ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE APPLICATION AND CHARACTERIZATION OF GRAPHENE DECORATED WITH TiO2 –Fe (1%)-N ON COTTON FABRICS

DUMITRESCU Iuliana[1], MITRAN Elena-Cornelia[1], DINCA Laurentiu Christian[1], IORDACHE George-Ovidiu[1], VARZARU Elena[1]

[1,]National R&D Institute for Textiles and Leather Bucharest (INCDTP) 16 Lucretiu Patrascanu, 030508, Bucharest, Romania, E-mail: certex@ns.certex.ro

Corresponding author: Mitran, Elena-Cornelia, E-mail: cornelia.mitran@certex.ro

Abstract: *Doped TiO2/graphene nanocomposites are studied due to their capacity to absorb the visible rays and large applicability in photo-catalytic applications. In this paper, we summarize our experiments on the development of photocatalytic fabrics based on deposition of doped TiO2/graphene nanocomposites by ultrasound method. We have investigated the surface morphology by scanning electron microscopy (SEM) and elemental composition was determinate through EDX. Other information were obtained from electrical resistivity analysis measured on Prostat PRS-801 instrument, evaluation of the cotton fabrics wettability by measuring the contact angle on a VCA Optima instrument and evaluation of the photo-catalytic properties of the treated fabrics under solar and visible light (Xenotest) by measuring the trichromatic coordinates of the treated and untreated textile materials. The results demonstrated that the ultrasound is an effective method to deposit nanoparticles on textile materials and that the uniform dispersion of TiO2- graphene composites depends on sonication parameters. Also, the treatment used on textile materials doesn't improve the electrical properties of the knit. The results obtain after evaluation of the photo-catalytic activity by photo degradation of methylene blue under visible and solar light show the performance of the developed fabrics and also that the photo-catalytic activity is high under visible light and solar light.*

Key words: *graphene-doped TiO2, photocatalyst, composite, nanoparticles, methylene blue.*

1. INTRODUCTION

Recent efforts to enhance the photocatalytic activity of TiO2 and develop self-cleaning[1], antibacterial[2] and antifungal cotton fabrics[3] are focused on the preparation of TiO2 composites with MWCNT[4], graphene[5] reduced graphene[6] or graphene oxide[7]. These composites increase the wavelength absorption across the entire visible light spectrum due to the graphene highly conjugated structure, and to the band gap reduction of carbon doped TiO2 [8]. Consequently, graphene-TiO2 show a high photocatalytic activity under visible light towards degradation of different contaminants [9,10]. The present research evaluated the potential photocatalytic activity of cotton fabrics coated with graphene decorated with TiO2 –Fe (1%)-N.

2. EXPERIMENTAL PART

2.1 Materials

Textile material: knitted cotton 188g/m2 weight; 0.927 mm thickness.

Chemical reagents:

- TiO2 doped with 1% iron and nitrogen and 2% graphene [TiO2 –Fe(1%)-N +2%GO, abbreviated GO] prepared by hydrothermal synthesis by National Institute of Materials Physics, Bucharest, Romania;
- Sodium dodecyl hydrogen sulphate (SDS) (Sigma-Aldrich),
- Distillate water.

2.2 Method

The cotton knit was treated with 0.16g/L GO prepared by dispersing the GO powder in 0.04g / L SDS for 180 minutes at 30^0C on ultrasound bath.

The fabric was immersed three times in above prepared dispersion and maintained 30 minutes at 60^0C on an ultrasonic bath.

After each immersion, the fabric was dried for 15 minutes under an IR lamp.

2.3 Characterization of knits treated with TiO_2

The morphology and presence of composites particles were evidenced by scanning electron microscopy and energy dispersive spectra (SEM/EDX, Quanta 200, FEI).

The hydrophily was determined by measuring the contact angles with a 5µl distilled water droplet on a VCA Optima (AST Products Inc., USA) instrument. The results are the average of ten measurements in different points on the samples surface.

The electrical resistivity of the textile materials was measured on Prostat PRS-801instrument (Prostat Corporation, USA) according standard SR EN 1149-1: 2006, at 20.70C and relative humidity of 28.8%.

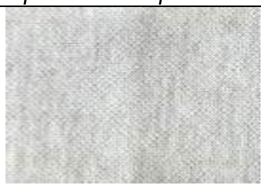
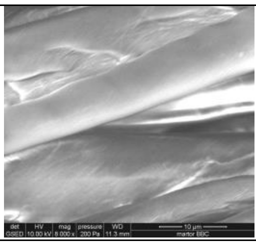
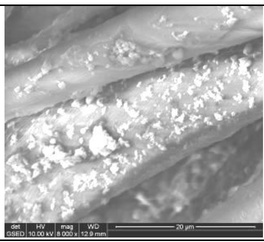
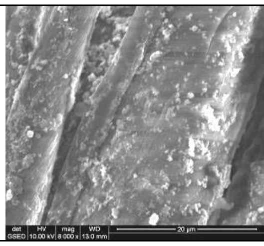
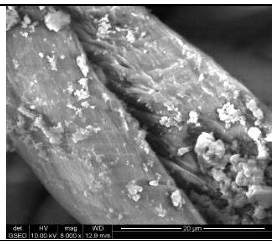
The photocatalytic efficiency under visible (Xenotest, Heraeus, Original Hanau) and solar light was evaluated by measuring the trichromatic coordinates (da*, db*, dL*, dE*) of the treated and un-treated fabrics stained with 0.0064 g/L methylene blue on a Hunter lab spectrophotometer, at 10° observer angle and D65 light.

3. RESULTS

3.1 Surface morphology

The aspect and the SEM images of fabrics treated with 0.16g/L GO are shown in the Table 1.

Table 1: *SEM images of the treated fabrics*

			
			
a.	b.	c.	d.

The treatment with TiO2 –Fe (1%)-N +2% GO completely changes the color of the material which becomes grey. The shade is intensified as the number of treatments increases. After the 1st treatment, the particles are randomly disposed on the material surface, most of them being agglomerated. After the 2nd treatment, the cotton fibers are covered with a large number of particles with different dimensions (329.8nm, 412.1nm, 450.6nm, 517.7nm. 778.7nm) less agglomerated than in the 1st treatment. The 3rd treatment leads to a more uniform coverage of the material surface with large particles which size vary from 257.6nm to 1.08µm.

The initial uneven distribution of particles is due to the non-uniformity of the fabrics and to the low adherence of the particles on the material surface. As ultrasonication time increases the nanoparticles size decreases and their dispersability in the treatment bath increases. Consequently, the number of particles deposited on the material increases. By lengthening the sonication time over 60 minutes, the slurry temperature increases which increases the number of collisions between the nanoparticles. As a result, the effect of dispersion decreases, nanoparticles form large aggregates, most of them remaining in suspension.

3.2 EDX elemental analysis of the fabrics treated with TiO2 –Fe (1%)-N +2%

The energy dispersive spectroscopic (EDX) microanalysis results are shown in the Table 2.

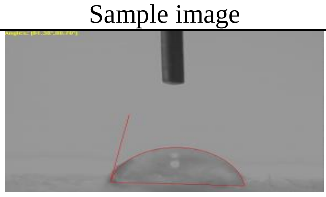
Table 2: *EDX elemental microanalysis of TiO2 –Fe (1%)-N +2% GO deposited on knit*

Element	1^{st} treatment	2^{nd} treatment	3^{rd} treatment
	Wt %	Wt %	Wt %
C K	39.70	31.42	30.72
N K	-	10.11	10.76
O K	53.70	41.85	41.58
TiK	**6.60**	**14.79**	**13.91**
FeK	-	1.83	3.03
Total	100	100	100

3.3 Evaluation of the cotton fabrics wettability

Table 3 shows results of the water contact angle measurements.

Table 3: *Contact angles of cotton knit treated with TiO_2 –Fe (1%)-N +2% GO*

Nr. crt	Sample	Sample image	Left angle	Right angle
1	after 2nd treatment		76.4°	80.70°
2	1st and 3rd treatment	-	Hydrofil material (10 measurements)	

The first and third treatment does not modify the hydrophilic properties of the initial cotton knit, the drop of water being absorbed instantly by the fabric. The contact angle after the 2nd treatment is about 80 degrees, which would indicate a slight hydrophobicity due to increasing amount of graphene deposited on material. However, taking into account the very small time of water absorption, of around 1 to 2 sec, it can be considered that the material is substantially hydrophilic.

3.4 Evaluation of electrical resistivity

The treatment with TiO_2 –Fe(1%)-N +2% GO doesn't improve the electrical properties of the knit.

Table 4: *Electrical resistivity of the treated cotton knit*

Sample	Surface resistivity, Ωsq	Volume resistivity, Ωcm	Thickness, mm
3rd treatment	$2.43x10^{13}$	$6.99\ x10^{14}$	0.90

3.5 Evaluation of the photocatalytic activity of the treated fabrics

The aspect and the color parameters of the exposed treated fabrics in comparison with the untreated fabrics are shown in the tables nr. 5 -7.

Table 5: *Aspect of the treated knit exposed to visible and solar light*

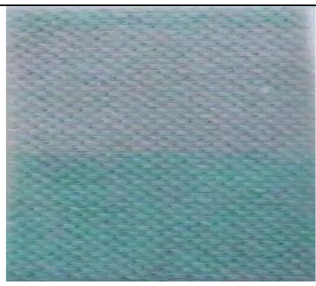
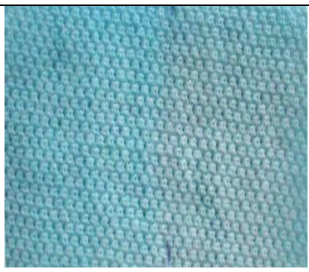
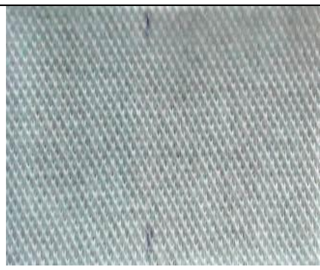
Fabrics exposed 4 hours to visible light	
Blank	3rd treatment
	
Fabrics exposed 4 hours to solar light	
Blank	3rd treatment
	

Table 6: *Trichromatic coordinates of the knit exposed 4 hours to visible light*

Sample	L*	a*	b*	dL*	da*	db*	dE*	Note
Blank	77.38	-8.33	-17.65					
Knit-3rd treatment	74.72	-2.63	-2.68	-2.66	-5.7	14.97	16.24	1.00

Table 7: *Trichromatic coordinates of the knit exposed 20 hours to solar light*

Sample	L*	a*	b*	dL*	da*	db*	dE*	Note
Blank	81.17	-5.54	-12.85					
Knit-3rd treatment	76.78	-1.85	-0.43	-4.39	3.69	12.42	13.68	1.00

The negative value of the difference of lightness coordinates (dL*) demonstrates that the treated fabrics exposed to visible and solar light are darker than the control sample, due to the black color of graphene and to the absorption of a higher amount of methylene blue by doped TiO_2 / graphene present on the material. At the same time, the color of the treated material is different from the treated blank as both da* and db * are positive, indicating the shift to red and yellow of the treated samples, respectively. Color differences indicated by high values of dE * and notes greyscale (differences are four tones to the blank) show a sharp degradation of the dye.

4. CONCLUSIONS

Ultrasound is an effective method to generate and apply the nano-particles on textile materials.

By selecting the suitable processing parameters, relatively uniform deposited layers with a high content of TiO_2-graphene could be deposited on materials.

The fabrics treated with TiO_2-graphene have photocatalytic activity demonstrated by intense discoloration of methylene blue both under visible and solar light.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from the UEFISCDI in the frame of programme PN II through the research project No. 87/2014 (CLEANTEX).

REFERENCES

[1]S. Liu, H. Sun, S. Liu and S. Wang, Graphene facilitated visible light photodegradation of methylene blue over titanium dioxide photocatalysts, Chemical Engineering Journal, 2013, vol. 214, pp 298–303.

[2] B. Cao, S. Cao, P. Dong, J. Gao, J. Wang, High antibacterial activity of ultrafine TiO2/graphene sheets nanocomposites under visible light irradiation, Materials Letters Journal, 2013, vol. 93, pp 349–352.

[3] L. Karimi, M. E. Yazdanshenas, R Khajavi, A. Rashidi, M. Mirjalili, Using graphene/TiO2 nanocomposite as a new route for preparation of electroconductive, self-cleaning, antibacterial and antifungal cotton fabric without toxicity,Cellulose, 2014, vol. 21(5), pp 3813.

[4] W. Wang, P. Serp, P. Kalck, C. G. Silva, J. L. Faria, Preparation and characterization of nanostructured MWCNT-TiO2 composite materials for photocatalytic water treatment applications, Materials Research Bulletin, vol. 43(4), pp 958–967.

[5] P. Muthirulan, C. N. Devi, M. M. Sundaram, TiO 2 wrapped graphene as a high performance photocatalyst for acid orange 7 dye degradation under solar/UV light irradiations, Ceramics International, 2014, vol. 40(4), pp. 5945-5957.

[6] P. Wang, J. Wang, X. Wang, H. Yu, J. Yu, M. Lei, Y. Wang, One-step synthesis of easy-recycling TiO2-rGO nanocomposite photocatalysts with enhanced photocatalytic activity, Applied Catalysis B: Environmental, 2013, vol. 132, pp. 452–459.

[7] M. S. A. S. Shah, A. R. Park, K. Zhang, J. H. Park, P. J. Yoo, Green Synthesis of Biphasic TiO2–Reduced Graphene Oxide Nanocomposites with Highly Enhanced Photocatalytic Activity, ACS Applied Materials & Interfaces, 2012, vol. 4(8), pp. 3893–3901.

[8] Y. Zhang, Z. R. Tang, X. Fu, Y. J. Xu, TiO2−Graphene Nanocomposites for Gas-Phase Photocatalytic Degradation of Volatile Aromatic Pollutant: Is TiO2−Graphene Truly Different from Other TiO2−Carbon Composite Materials?, ACS Nano, 2010, vol. 4 (12), pp. 7303-7314.

[9] T. D. Nguyen-Phan, V. H. Pham, H. Kweon, J. S. Chung, E. J. Kim, S. H. Hur, E. W. Shin, Uniform distribution of TiO2 nanocrystals on reduced graphene oxide sheets by the chelating ligands, Journal of Colloid and Interface Science, 2012, vol. 367(1), pp. 139-147.

[10]M. Shateri-Khalilabad, M. E. Yazdanshenas, Preparation of superhydrophobic electroconductive graphene-coated cotton cellulose, Cellulose, 2013, vol. 20(2), pp. 963–972.