Indian Journal of Fibre & Textile Research
Vol. 45, June 2020, pp. 207-210

Short Communications

Enhancing electro conductivity, antibacterial and UV blocking of cotton fabric by using graphene/zirconium dioxide nano composite

Mahsa Mohamadiyan, Salar Zohoor[a] & Abolfazl Davodiroknabadi

Department of Design and Clothing, Yazd Branch, Imam Javad University College, Yazd, Iran

Received 11 August 2018; revised received and accepted 29 January 2019

Nano composite of graphene/zirconium dioxide has been produced and then coated on the surface of cotton fabric. Scanning electron microscope and transmittance electron microscope of sample prove the existence of nano zirconium dioxide distribution on the surface of cotton fabric. Results show that the electrical conductivity of treated sample has increased in comparison with sample without graphene/zirconium dioxide. It is also observed that the use of graphene/zirconium dioxide composite increases UV blocking of fabric. Furthermore, the nanocomposites are found to have antibacterial property against both *Staphylococcus aureus* and *Escherichia coli* bacteria according to AATCC test method.

Keywords: Antibacterial, Electro conductivity, Graphene, Nano zirconium dioxide, UV-blocking

Cotton is the most plentiful and popular biopolymer in the world. Also it is the most valuable raw material in the world of textile industry. Cotton fibres and fabrics have been used from ancient periods. Owing to its plenty availability, biodegradability and some 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, exactly separate from its traditional and great use in paper manufacturing and textile industry. Cotton fibres present a symmetric surface, inter-communicated with the hydroxylated nature of the organizing anhydroglucose units. This property gives high hydrophilicity of cotton, provides the formation of powerful hydrogen bonding between cotton fibers and the organization of three-dimensional fibre-based structures[1-5].

[a]Corresponding author.
E-mail: s_textile@yahoo.com

In last decade, an extensive range of nano particles and nano structures were used in fabrics, which gave new features to the ultimate fabric supply. Nowadays, more consideration has been made on the usage of semiconductors such as CdS, Fe_2O_3, ZnO (refs 6,7) and carbon compounds[8-14].

Graphene is one of the carbon compounds which has specific properties[15]. Graphene is a semiconductor material which can enhance many properties of fabrics, such as electrical conductivity, optical properties, thermal conductivity, high carrier mobility and high surface area[16,17]. Zhao *et al.*[18] reported the electrical conductivity of graphene ranging about 106 S/cm. Also, Lee *et al.*[19] reported the Young's modulus of 1 TPa and strength of 130 GPa. Some researchers coated graphene on surface of fabrics[20]. Moafi *et al.*[21] reported that using ZrO_2 can improve the fabric properties such as photocatalitic activity.

In this study, nano geraphene/nano zirconium dioxide composite has been prepared and then coated on the surface of cotton fabric. The coated fabric is then studied for the properties, such as antibacterial, electrical conductivity and UV-blocking.

Experimental

Cotton fabric with a warp density 26 yarn/cm (warp count, 19.6 tex), weft density 22 yarn/cm (weft count, 29.5 tex) and fabric weight 126.8 g/m^2 was produced from Yazdbaf Company, Iran. Also, nanopowder of zirconium dioxide (average particle size <100nm, purity 99.2% and specific surface area ≥25m^2/g) from Aldrich Company (CAS Number 1314234), sulfuric acid and hydro chloridric acid (99%) from Merck, potassium permanganate from Merck, hydrogen peroxide from Merck, graphite powder from Graphene-Supermarket Company were used for the study. A Euronda ultrasonic bath model Eurosonic 4D, 350 W, 50/60 Hz (Italy) was used. The morphology of samples was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). UV-blocking properties of samples were determined using Perkin Elmer Lambda UV-vis spectrophotometer. Electrical surface resistivity was investigated by Hioki digital multimeter (model 3256-50, Japan). A centrifugal device (model Eppendorf AG 22331, Hamburg) was used.

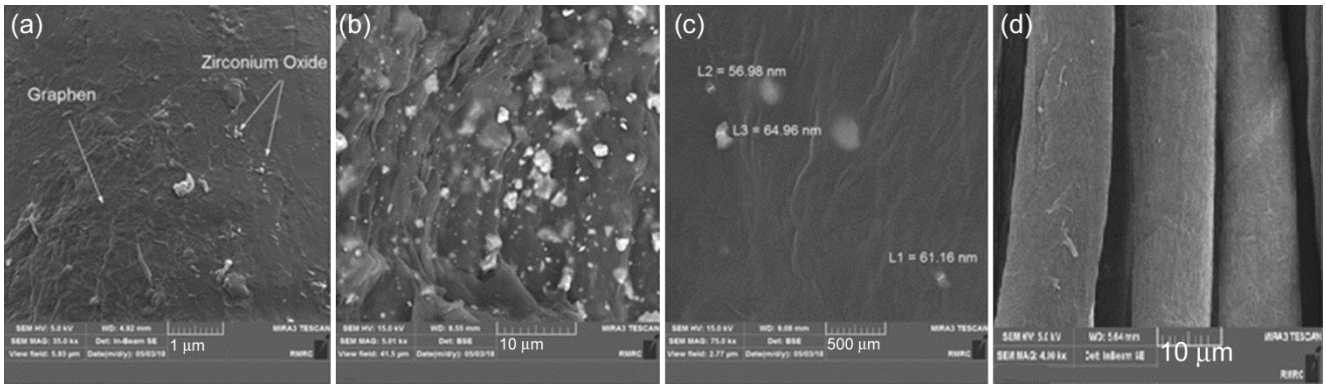

Fig.1 — SEM images of (a) graphene nano sheets and ZrO_2 on surface of fabric, (b) distribution of nano materials on fabric, (c) diameter of nano materials on fabric and (d) raw sample

First of all, graphite was added to sulfuric acid and shaken for one day. Potassium permanganate was added to above solution in ice bath followed by the addition of distilled water and hydrogen peroxide. Then the solution was centrifuged (4000rpm) for 15min, followed by washing with hydrochloridric acid, and distilled water. In order to obtain graphene oxide, the solution was sonicated in ultrasonic bath for an hour. The ultrasonic bath was used in order to separate the sheets of graphene. During this, nano ZrO_2 was added. The scoured cotton fabric was added to bath and kept for one hour at 50°C. Then, fabric was washed with distilled water and dried. The sample was again washed with hydrochloric acid and distilled water. Thus, the fabric with 0.3% graphene oxide and 0.15% nano zirconium dioxide was obtained.

Results and Discussion

SEM, TEM Images & EDX Analysis

In order to study the morphology of samples, SEM images of samples have been obtained. The SEM has been done at 5 and 15 kV and its magnification was ×5k, ×35k and ×75k. Figure 1 (a) clearly shows the distribution of graphene sheets and nano ZrO_2 on the samples at higher magnification. Figure 1 (b) shows the distribution of particles on surface of fabric. Fortunately, this image proves that there is not any aggregation of nano material. Figure 1(c) indicates that the particle size of the deposited ZrO_2 on the fabric surface is about 60nm. As shown in Fig. 1(d), the surface of blank cotton fabric is clean and smooth. It is clearly possible to recognize the nanocomposite particles on the surface of treated cotton fabric. Also, it is obvious that the nanoparticles are well distributed on the fibre surface.

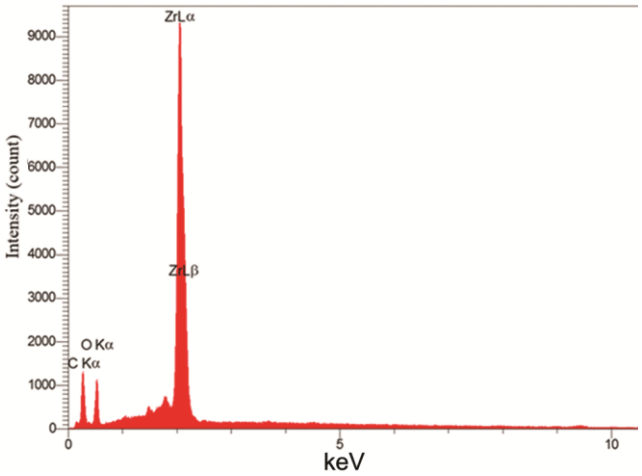

Fig. 2 — EDX images of nano ZrO_2

On the basis of EDX analysis (Fig. 2), it is observed that the samples of ZrO_2 on fabric contain significant amount of Zr after treatment, which indicates the presence of C, O and Zr elements on the surface of fabric. In order to study the size of ZrO_2 particles used in forming the coatings, TEM analyses has been done. TEM image of nano ZrO_2 is illustrated in Fig. 3. It is noticeable that the particle size and morphology of the nano ZrO_2 is less than 100nm.

Electrical Conductivity Analysis

In recent years, fabric electrical conductivity has attracted more consideration[22]. One of the most important physical properties of graphene/zirconium dioxide composite is electrical conductivity. The electrical resistance of raw sample (cotton fabric with 0.00% graphene/ziconum dioxide) and treated sample has been investigated by Hioki digital multimeter (model 3256-50). The conductivity of raw sample is zero, but by loading composite of graphene/ZrO_2, the electrical conductivity increases significantly. It can be

explained by percolation theory. Thirty tests have been done and the electrical resistance average of treated sample is obtained. Electrical resistance of cotton fabric, coated with graphene/ZrO_2, is found 103 Ω. It means that by increasing the graphene/ZrO_2 concentration on surface of fabric, the electrical conductivity of cotton fabric increases. By comparing the electrical conductivity of cotton fabric coated with graphene[23], it can be observed that ZrO_2 improves the electrical conductivity as compared to samples without ZrO_2. This can be described by better contact between nano materials on surface of fabric.

UV Blocking Analysis

The UV transmission of untreated and treated cotton samples with graphene/ZrO_2 in the range of 200-800nm is illustrated in Fig. 4. As it is demonstrated, the transmittance of raw sample is higher than that of the treated sample. It means that UV protection of cotton fabric which is coated with graphene/ZrO_2 is higher than raw sample. This is owing to UV adsorption capability of carbon and zirconium. Moreover, the UV-blocking activity of the graphene is improved by the presence of nano ZrO_2 on the surface of cotton fabrics, which is due to the synergetic UV absorption of ZrO_2. On the other hand, the UV protection factor (UPF) values are also calculated. The UPF value of raw cotton fabric is 9.48. An UPF value of less than 15 indicates no protection against transmittance of UV radiation through fabric onto skin. The UPF value of the treated cotton fabric is measured to be 204.78. Therefore, results confirm the excellent UV-blocking activity of treated cotton fabric.

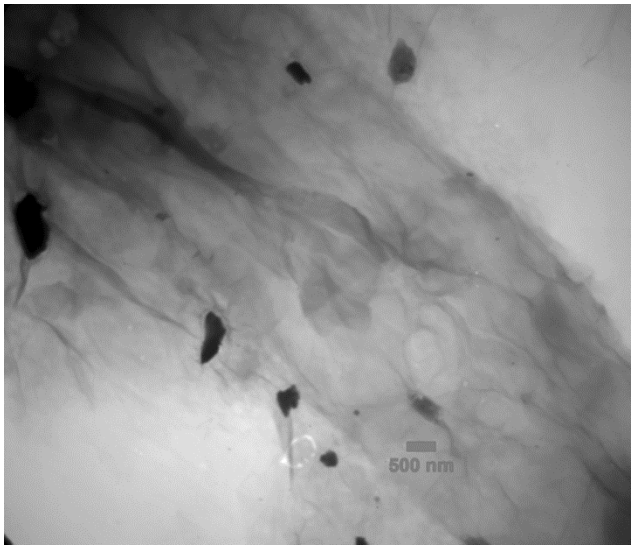

Fig. 3 — TEM images of nano ZrO_2

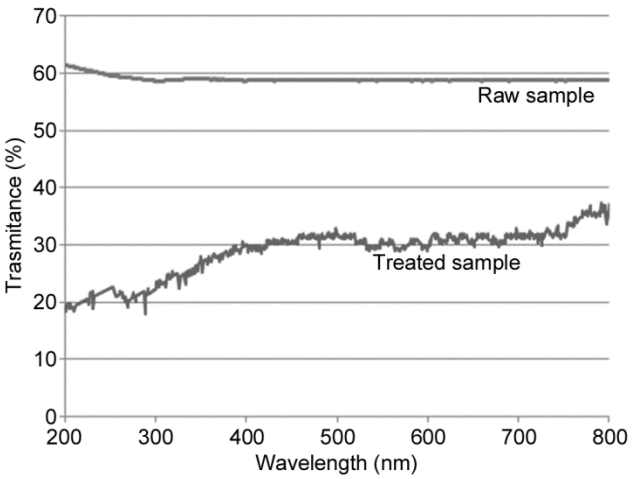

Fig. 4 — UV transmittance diagram of samples

Antibacterial Properties Analysis

In this study, two kinds of bacteria *Escherichia coli* and *Staphylococcus aureus* have been used in order to investigate the antibacterial efficiency of samples. The E. coli and S. aureus bacteria are pathogenic microorganism which can cause many illnesses, such as poisonous shock, purulence, abscess, fibrin coagulation, and endocarditic[24].

The outcome of the antibacterial experiment is presented in Fig. 5. The results show that there is not any antibacterial property on raw sample, while the samples

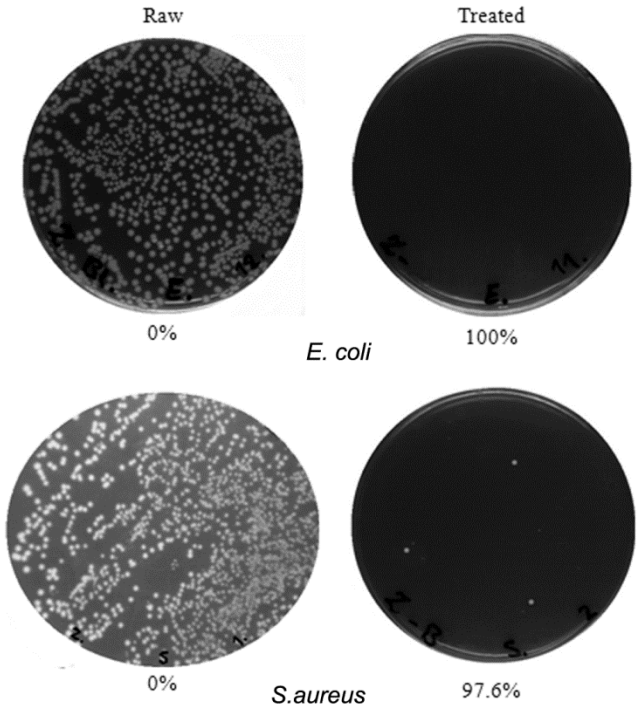

Fig. 5 — Antibacterial efficiency of raw and treated samples

treated with graphene/ZrO_2 have the antibacterial activity against both Gram-negative and Gram-positive bacteria. The antibacterial activity of the sample, which is coated with graphene/ZrO_2, is about 100% and 97.6% for *E. coli* and *S. aureus* respectively. The reason of better efficiency against *E. coli* in comparison with *S. aureus* is due to difference in the thicknesses of the cell walls; *S. aureus* has a thicker cell wall. The reason of antibacterial property is because of Zr^{2+} ions in the bacterial culture. These positive ions react with negatively charged at the cell surface of microorganism causing variation in cell permeability, and transforming normal metabolism of microorganisms, which may lead to microorganism death.

It is inferred that the electrical conductivity of samples treated with graphene/ZrO_2 is good and also the presence of ZrO_2 enhances the conductivity of fabric, as compared to previous works[23] wherein only graphene was used. UV blocking property of treated samples shows that nano composite of graphene/ZrO_2 can prevent the body from ultra violet spectrum. The UPF value of raw cotton fabric is 9.48, while that of treated cotton fabric is found to be 204.78. On the other hand, presence of graphene/ZrO_2 composite shows excellent antibacterial property. The treated fabric has 100% and 97.6% antibacterial property for *E. coli* and *S. aureus* respectively. This is due to the presence of Zr^{2+} ions in the bacterial culture, which is able to react with negatively charged cell surface of microorganism, causing a variation in cell permeability, thus transforming normal metabolism of microorganisms, which may lead to microorganism death. Through SEM and TEM images, the successful distribution of graphene/ZrO_2 on the surface of cotton is verified. Moreover, the morphologies of nano materials are illustrated clearly.

References

1 Goncalves G, Marques P A A P, Pinto R J B, Trindade T & Neto CP, *Composites Sci Technol*, 69 (2009) 1051

2 Subramanian K, D'Souza L & Dhurai B, *Mater Sci-Medzg*, 15 (2009) 75.

3 Li Q, Chen SL & Jiang WC, *J Appl Polym Sci*, 103 (2006) 412.

4 Yadav A, Prasad V, Kathe A A, Raj S, Yadav D, Sundaramoorthy C & Vigneshwaran N, *Bull Materials Sci*, 29 (2006) 641.

5 Yuranova T, Mosteco R, Bandara J, Laub D & Kiwi J, *J Molecular Catalysis*, 244 (2006) 160.

6 Yan Y, Mi W, Zhao J, Yang Z, Zhang K & Luan C, *Vacuum*, 155, (2018) 210.

7 Jung H J, Koutavarapu R, Lee S, Kim J. H, Choi H. C & Choi M Y, *J Environ Sci*, 74 (2018) 107.

8 Li Q, Shi T, Li X, Lv K, Li M, Liu F, Li H & Lei M, *Appl Catalysis*, 229 (2018) 8.

9 Ali A A, Nazeer A A, Madkour M, Bumajdad A & Sagheer F, *Arab J Chem*, 11 (2018) 692.

10 Rahmani A, Emrooz H B M, Abedi S & Morsali A, *Mat Sci Semiconductor Proc*, 80 (2018)44.

11 Zhao J, Ge K, Zhao L, Zhang S & Zeng Y, *J Alloys Comp*, 729 (2017)189.

12 Choi J, Song T, Kwon J, Lee S, Han H, Roy N, Terashima C, Fujishima A, Paik U & Pitchaimuthu S, *Appl Surf Sci*, 447 (2018)331.

13 Zhang Z, Liu G & Mao Y, *Inter J Hydr Energy*, 38 (2013) 9349.

14 Bai S, Tian K, Fu H, Feng Y, Luo R, Li D, Chen A & Liu CC, *Sens Actuators*, 268 (2018) 136.

15 Mansour M, Bechelany M, Habchi R & Eid C, *Physics Lett A*, 381 (2017) 658.

16 Pant H. R, Adhikari S P, Pant B, Joshi M K, Kim H J, Park C H & Kim C S, *J Coll Inter Sci*, 457 (2015)174.

17 Karimi L, Yazdanshenas ME, Khajavi R, Rashidi A & Mirjalili M, *Cellulose*, 21 (2014) 3813.

18 Zhao X, Tian H, Zhu M, Tian K, Wang J J, Kang F & Outlaw R A, *J Power Sources*, 194 (2009) 1208.

19 Lee C, Wei X, Kysar J W & Hone J, *Sci*, 321 (2008) 385.

20 Shateri-Khalilabad M & Yazdanshenas M E, *Carbohydr Polym*, 96 (2013) 190.

21 Moafi H F, Shojaie A F & Zanjanchi M A, *Appl Surf Sci*, 256 (2010) 4310.

22 Jin X, Xiao C, An S & Jia G, *J Mater Sci*, 42 (2007) 4384.

23 Zohoori S, Latifi M, Davodi A & Mirjalili M, *Polish J Chem Technol*, 19 (2017) 0049.

24 Montazer M, Behzadnia A, Pakdel E, Rahimi M K & Moghadam M B, *J Photochem Photobiol*, 103 (2011) 207.