca. 66% and 83.3 % for both UV-A and UV-B, respectively. As seen in Fig. 7, the blocking percent of the treated fabrics indicated with minor transmittance of UV radiation compared to untreated ones (UVA blocking percent 34.0% & UVB blocking16.7%), i.e., T% of all the prepared samples was observably diminished after implantation of palladium nanopanciles compared to that of the untreated fabric (UVA T% 66.0 & UVB T% 83.3). The blocking percentage of treated cotton fabrics showed that the percent of blocking for UV-B radiation is higher than that of UV-A for all samples prepared from native cotton, in contrast to that prepared from cationized cotton (Table 4). The increment of concentration of palladium precursor (UVB T% for Pd-C3 was 1.6 %, while, for Pd-C4 was 1.0 %) and processing the palladium implantation under alkaline conditions resulted in lowering the detected transmission percent. Therefore, Pd-C4 sample (UVA T% 0.9 & UVB T% 1) was exhibited by the highest UVA & UVB blocking percent of 99.1% and 99.0 %, respectively, compared to the other three samples pristine cotton (Fig. 8a).

Figure 8b & c demonstrated that, the decrement of transmission was significantly higher for the cationized cotton samples compared to that prepared from native cotton. Duplication of cationization percent and alkalinity were notably affected on diminishing of transmission percent, whereas, increment of concentration for palladium salt under alkaline conditions was shown to insignificantly affecting on the transmission. The estimated results showed that UVA T% & UVB T% was sharply decreased from 34.6 % & 41.4 % for cationized (50) cotton (UVA blocking 53.4 %& UVB blocking 41.4 %) to 2.7 % & 1.8 % for Pd-CC (50)2 (UVA blocking 97.3 %& UVB blocking 98.2 %) and superiorly to 0.7 % and 0.5 % for Pd-CC (50)3 (UVA & UVB blocking 99.3 %) and Pd-CC (50)4 (UVA & UVB blocking 99.5 %), respectively (Fig. 7b). Whereas, the lowest transmission percent of 0.4% for all the prepared samples was exhibited by Pd-CC (100)4 (the highest UVA & UVB blocking percent of 99.6 %). These could affirm the effects of cationization, alkalinity and concentration of palladium precursor in implantation of greater amounts from palladium nanopanciles.

Table 4
Ultraviolet protection results for the Pd-modified cotton fabrics.

Samples	UVA (T%)	UVB (T%)	UVA Blocking	UVB Blocking	UPF	UPF rate
Cotton	66.0	83.3	34.0	16.7	1.3	In sufficient
Pd-C1	13.4	13.5	86.6	86.5	7.4	In sufficient
Pd-C2	4.0	4.2	96.0	95.8	24	In sufficient
Pd-C3	1.6	1.6	98.4	98.4	76.2	Excellent
Pd-C4	0.9	1.0	99.1	99.0	103.4	Excellent
Cationized (50) Cotton	34.6	41.4	53.4	46.6	5.6	In sufficient
Pd-CC (50)1	2.9	2.3	97.1	97.7	39.8	Very good
Pd-CC (50)2	2.7	1.8	97.3	98.2	50.1	Excellent
Pd-CC (50)3	0.7	0.7	99.3	99.3	147.8	Excellent
Pd-CC (50)4	0.5	0.5	99.5	99.5	198.9	Excellent
Cationized (100) Cotton	15.3	11.6	84.7	88.4	8.1	In sufficient
Pd-CC (100)1	2.1	1.2	97.9	98.8	76.2	Excellent
Pd-CC (100)2	1.9	1.2	98.1	98.8	76.2	Excellent
Pd-CC (100)3	0.8	0.7	99.2	99.3	137.9	Excellent
Pd-CC (100)4	0.4	0.4	99.6	99.6	256.6	Excellent

UPF & UV protection rating were also evaluated in accordance to the estimated values of transmission percent (Table 4). The UPFs of native cotton, cationized (50) cotton and cationized (100) cotton fabrics were 1.3, 5.6 and 8.1, respectively. They were estimated to increase up to 103.4, 198.9 and 256.6 for Pd-C4, Pd-CC (50)4, and Pd-CC (100)4, respectively. The highest UPF was found in Pd-CC (100)4 to affirm the superior cationization effect on the efficient implantation of higher amounts of palladium nanopanciles within the fabric matrix to reveal higher blocking of ultraviolet radiation, while, palladium nanopanciles were superiorly aid as excellent UV absorbers for preparation of UV protective textiles. Moreover, the demonstrated data for ultraviolet protection rating it could be declared that, all the samples that were prepared under alkaline conditions showed very good to excellent rating, for substantiation the excellency of palladium nanopanciles as UV blocking structures.

Compared with other reported approaches in literature the UV protection properties of cotton fabrics that were currently prepared via the self-implantation of palladium nanopanciles are extensively higher than for fabrics prepared in literature via the immobilization of metallic based ultraviolet absorbers metals like silver, gold, zinc, copper, or titanium (Emam and Bechtold 2015; Ahmed et al. 2017; Emam et al. 2016), or via the impregnation of MOFs within the polymeric matrix of fabric (Emam and Abdelhameed 2017; Emam et al. 2020b). Therefore, the results represented currently suggested that palladium nanopanciles-coated fabrics could be expressed as potential candidates for ultraviolet shielding in textile functionalization, packaging applications and optoelectronics.

Conclusion

In the current study, for the first time, self-implantation of palladium nanopanciles within cotton fabrics was proceeded in order to aid as strong ultraviolet absorbers to acquire the treated fabrics excellent ultraviolet protection potency with full shielding effects. The self-implanted palladium nanopanciles were immobilized within the polymeric matrix of both native and cationized cotton fabrics. For all the prepared specimens, the effects of the concentration of palladium precursor, pH, and cationization percentage on the particle size of the implanted nanopanciles, in addition to, the color coordinates, yellowness index, whiteness index, color strength, tensile strength, elongation percentage were monitored. From all of the illustrated data it could be summarized that, palladium nanopanciles aided superiorly as strong ultraviolet shielding sites within the fabric matrix. The yellowness degree and UV protection potency were shown to follow the trend of Pd-CC (100)4 > Pd-CC (50)4 >> Pd-C4 > > Cationized (100) Cotton > Cationized (50) Cotton > native cotton. Pd-CC (100)4 exhibited good mechanical properties and excellent ultraviolet protection potentiality, that could be attributed to the effect of cationization in the stronger implantation of palladium nanopanciles within the fabrics. It could be eventually reported that, the textile industry should address the unique presented challenge for production of excellent ultraviolet protective cotton fabrics with full shielding effect, via self-implantation of palladium nanopanciles. The ingrained palladium nanopanciles could also be promisingly exploited in other several purposes, such as textile functionalization, packaging applications and optoelectronics.

Declarations

Compliance with ethical standards

The authors declare that they have no competing financial interest

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Figures

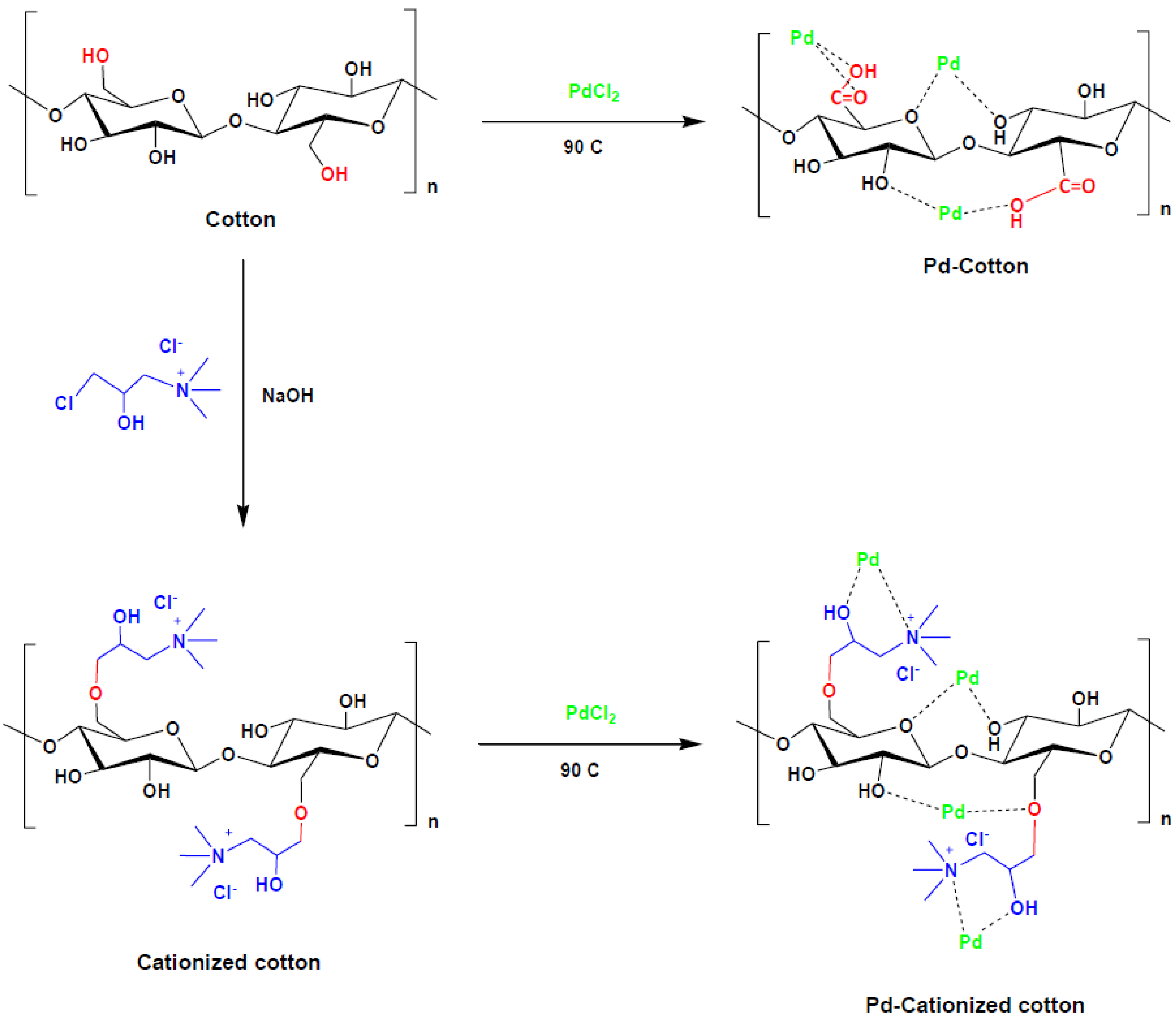

Figure 1

Schematic for formation of Pd-modified cotton fabrics.

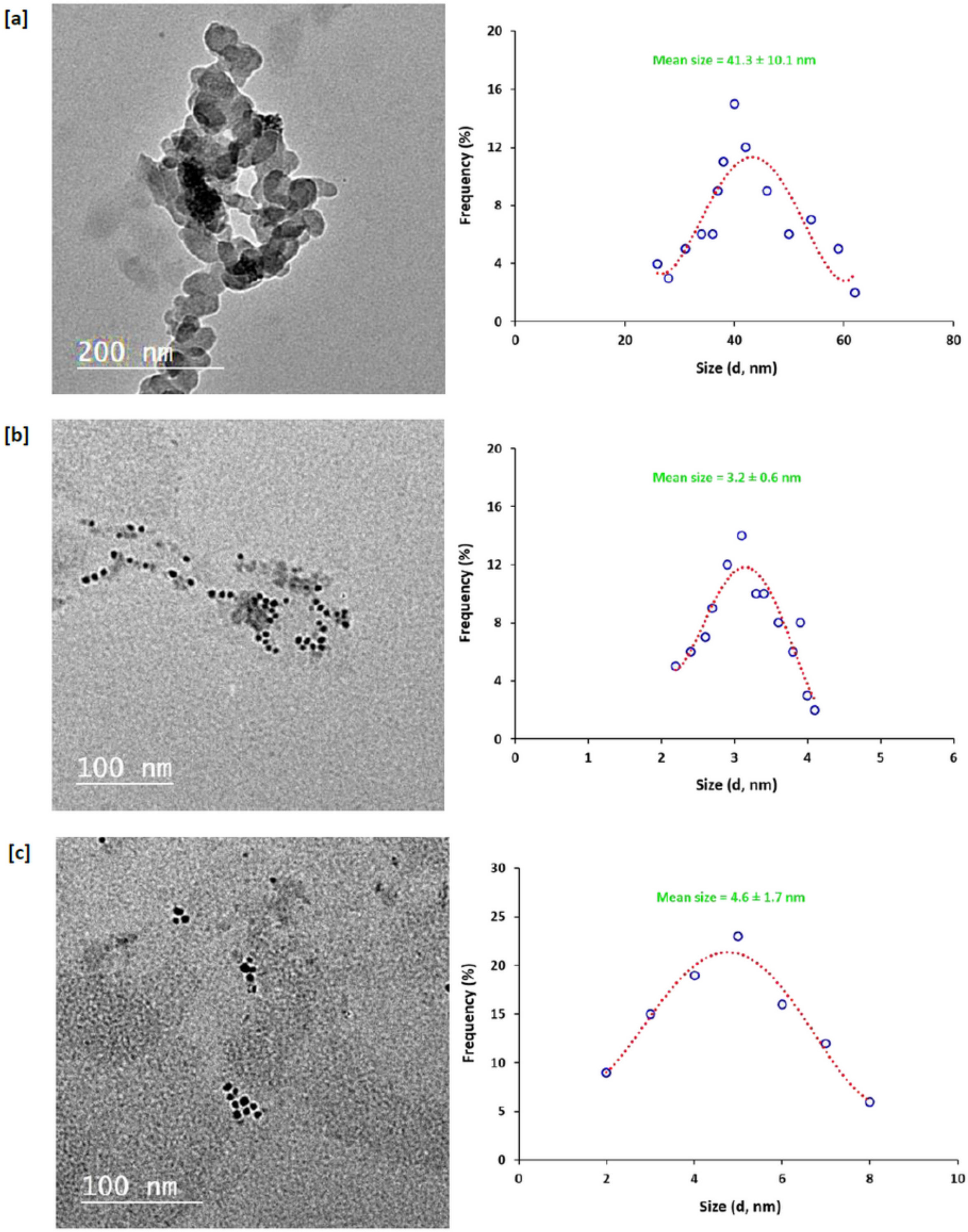

Figure 2

TEM images for the supernatant solution of Pd after modification of cotton fabrics; [a] Pd-C3, [b] Pd-CC (50)3 and [c] Pd-CC (100)3.

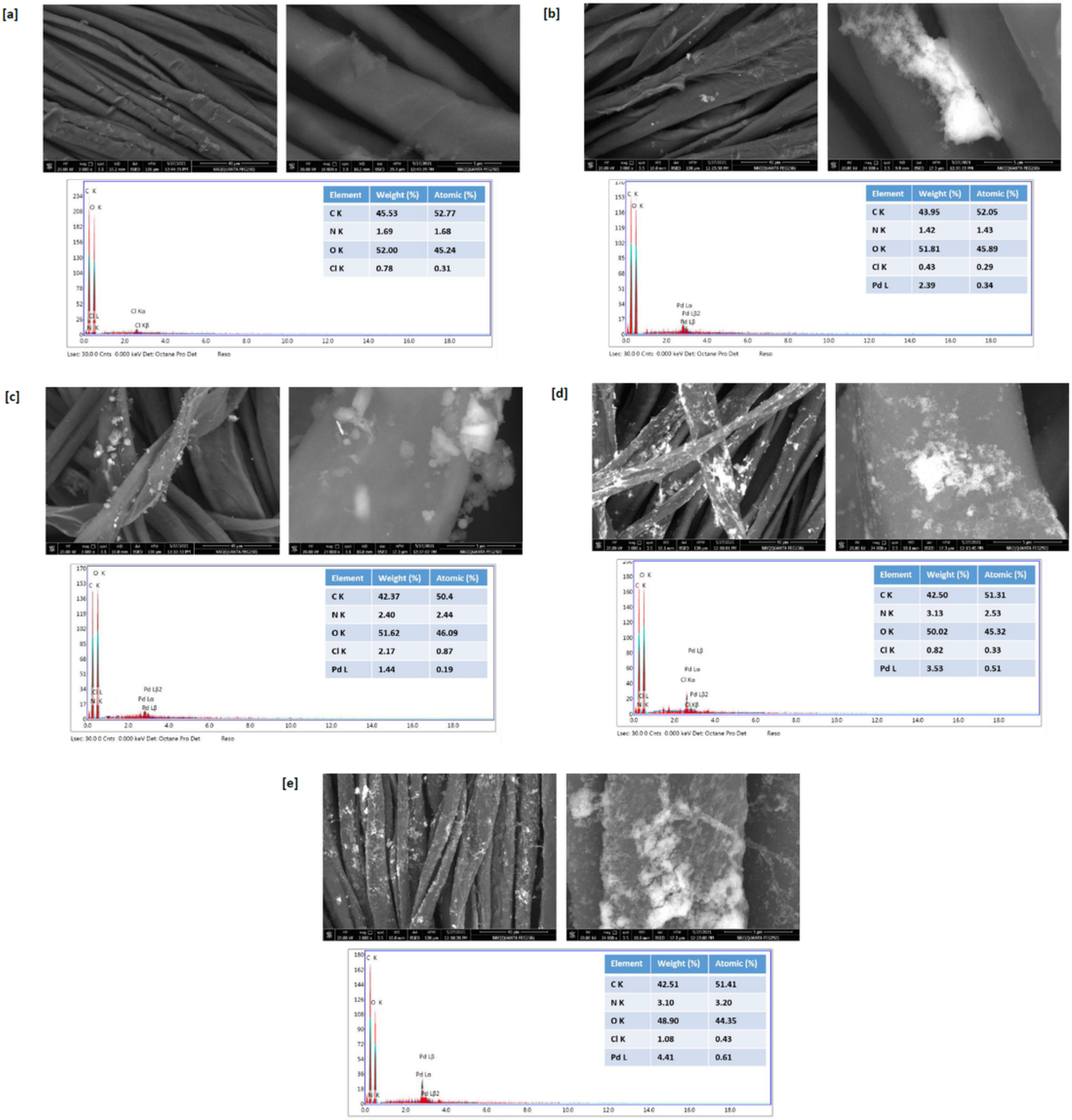

Figure 3

SEM photos for the Pd-modified cotton fabrics; [a] cationized cotton, [b] Pd-C4, [c] Pd-CC (50)4, [d] Pd-CC (100)3 and [e] Pd-CC (100)4.

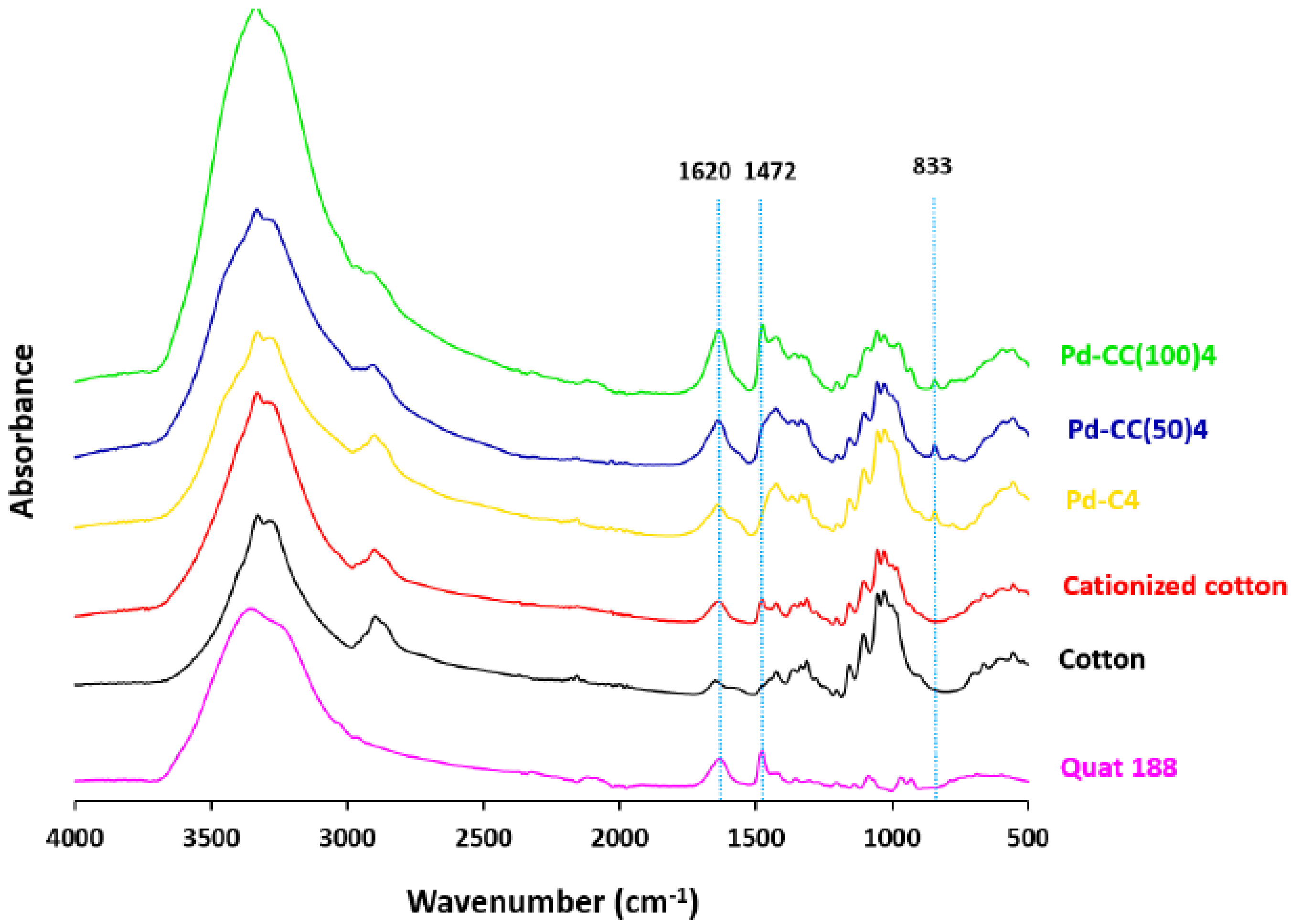

Figure 4

FTIR for the Pd-modified cotton fabrics.

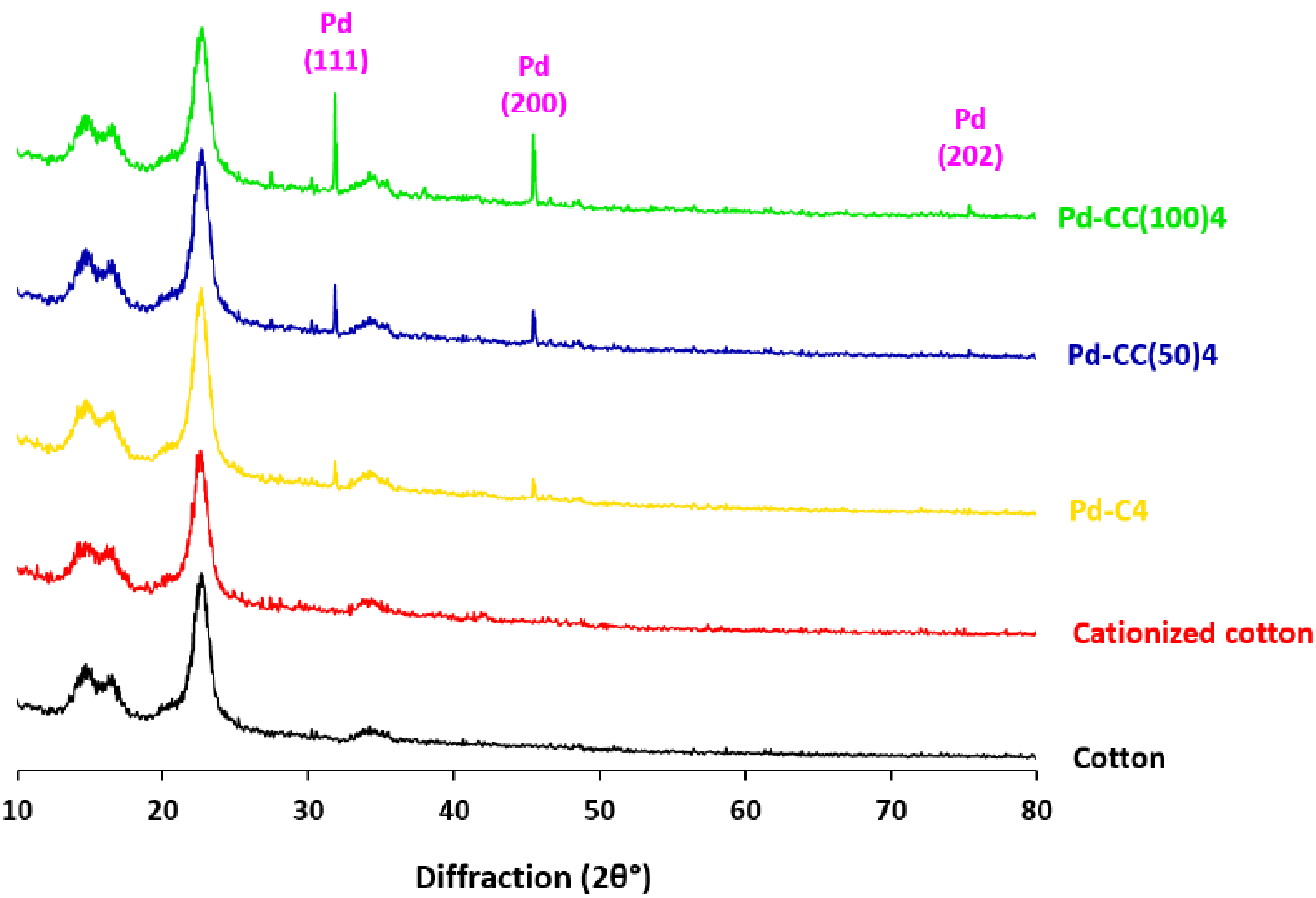

Figure 5

XRD for the Pd-modified cotton fabrics.

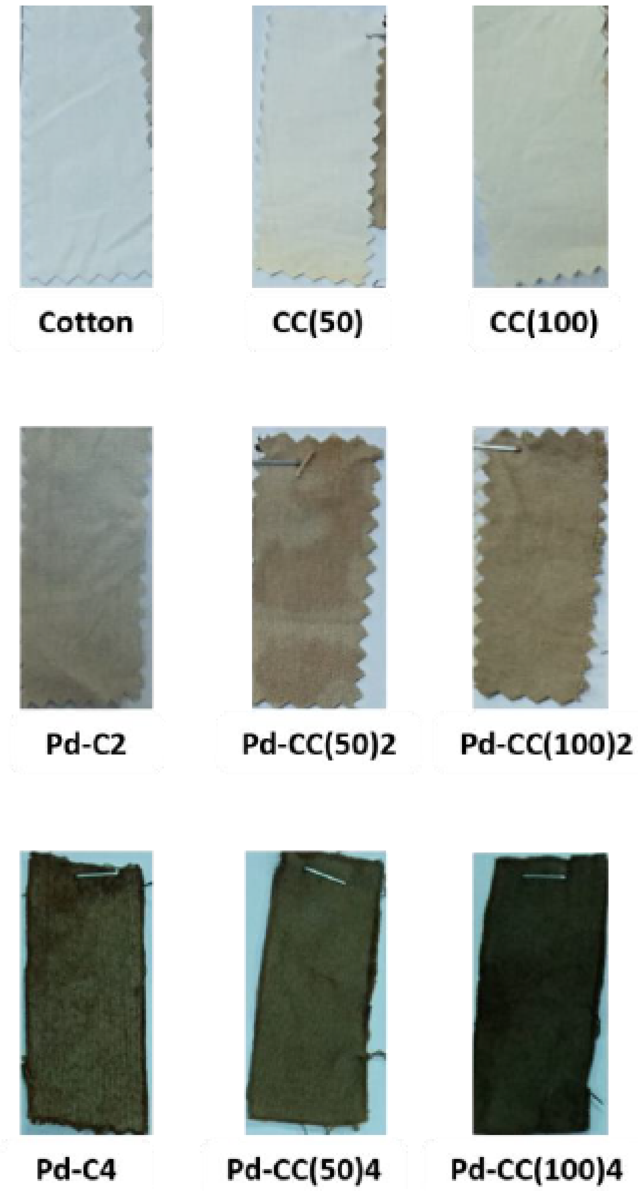

Figure 6

Photographs for the Pd-modified cotton fabrics.

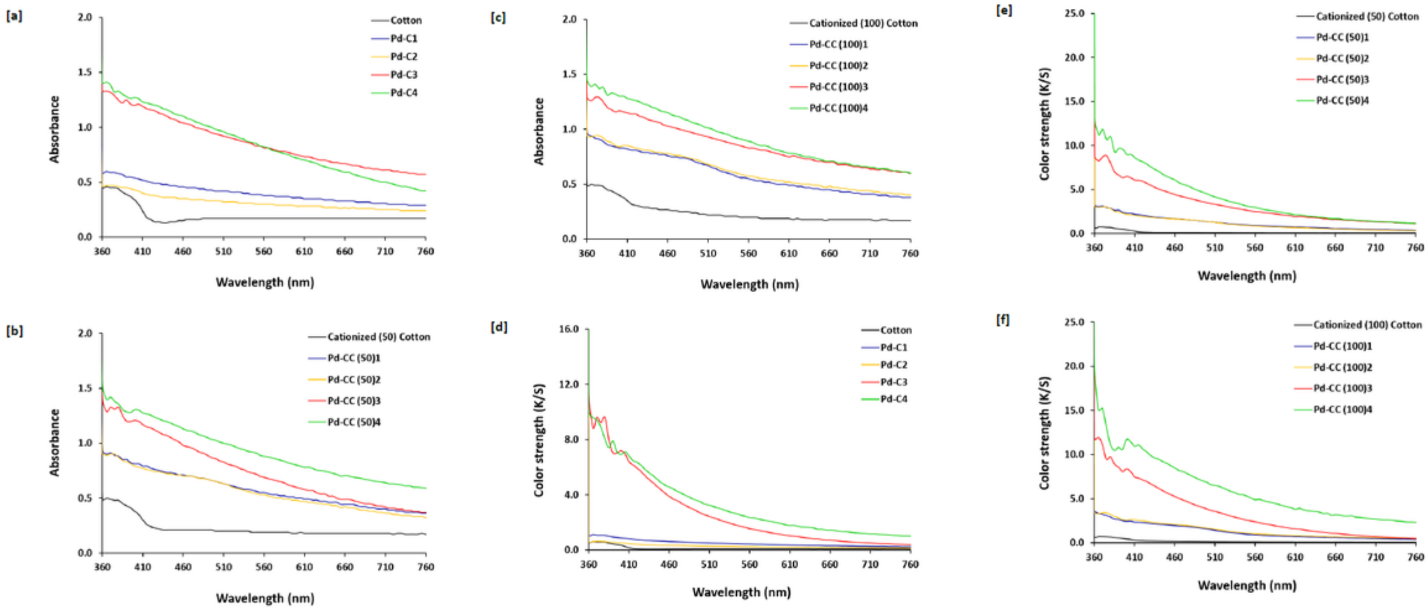

Figure 7

Colorimetric data for the Pd-modified cotton fabrics; [a, b, c] absorbance and [d, e, f] color strength.

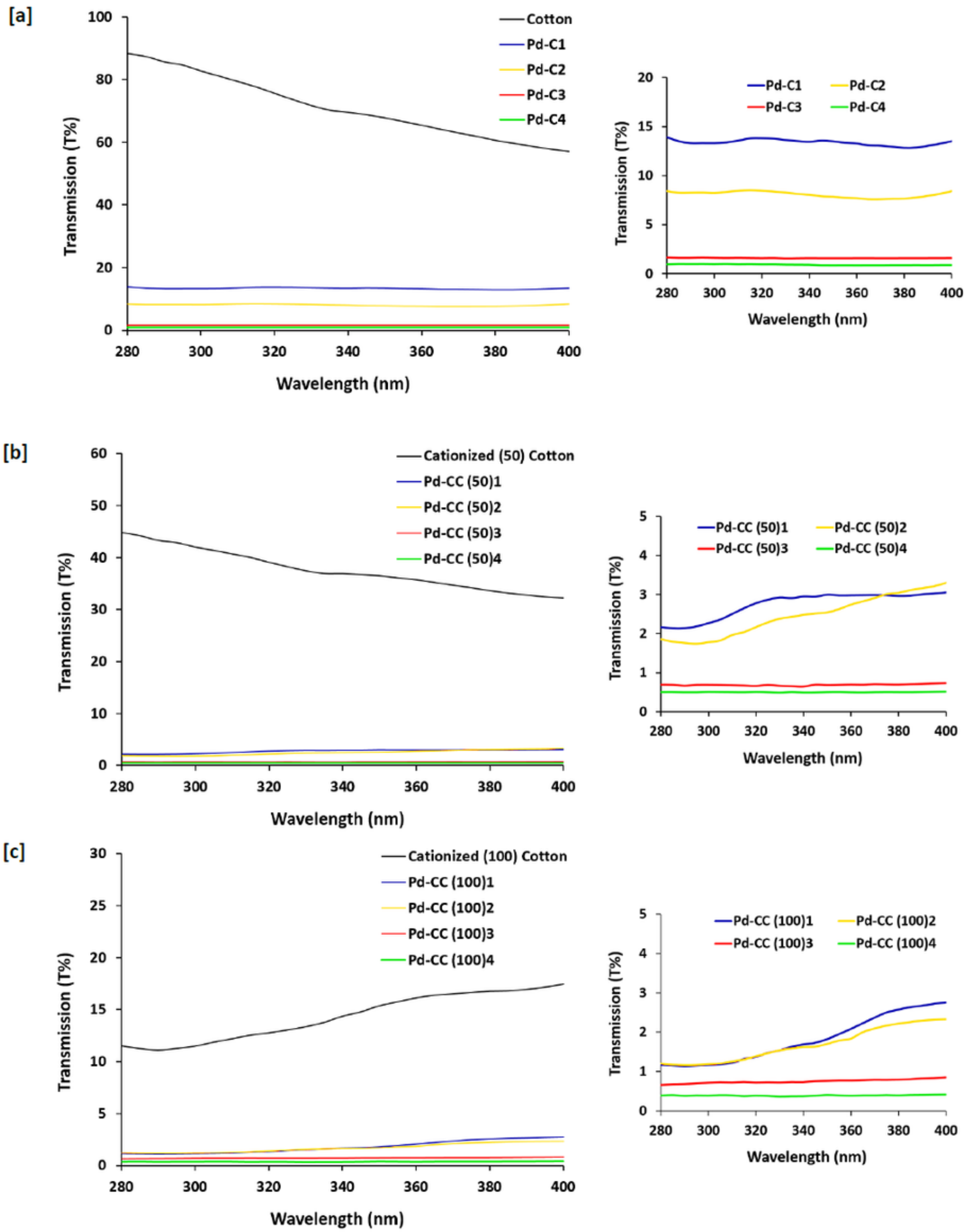

Figure 8

Transmission of ultraviolet radiation through the Pd-modified cotton fabrics.

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