Indian Journal of Fibre & Textile Research
Vol. 46, March 2021, pp. 57-62

Antibacterial, self-cleaning and UV blocking of wool fabric coated with nano Ce/ZnO and Ce/ TiO_2

Salar Zohoori[1], Pedram Payvandy[1,2,a] & Maryam Bekrani[1]

[1]Center of Excellence for Machine Vision in Textile and Apparel Industry, [2]Department of Textile Engineering, Yazd University, Yazd, Iran

Received 21 April 2019; revised received and accepted 14 June 2020

Ultrasonic method has been used in order to load nano Ce, ZnO and TiO_2 on the surface of wool fabric. Three types of nano composite fabric have been prepared (wool /Ce, wool /Ce/ZnO, and wool /Ce/ TiO_2) and their physical properties are examined. Field emission scanning electron microscope images of the samples show a good distribution of nano material, and EDX and XRD findings prove the amount usage of nano materials. On the other hand, elemental mapping is used to study separately the distribution of each nano material. Antibacterial property of the samples shows excellent result against both Gram-negative and Gram-positive bacteria. Also, UV blocking of treated samples shows low transmission from all samples, when exposed to ultra violet irradiation. Self-cleaning property of wool samples illustrates that doping of nano materials on the surface of wool fabric has an excellent effect on increasing the self-cleaning efficiency.

Keywords: Antibacterial, Cerium, Self-cleaning property, UV-blocking, Wool

1 Introduction

Wool is one of the popular natural fibers, which has special properties such as flexibility, warmness, antistatic, etc.[1-4]. Another fact of wool fabric is the special formula which plays a unique role in its physical and chemical properties. For example, sulphur of cysteine gives the strength of wool and cortex provides hydrophilic property[5-7].

In the last decade, an extensive range of nano particles and nano structures have been used in fabrics, which gives new features to the ultimate fabric supply. Nowadays, the use of semiconductors such as CdS, Fe_2O_3, ZnO and Ce are being considered more[8-11].

Cerium is considered as one of the rare-earth elements, which has no biological role and is not so toxic. Cerium has variable electronic structure. The energy of 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[12]. Cerium has different properties, such as environment friendly and good photocatalytic effect[13], and has very good antibacterial property[14].

One of the famous semiconductor materials is zinc oxide. Its energy band gap is 3.3eV. Nano zinc oxide has many applications, such as photocatalytic activity, 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 nanoparticles on fabric without any agglomeration[15]. Titanium dioxide nanoparticles are highly considered by researchers because of their unique properties, such as electrical conductivity, photo activity, anti-bacterial property[16-17], self-cleaning[18-21], non-toxicity[22-23] and preventing the transmission of ultra violet spectra[24-25]. The problem of using nano photocatalyses, such as nano ZnO and nano TiO_2 is that they are exited under UV irradiation which is low in day light[26-27]. So, in order to overcome this problem doping of these nano particles are essential[28]. By doping, the energy band gap is changed and leads to enhance the adsorption range of light acquisition[29-30]. However, based on unparalleled electronic construction of some rare earth metals, doping of these materials can produce photo electrons, which can increase electrons and holes. Therefore, the number of photo charges are proliferate and leads to better photocatalytic activity and anti-bacterial processes[31-34]. In presence of light, the electrons of valence band are activated to the conduction bond which produces electrons (e-) and holes (h+), showing that these groups can generate O_2- and OH-, so as to react with organic composition

[a] Corresponding author.
E-mail: peivandi@yazd.ac.ir

of any fungi cells to destroy them[35-38]. The effect of ultrasonic is reported in many papers in order to prepare a homogenous solution for spinning[39-40]. Ultrasonic can cause to shift the energy in to nano materials via cavitation process[41]. This process contain foundation, development and severe breaking of energy on surface of nano materials. This energy is about 100 kJ/mol[42].

In this study, nano cerium/zinc oxide and nano cerium/titanium dioxide have been synthesized on the surface of wool fabric and the treated fabric properties, such as antibacterial, photocatalytic activity and UV-blocking are investigated and compared.

2 Materials and Methods

2.1 Materials

Plain weave wool fabric (173 g/m^2) was used. Powder of nano cerium oxide (average particle size<50nm, purity>99.95%, specific surface area of 30m^2/g) from Aldrich (CAS Number 1306383) and nano titanium dioxide (average particle size<50nm) (Degussa P-25) were prepared and used. 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), and UV-blocking properties of samples were determined using Perkin Elmer Lambda UV-vis spectrophotometer. FESEM images were obtained with 5kV at different mahnifications. The X-ray diffraction (XRD) analysis was performed using a Bruker (model D8 Discover) X-ray Diffractometer, Germany.

2.2 Methods

Initially, the wool fabric was washed with distilled water in order to remove any extra materials. The wool fabric was then coated with nano materials; nano materials suspensions were sonicated for 30 min at 50^{o}C. The washed wool fabric was immersed into the aqueous suspension of nano materials and heated at 80^{o}C. Then, for fixation of nano materials, the fabric was kept in an oven at 100^{o}C for 30 min. Finally, the unbounded nano materials were washed off under sonication in distilled water for 10 min. Table 1 shows the formulations of samples investigated in this study.

3 Results and Discussion

3.1 FESEM, EDX, XRF & Elemental Mapping Analyses

Figure 1 shows the obtained images, clearly indicating the presence of nano materials. On the

Table 1 — Specification of samples

Sample code	Percentage of nano materials		
	Nano Ce	Nano TiO_2	Nano ZnO
A	2	0	1
B	2	1	0
C	2	0	0
D	0	0	0

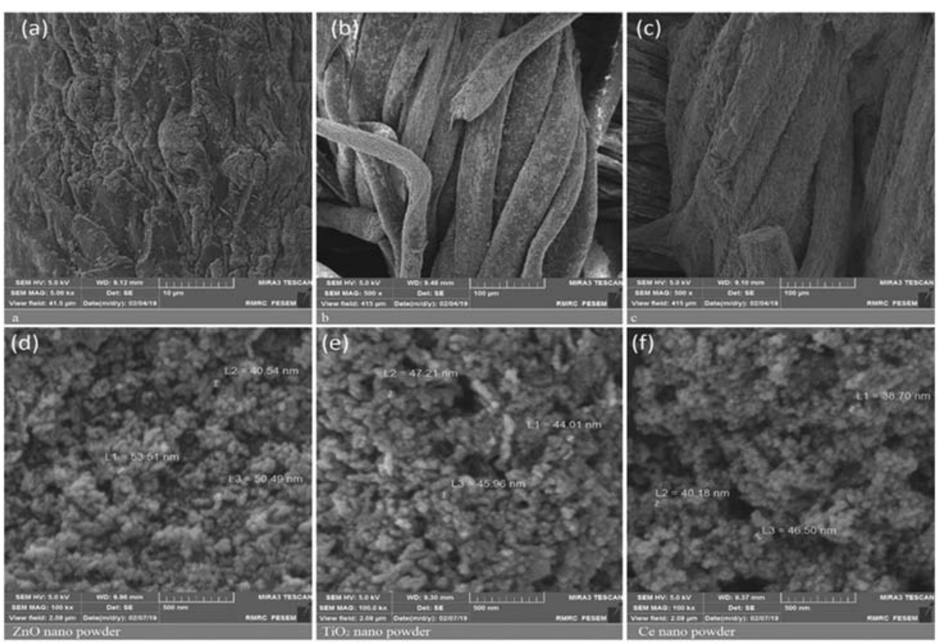

Fig. 1 — FESEM images of (a) sample A, (b) sample B, (c) sample C, (d) ZnO nano powder, (e) TiO_2 nano powder, and (f) Ce nano powder

other hand, the most importantly there is no aggregate or agglomeration of nano materials, which proves the right method of loading nano materials on the surface of fabric. Figure 1(a) shows the distribution of nano Ce and nano ZnO on the surface of washed fabric, Figure 1(b) shows the distribution of nano Ce and nano TiO_2 on the surface of washed fabric, Figure 1(c) shows the distribution of nano Ce on the surface of washed fabric, although the nano powders of Ce, ZnO and TiO_2 are illustrated respectively. It has been observed that the particle sizes of these nano materials are less than 50nm.

On the other hand, the EDX analysis of treated samples shows that the samples have significant amount of nano materials, which proves the presence of Ce, ZnO and TiO_2 (Fig. 2). The other elements shown in EDX are referred to wool. Elemental mapping is used to study separately the distribution of nano Ce, Ti and Zn particles separately (Fig. 3). The excellent distribution of these three nano elements are perspicuously illustrated on the surface of wool fabric and this can prove the prosperous distribution of nano materials on surface of fabric.

XRD patterns are used to confirm the presence of cerium, zinc oxide and titanium dioxide on the fabric surface and to estimate the crystalline size. Figure 4 illustrates the XRD patterns of wool/Ce/ZnO and wool/Ce/TiO_2. The diffraction peaks monitor around 2θ=30.7° and 34.5°, which is related to the structure of wool and α-keratin. Six reflection peaks that appeared at 2θ values of 25.4°, 37.0°, 37.7°, 48.8°, 54.1°, and 55.1° could be indexed as the anatase structure of titanium dioxide and the reflection peaks that appear at 2θ values of 28.7°, 33.0°, 47.6°, 56.3°, could be indexed as the cubic structure of cerium. In Fig. 4(a), six reflection peaks that appear at 2θ values of 31.2°, 36.1°, 56.5°, 62.8°, 67.7°, and 69.1°, could be indexed as the hexagonal structure of zinc oxide.

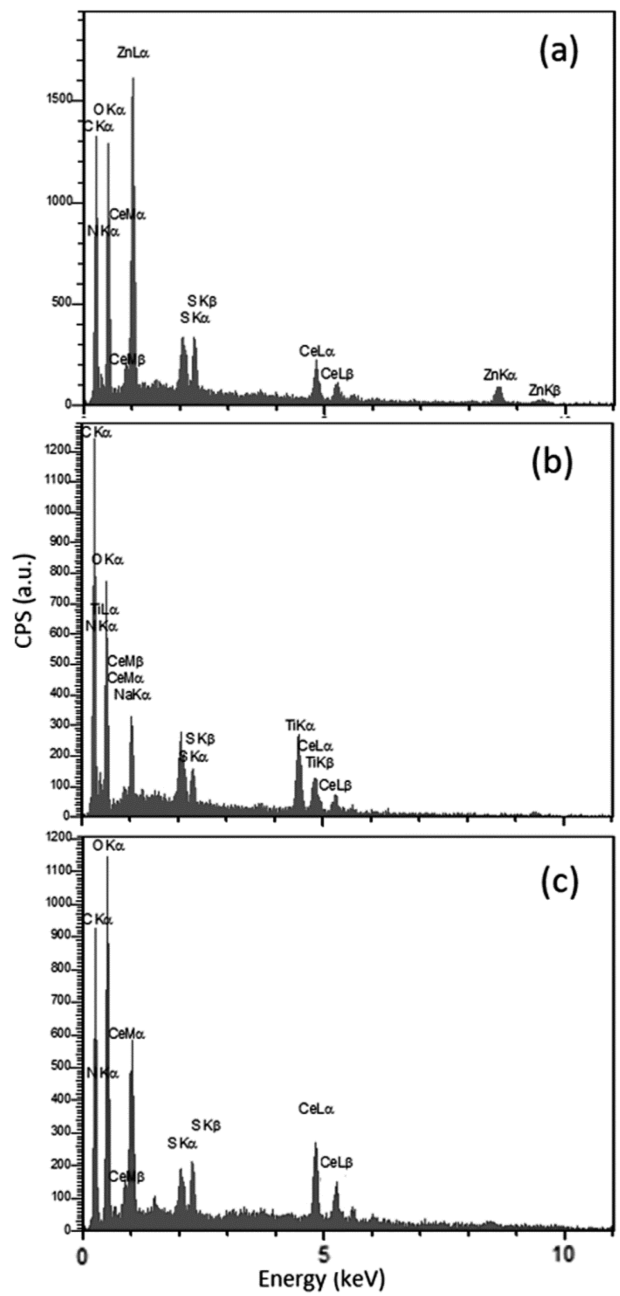

Fig. 2 — EDX images of treated samples (a) sample A, (b) sample B, (c) sample C

3.2 UV Blocking Analysis

Figure 5 shows the ultra violet transmission of samples in the range of 200-800 nm (according to AATCC 183-2004). It is observed that the treated samples have lower spectrum than raw sample. In other words, UV protection of samples loaded with nano materials is higher than raw samples. By analyzing the spectrums, it can be demonstrated that the sample treated with nano Ce has lower protection against UV irradiation in comparison with samples treated with Ce/ZnO and Ce/TiO_2. This is due to the UV adsorption capability of titanium dioxide and zinc oxide. Moreover, the UV-blocking activity of these nano materials is due to the synergetic UV absorption of Ce, ZnO and TiO_2.

3.3 Antibacterial Analysis

The result of the cultivating bacteria test (according to AATCC 100-2004) is presented in Fig. 6. The test result shows that raw sample is suitable for the growth of both bacteria. It means

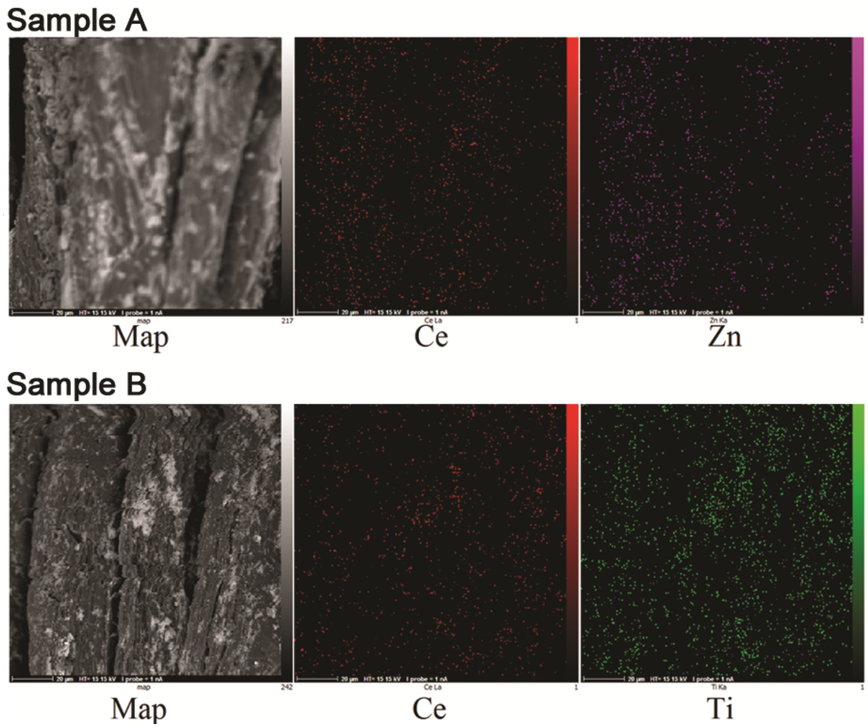

Fig. 3 — Elemental mapping of samples A and sample B with magnification × 1.5k

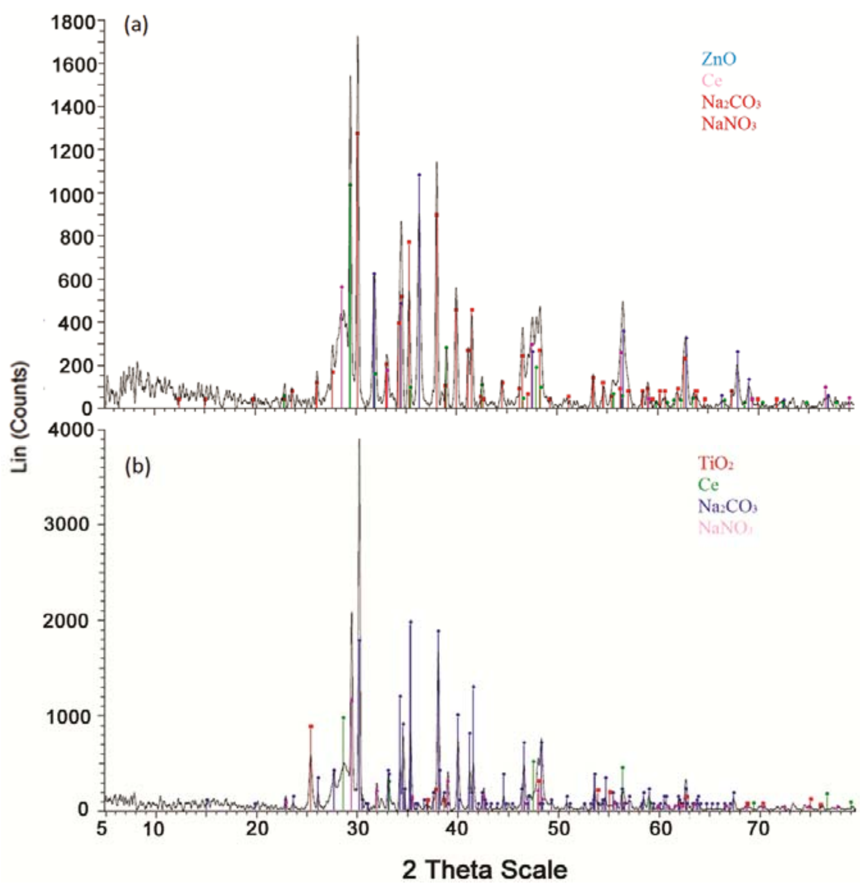

Fig. 4 — XRD diagram of (a) sample A and (b) sample B

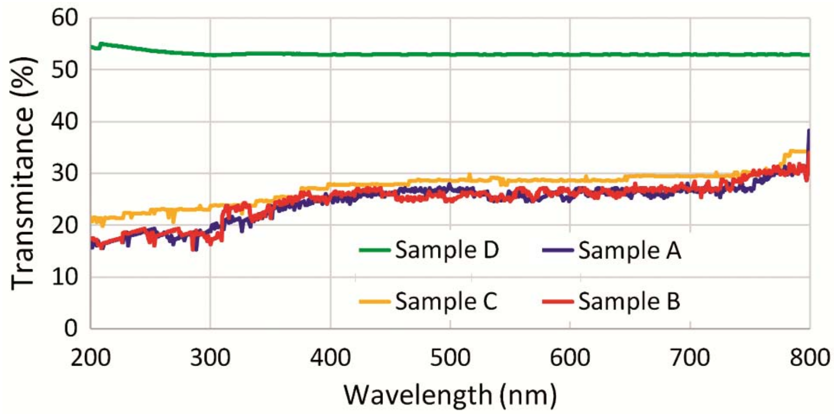

Fig. 5 — UV transmittance diagram of samples

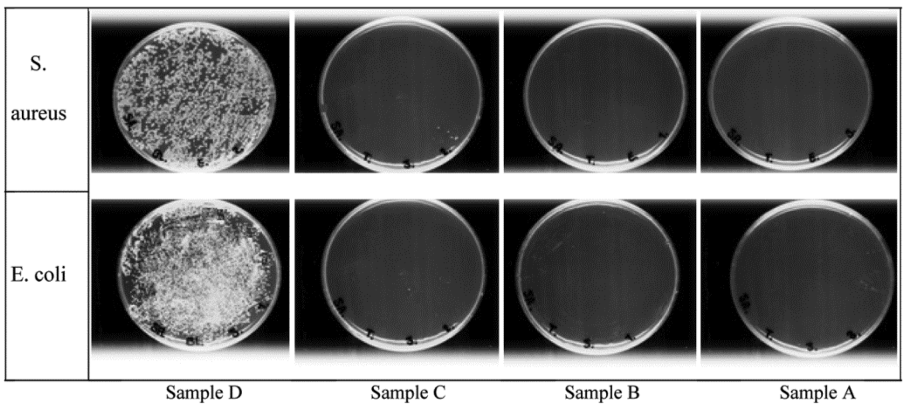

Fig. 6 — Antibacterial efficiency of raw and treated samples

that the antibacterial property of raw sample is zero. However, the samples which are treated with nano materials have antibacterial property against Gram-negative and Gram-positive bacteria. The antibacterial activity of samples A and B coated with nano Ce/ZnO and Ce/TiO_2 respectively is found 100% against both the bacteria, while the antibacterial activity of sample C coated with nano Ce is 99.8% for *Escherichia coli* and 98.4% for *Staphylococcus aureus* respectively. The reason of higher antibacterial property of samples A and B as compared to sample C is 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 sample C against *E.coli* is found better than that against *S.aureus*. This can be explained due to the difference in thickness of the cell walls of these bacteria. *E.coli* has thinner cell wall than *S.aureus*.

3.4 Self-cleaning Property

Self-cleaning property of samples which are stained with methylene blue dye has also been assessed. The raw sample shows no photocatalytic activity under UV irradiation. The results show that by increasing nano materials on surface of wool, the ΔE of the samples decreases. It means that the self-cleaning property increases and stain degradation enhances. Due to the obtained results, ΔE of raw sample is 38.61 which is higher and doesn't have any self-cleaning property. On the other hand, the ΔE of samples A and B is about 17.64 and 17.42 respectively, which is excellent for self-cleaning. The ΔE of sample C is a little higher (21.83) than the samples A and B and this is due to the doping of nano Zn and Ti on Ce.

4 Conclusion

In this study, nano Ce has been loaded on the surface of wool fabric and nano ZnO and TiO_2 are doped on it. Three types of fabric (wool /Ce, wool /Ce/ZnO, wool /Ce/TiO_2) are prepared and physical properties of the obtained fabric are investigated. The ultra violet protecting property of loaded samples shows that the transmission of UV from these fabrics is lower than raw sample. On the other hand, by comparing Ce loaded fabric with Ce/ZnO and Ce/TiO_2 loaded fabrics, UV blocking property of samples with ZnO and TiO_2 is found better than the Ce loaded fabric. This is due to UV-blocking activity of the nano materials and synergetic UV absorption. Also, antibacterial property of treated samples is investigated using both Gram-negative and Gram-positive bacteria and the result shows that all samples have excellent antibacterial property. So, samples which contain ZnO and TiO_2 have 100% antibacterial and the sample treated just with Ce has more than 98% antibacterial property. The morphology of samples is illustrated by FESEM and it confirms the good distribution of nano materials on the surface of fabric. EDX and XRD analyses prove the percentage usage of nano materials. On the other hand, self-cleaning property of samples shows that the samples having nano materials have this property but the samples which contain Ce/ZnO and Ce/TiO_2 has more self-cleaning in comparison to the sample which has Ce due to doping of nano Zn and Ti on Ce.

References

1 Marshall RC, Orwin DFG & Gillespie JM, *Electron Microscopy Rev*, 4(1) (1991) 47.
2 Hassan MM & Leighs SJ, *Appl Surface Sci*, 419 (2017) 348.
3 Kaur A & Chakraborty JN, *J Cleaner Production*, 108 (2015) 503.
4 Zanini S, *Surface Coatings Technol*, 292 (2016) 155.
5 Cheng XW, *Thermochimica Acta*, 665 (2018) 28.
6 Scobie DR, *Small Ruminant Res*, 133 (2015) 43.
7 Eren E, *J Electrostatics*, 77 (2015) 69.
8 Yan Y, *Vacuum*, 155 (2018) 210.
9 Jung HJ, *J Environmental Sci*, 74 (2018) 107.
10 Gao D, *Materials Res Bull*, 89 (2017) 102.
11 Gao D, *Carbohydrate Polym*, 200 (2018) 221.
12 Johansson B, *Scientific Reports*, 4 (2014) 6398.
13 Kumar R, *Ceramics Int*, 41(6) (2015) 7773.
14 Wang Y, *Appl Surface Sci*, 292 (2014) 608.
15 Perelshtein I, *ACS Appl Mat Interfaces*, 1(2) (2009) 361.
16 Montazer M, Pakdel E & Behzadnia, *J Appl Polym Sci*, 121(6) (2011) 3407.
17 Khurana N & Adivarekar RV, *Fibre Polym*, 14(7) (2013) 1094.
18 Veronovski N, *Fibre Polym*, 10(4) (2009) 551.
19 Karimi L, *Photochem Photobiol*, 86(5) (2010) 1030.
20 Palamutcu S, *Desalination Water Treatment*, 26(1-3) (2011) 178.
21 Montazer M, Lessan F & Moghadam MB, *J Text Inst*, 103(8) (2012) 795.
22 Chen X & Mao SS, *Chem Rev*, 107(7) (2007) 2891.
23 Chen X & Selloni A, *Chem Rev*, 114(19) (2014) 9281.
24 Uğur ŞS, Sarıšık M & Aktaş AH, *Fibre Polym*, 12(2) (2011) 190.
25 Khan MZ, *Fibre Polym*, 16(5) (2015) 1092.
26 Gaya UI & Abdullah AH, *J Photochem Photobiol C*, 9(1) (2008) 1.
27 Dural-Erem A, *J Text Inst*, 106(6) (2015) 571.
28 Behzadnia A, Montazer M & Rad MM, *Ultrasonics Sonochem*, 27 (2015) 200.
29 Montazer M, *J Photochem Photobiol B*, 103(3) (2011) 207.
30 Montazer M, Behzadnia A & Moghadam MB, *J Appl Polym Sci*, 125(S2) (2012) 356.
31 Wang W, *J Phys Chem C*, 114(32) (2010) 13663.
32 Caratto V, *ACS Appl Materials Interfaces*, 6(20) (2014) 17346.
33 Faisal M, *Chemical Eng J*, 229 (2013) 225.
34 Ibănescu M, *J Alloys Compounds*, 610(2014) 244.
35 Fu F, *ACS Appl Materials Interfaces*, 7(4) (2015) 2597.
36 Manna J, *ACS Appl Materials Interfaces*, 5(10) (2013) 4457.
37 Gao D, *Chem Eng J*, 258(2014) 85.
38 Hatamie A, *Langmuir*, 31(39) (2015) 10913.
39 Hu Z, *Int J Polym Sci*, 2017(2017) 1-91.
40 Szymańska-Chargot M, *Cellulose*, 25(8) (2018) 4603.
41 Tischer PCSF, *Biomacromolecules*, 11(5) (2010) 1217.
42 Suslick KS, *Science*, 247 (1990) 1439.