PRODUCING MULTIFUNCTIONAL COTTON FABRICS USING NANO CeO_2 DOPED WITH NANO TiO_2 AND ZnO

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Abstract:

Cross-link method has been used to load nano CeO_2, ZnO, and TiO_2 on the surface of cotton fabric. Three types of nanocomposite fabrics are prepared (cotton/CeO_2, cotton/CeO_2/ZnO, and cotton/CeO_2/TiO_2) and their properties were investigated. Field emission scanning electron microscopic (FESEM) images of the samples showed good distribution of nanomaterial, and energy dispersive X-ray spectroscopy (EDX) and X-ray fluorescence (XRF) samples proved the usage of amount of nanomaterials. On the other hand, elemental mapping was used to study the distribution of each nanomaterial separately. Antibacterial property of the samples showed excellent results against both Gram-negative and Gram-positive bacteria. Also ultraviolet (UV)-blocking of treated samples showed that all samples have very low transmission when exposed to UV irradiation.

Keywords:

Nano cerium dioxide, zinc oxide, titanium dioxide, UV-blocking, antibacterial

1. Introduction

Cotton is the most abundant and popular biopolymer and valuable raw material in the world of textile industry. Cotton fibers and fabrics have been used from ancient periods. Owing to its abundance, biodegradability, and physical properties such as high humidity absorption, glossy, high stability, alkaline resistance, and amorphous structure, cotton is an extremely great renewable resource for the improvement of environment friendly, and utilized in paper manufacturing and textile industry. Cotton fibers present a symmetric surface intercommunicated with the hydroxylated nature of the organizing hydro-glucose units. This property results in the high hydrophilicity of cotton, which provides the formation of powerful hydrogen bonding between cotton fibers and the organization of three-dimensional fiber-based structures [1–5].

In the last decade, an extensive range of nanoparticles and nanostructures can be fixed in fabrics, which gives new features to the ultimate fabric supply. Nowadays, more consideration has been paid to the usage of semiconductors such as CdS, Fe2O3, ZnO, Ce, respectively [6–9].

Cerium is considered as one of the rare-earth elements which has no biologic role and is not so toxic. Cerium has variable electronic structure. The energy of the 4f electron is nearly the same as the outer 5d and 6s electrons which are delocalized in the metallic state, and only a small amount of energy is required to change the relative occupancy of these electronic levels, giving rise to dual valence states [10]. Cerium has different properties such as being environment friendly, good photocatalytic material [11], and has very good antibacterial property [12].

One of the famous semiconductor material is zinc oxide. Its energy band gap is 3.3 eV. Nano zinc oxide has many applications such as photocatalytic activity, ultraviolet (UV) resistance, antibacterial, low toxicity, etc. Ultrasonic is one of the methods to sediment nano zinc oxide on fabric surface. In this method, the energy of irradiation can deposit the nanoparticles on fabric without any agglomeration [13]. Titanium dioxide nanoparticles are highly considered by researchers due to their unique properties such as electrical conductivity, photo activity, antibacterial property [14, 15], self-cleaning [16–19], non-toxicity [20, 21], and preventing the transmission of UV spectra [22, 23]. The problem of using nano photocatalysts such as nano ZnO and nano TiO_2 is that they are exited under UV irradiation which is low in day light [24, 25]. So, to overcome to this problem, doping of these nanoparticles is essential [26]. By doping, the energy band gap is changed and leads to enhance the adsorption range of light acquisition [27, 28]. However, based on unparalleled electronic construction of some rare-earth metals, doping of these materials can produce photoelectrons which can increase electros and holes;

therefore, the number of photo charges proliferates and leads to better photocatalytic activity and antibacterial processes [29–32]. In the presence of light, the electrons of valence band are activated to the conduction bond which produces electrons (e−) and holes (h+) that these groups can generate O_2^- and OH^- so as to react with organic composition of any fungi cells and to destroy them [33–36].

In this paper, nano cerium dioxide/zinc oxide and nano cerium dioxide/titanium dioxide synthesis on the surface of cotton fabric with their properties such as antibacterial, photocatalytic activity, and UV-blocking were investigated and compared.

2. Experimental

2.1 Materials

According to the purpose of this project, we prepared 100% bleached cotton fabric with a warp density of 26 yarn/cm (warp count, 19.6 tex), weft density of 22 yarn/cm (weft count, 29.5 tex), and fabric weight of 126.8 g/m2 from Yazdbaf company, Iran. Also, we prepared nanopowder of cerium dioxide from Aldrich (CAS Number 1306383) Company with an average particle size of less than 50 nm and purity of more than 99.95% with specific surface area of 30 m^2/g; nano titanium dioxide (Degussa P-25) with average particle size of less than 50 nm; nano ZnO with CAS number of 1314132 and average particle size of less than 50 nm with surface area of 15–25 m^2/g from Sigma Aldrich company; sodium hypo-phosphate from Merck as a catalyst and succinic acid as a cross-link agent from Merck were prepared. A Euronda ultrasonic bath model Eurosonic 4D, 350 W, 50/60 Hz (Italy) was used. The morphology of samples was observed by field emission scanning electron microscope (FESEM), UV-blocking, and photocatalytic properties of samples were determined using Perkin Elmer Lambda UV-vis spectrophotometer.

2.2 Methods

First of all, cotton fabric was rinsed with distilled water. The cotton fabric was coated with nanomaterials, using cross-link method as follows: Samples of washed cotton were immersed in an aqueous solution of succinic acid in the presence of sodium hypophosphate for 1 hour. Then, the samples were dried for 3 min at 80°C. During this process, nanomaterial suspensions were sonicated for 30 min at 50°C. Afterward, the cotton fabrics with loaded carboxylic acid were immersed into this aqueous suspension of nanomaterials and heated at 80°C. Then, for fixation of nanomaterials, the fabric was kept in an oven at 100°C for 30 min. Finally, the unbounded nanomaterials were washed under sonication in distilled water for 10 min. Table 1 shows the formulations of samples investigated in this study.

Table 1. Specification of samples

Sample code	Percentage of nanomaterials		
	Nano CeO_2	Nano TiO_2	Nano ZnO
A	2%	0%	1%
B	2%	1%	0%
C	2%	0%	0%
D	0%	2%	0%
E	0%	0%	2%
F	0%	0%	0%

3. Results and Discussion

3.1 FESEM, EDX, XRF, and elemental mapping analysis

FESEM images of treated samples and raw samples were obtained to investigate their morphology. The condition of FESEM was 5 kV at different magnifications. Figure 1 shows the obtained images, and it clearly illustrates the presence of nanomaterials. On the other hand, the most important point is that there are not any aggregate or agglomeration of nanomaterials which prove the right method of loading nanomaterials on the surface of fabric. Figure 1A shows the distribution of nano CeO_2 and nano ZnO on the surface of cotton fabric, (b) shows the distribution of nano CeO_2 and nano TiO_2 on the surface of cotton fabric, and (c) shows the distribution of nano CeO_2 on the surface of cotton fabric and although the nanopowders of CeO_2, ZnO, and TiO_2 are illustrated, respectively. It has been shown that the particle size of these nanomaterials is less than 50 nm.

On the other hand, the energy dispersive X-ray spectroscopy (EDX) analysis of treated samples show that the samples have significant amount of nanomaterials which proves the presence of CeO_2, ZnO, and TiO_2 (Figure 2). The other elements that are in EDX are referred to cotton. Elemental mapping was used to study the distribution of nano CeO_2, Ti, and Zn particles separately (Figure 3). The excellent distribution of these three nanoelements are perspicuously illustrated on the surface of cotton fabric and this can prove the prosperous distribution of nanomaterials on surface of fabric.

X-ray fluorescence (XRF) spectrometry is an affirmative analytical method extensively used in industrial and research utilization for elemental composition analysis. Table 2 shows the results of XRF analysis of samples before and after washing. The results show the correct ratio of nanomaterial in samples which confirms the used amount of nanomaterials. Also after washing, there was no much change in data and this can prove that the samples have good washing fastness.

3.2 UV-blocking analysis

Figure 4 shows the UV transmission of samples in the range of 200–800 nm. As shown, the treated samples have lower spectrum than raw samples. In other words, UV protection of samples loaded with nanomaterials are higher than raw samples. By analyzing the spectrums, it can be demonstrated that the sample treated with nano CeO_2 has lower protection against UV irradiation in comparison with samples that are treated with CeO_2/ZnO and CeO_2/TiO_2. This is due to the UV adsorption capability of titanium dioxide and zinc oxide.

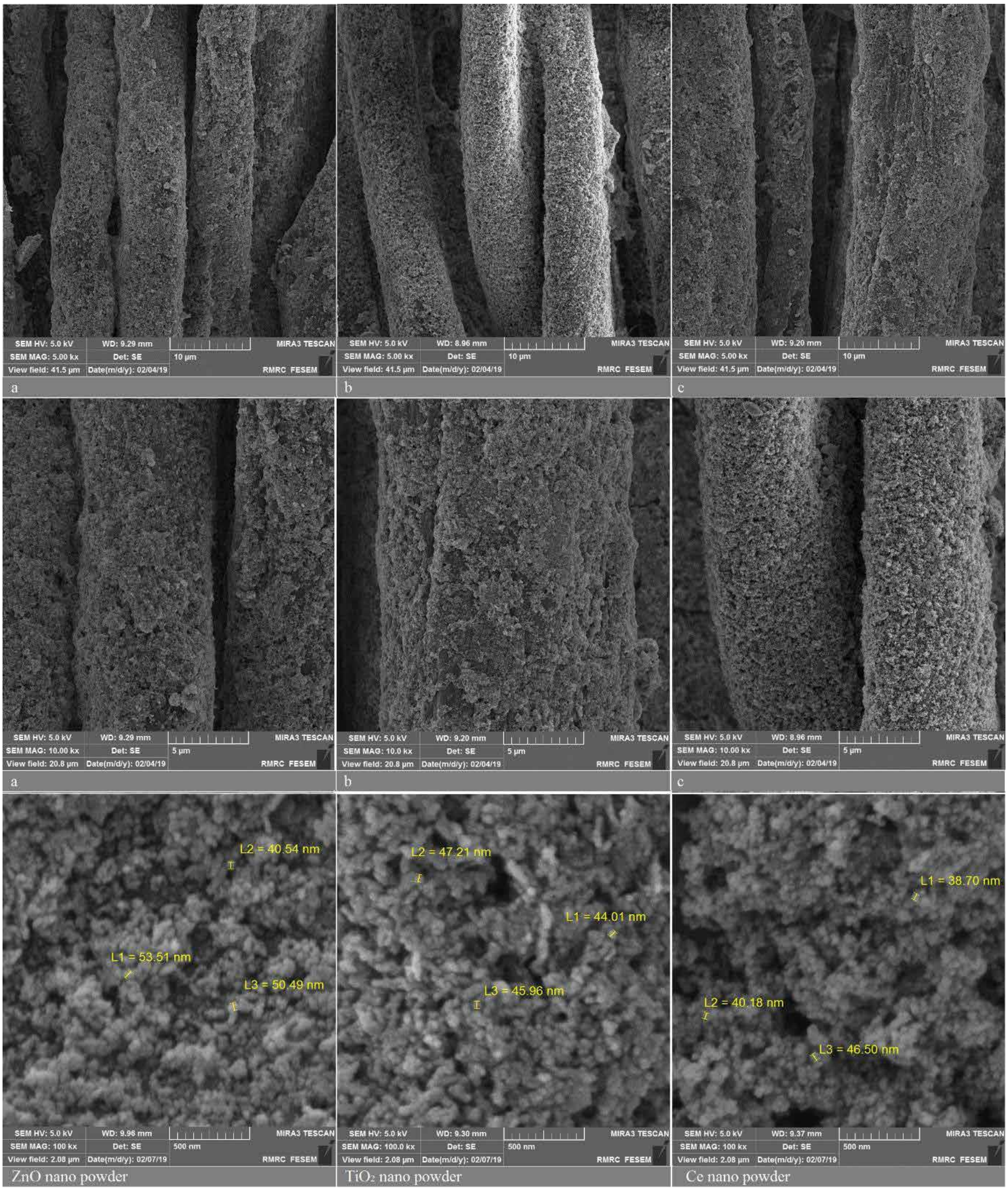

Figure .1. FESEM images of (A) sample A with two magnifications, (B) sample B with two magnifications, and (C) sample C with two magnifications, and ZnO, TiO_2, CeO_2 nano powders, respectively.

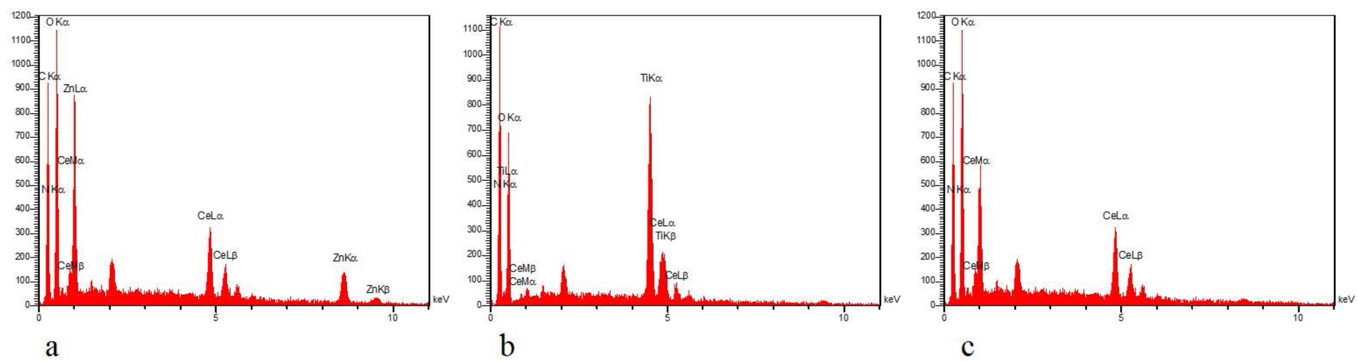

Figure 2. EDX images of treated samples.

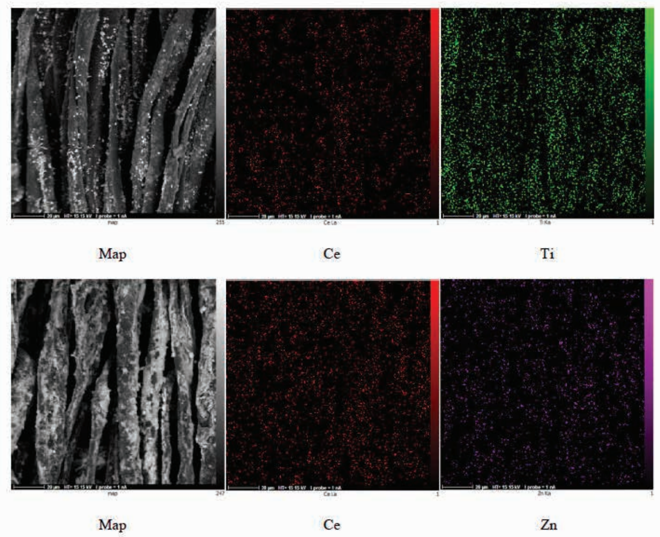

Figure 3. Elemental mapping of samples.

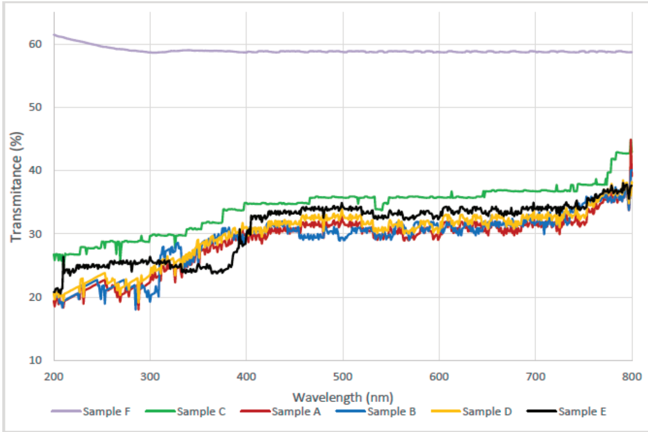

Figure 4. UV transmittance diagram of samples.

Moreover, the UV-blocking activity of these nanomaterials is due to the synergetic UV absorption of CeO_2, ZnO, and TiO_2. UV-blocking property of fabrics is illustrated by UV protection factor (UPF). This factor is measured via Eq. (1). In this equation, *Eλ* is the relative erythemal spectral effectiveness, *Tλ* is the spectral transmittance of the specimen, *Sλ* is the solar UV spectral irradiance, and *dλ* is the wavelength increment. The UPF of the raw sample is 5, which has no protection against transmittance of UV irradiation. However, the measured UPF of the treated samples are 68, 101, 53, 88, and 49 for samples A, B, C, D, and E, respectively. As a consequence, the samples with CeO_2/TiO_2 have better UV protection compared with the other samples due to UV absorption ability of nanoparticles.

$$UPF = \frac{\int_{200}^{400} E\lambda \times S\lambda \times d\lambda}{\int_{200}^{400} E\lambda \times S\lambda \times T\lambda \times d\lambda} \quad \text{Eq. (1)}$$

3.3 Antibacterial analysis

The result of the cultivating bacteria test is presented in Figure 5. The test result shows that raw sample is a suitable place for the growth of both bacteria. It means that the antibacterial property of raw sample is zero. However, the samples that are treated with nanomaterials have antibacterial property against Gram-negative and Gram-positive bacteria. The antibacterial activity of samples A and B coated with nano CeO_2/ZnO and CeO_2/TiO_2 was 100% against both bacteria, whereas the antibacterial activity of sample C coated with nano CeO_2 is 98.3% for *Escherichia coli* and 96.8% for *Staphylococcus aureus*, respectively. Also, the antibacterial activity of sample D which is coated with nano TiO_2 is 99.6% for *E. coli* and 98.9% for *S. aureus*, and antibacterial activity of sample E which is coated with nano ZnO is 98.5% for *E. Coli* and 88.7% for *S. aureus*. The reason for higher antibacterial property of samples A and B compared with sample C is due to the presence of another material (ZnO and TiO_2) which can reinforce the antibacterial property of nano cerium. On the other hand, the antibacterial property of samples against *E. coli* has been better than *S. aureus*. This can be explained by difference in the thicknesses of the cell walls of these bacteria. *E. coli* has thinner cell wall than *S. aureus*.

3.4 Photocatalytic performance and water drop analysis

Figure 6 illustrates the photocatalytic property of samples which are stained with methylene blue dye. The raw sample shows no photocatalytic activity under UV irradiation. The results show that by increasing nanomaterials on surface of cotton, the ΔE of the samples decreases. It means that the self-cleaning property is increased and stain degradation is enhanced. Due to the obtained results, ΔE of raw sample is 39.91 which is so high and does not have any self-cleaning property. On the other hand, the ΔE of samples A and B is about 19 and 18 that is excellent for self-cleaning. ΔE of sample C is a little higher that samples A and B and this is due to doping nano ZnO and TiO_2 on CeO_2 in samples A and B. By comparing the samples, we come to conclusion that doping nano CeO_2 to nano TiO_2 has gain much photocatalytic activity on cotton.

Table 2. XRF data of samples

Oxides	Weight percent before washing (wt.%)			Weight percent after washing (wt.%)		
	A (%)	B (%)	C (%)	A (%)	B (%)	C (%)
TiO_2	0	12	0	0	12	0
CeO_2	25	23	32	24	21	32
ZnO	14	0	0	13	0	0
Na_2NO_3	26	24	29	26	23	27
Na_2CO_3	35	41	39	35	41	39

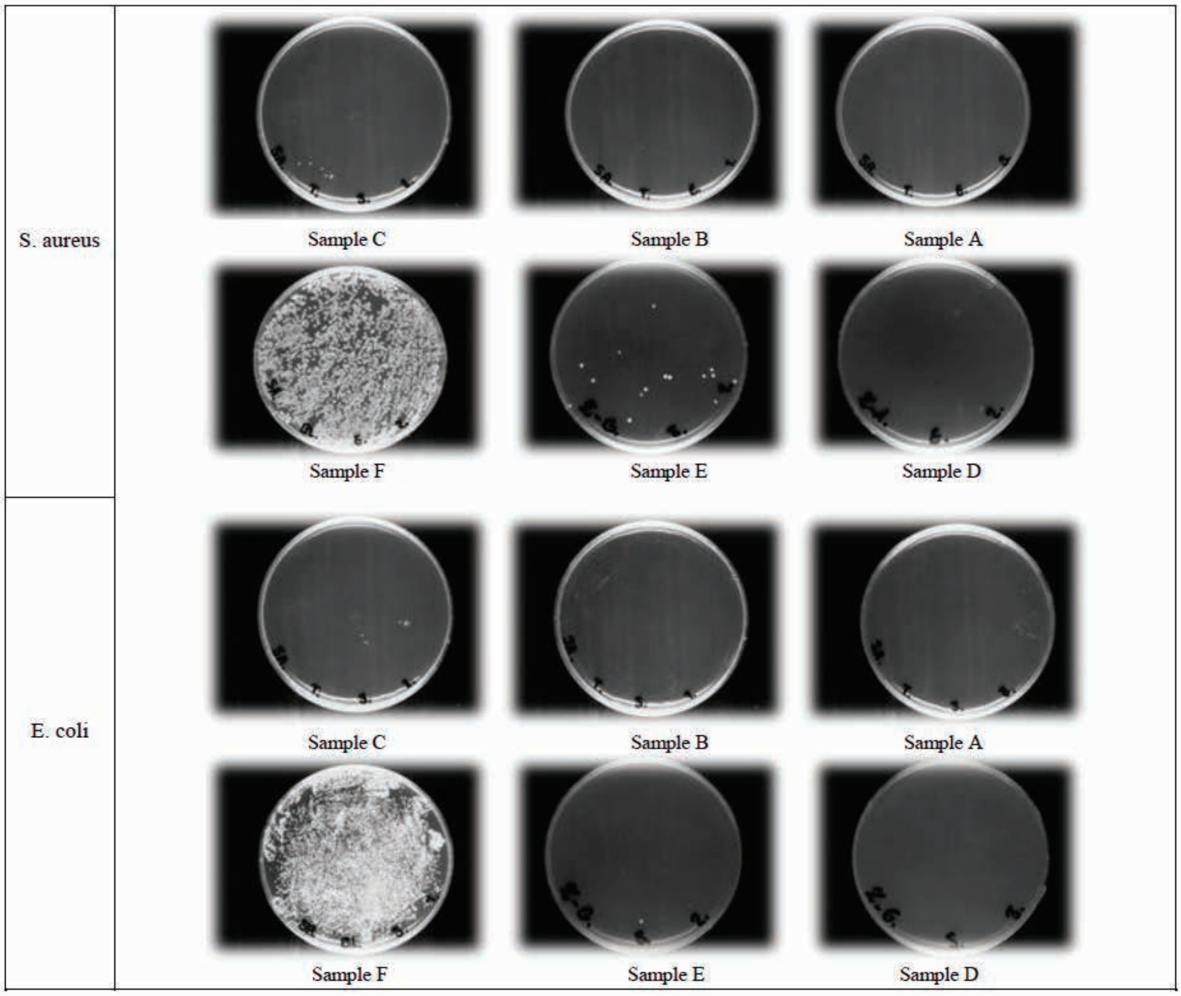

Figure 5. Antibacterial efficiency of raw and treated samples.

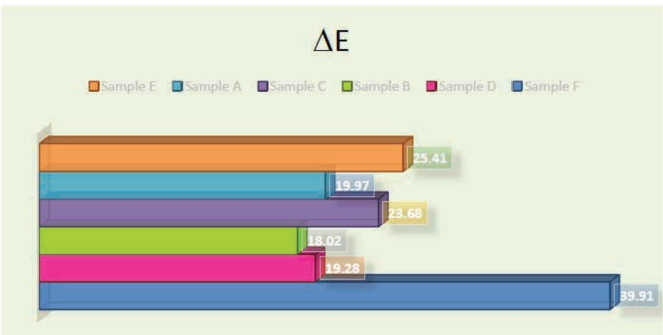

Figure 6. ΔE of raw and treated samples.

Table 3. Water dropping data of samples

Sample	Water drop absorption (s)	Water drop absorption after UV irradiation (s)
A	1″:97‴	1″:18‴
B	2″:06‴	1‴:15‴
C	1″:82″	1″:28″
D	1″:93‴	1″:21‴
E	1″:56‴	1″:26‴
F	1″:37‴	1″:37‴

On the other hand, the water drop test was done before and after UV irradiation. The results after UV irradiation show that by adding nanomaterials, the water adsorption is good. This can be due to the introduction of base on hydroxyl groups after activation under UV. Table 3 shows the results of water dropping.

4. Conclusion

In this study, nano CeO_2 has been loaded on the surface of cotton fabric and nano ZnO and TiO_2 was doped on it. Three types of fabric (cotton/CeO_2, cotton/CeO_2/ZnO, and cotton/CeO_2/TiO_2) were prepared and properties of the obtained fabric were investigated. The UV protecting property of loaded samples showed that the transmission of UV from these fabrics is lower than raw sample. On the other hand, by comparing CeO_2-loaded fabric in comparison of CeO_2/ZnO and CeO_2/TiO_2, UV-blocking property of samples with ZnO and TiO_2 was better than CeO_2-loaded fabric. This is due to UV-blocking activity of the nanomaterials and synergetic UV absorption. On the other hand, by investigating the photocatalytic performance of samples, doping nano CeO_2 to nano TiO_2 has gain much photocatalytic activity on cotton. Also antibacterial property of treated samples was investigated by both Gram-negative and

Gram-positive bacteria and the result showed that all samples have excellent antibacterial property. So that samples that contain ZnO and TiO_2 have 100% antibacterial and the sample that treated just with CeO_2 has more than 96% antibacterial property. The morphology of samples is illustrated by scanning electron microscopy (SEM) and it confirms the good distribution of nanomaterials on the surface of fabric and also EDX and XRF analyses proves the percentage usage of nanomaterials.

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