PHOTOCATALYTIC PERFORMANCES OF TEXTILES COATED WITH GRAPHENE OXIDE/TIO_2 NANOCOMPOSITES – PART 2

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The objective of this work was dedicated to the preparation of photocatalytic textiles based on graphene (0.5%wt)/TiO_2 composite. Four different methods were tested to coat the cotton knit: dipping twice the knit in composite (a); dipping twice the knit in composite and finally in a polyacrylate binder (b); dipping the knit in a mixture composite/polyacrylic binder (c) and treatment of the materials in adhesive polymer followed by immersion in composite dispersion (d). To evaluate the photocatalytic effect of the materials after washing treatment, samples were exposed to ultraviolet and visible light. The trichromatic coordinates of the exposed and non-exposed samples were measured on Hunterlab spectrophotometer. Morphological aspect and TiO_2 existing on the materials surface after washing were evaluated by scanning electron microscopy and energy dispersive analysis. Cotton fabric treated by method b has the most pronounced photocatalytic effect under UV light, probably because of carboxylic groups of polyacrylic binder that facilitates photooxidation.

Keywords: cotton, graphene/ TiO_2, photocatalytic.

INTRODUCTION

TiO_2 is recognized as one of the best photocatalytic material, intensively investigated for water purification and environment decontamination. The main disadvantage of TiO_2 is its low efficiency on visible range. To overcome this limitation it was doped with different metals and non-metals, and more recently by preparing TiO_2/graphene nanocomposite (Xuan *et al*., 2013). The studies (Tolasz *et al*., 2015) have shown that graphene could acts as a sensitizer, and TiO_2 as a substrate in the heterojunction system, promoting the separation of photo-induced electron-hole pairs, the electrons being transferred from TiO_2 to graphene, while the holes remaining in TiO_2 drive the oxidation process (Pan *et al*., 2012).

Our study was focused on the analysis of the photocatalytic effects of Graphene (0.5% wt.)-TiO_2 deposited on textile materials under visible, UV light and their durability at washing.

EXPERIMENTAL

Materials

Graphene (0.5% wt)-TiO_2 prepared by sonication process was provided by NanoXplore (Canada). Itobinder AG, polyacrylic binder was purchased from LJ Specialities, UK. Ethanol pro-analysis and distilled water were used to prepare Graphene (0.5% wt)-TiO_2 (GT) dispersions.

Textile fabric: 100% cotton knit, 213 g/m2, 1.08 mm thick.

Methods

Preparation of Graphene-TiO_2 Composites Dispersion

0.05g graphene (0.5% wt.) -TiO_2 were introduced in a mixture of distilled water / ethanol and placed in an ultrasonic bath for one hour at 30°C. A milky unstable dispersion was obtained (experiment 1). To stabilize the dispersion an acrylic polymer, Itobinder AG, is added dropwise over 30 minutes under ultrasonic stirring.

Treatment Methods of Textile Materials

Method a: cotton knit is immersed into the graphene/TiO_2 dispersion (experiment 1) and maintained 10 minutes in an ultrasonic bath at 30°C and then for another 20 minutes without ultrasound at 20°C, with occasionally stirring. The knit was removed from the bath and dried at 100°C. The dried fabric was re-immersed in the dispersion prepared according to experiment 1 and maintained 10 minutes at 30°C on ultrasonic bath, then squeezed and dried in an oven at 100°C. Knit notation: *T_1S_2-2*.

Method b: in the solution prepared according to experiment 1, remaining from the 2nd treatment of cotton fabric, 82.3mL of water and 60 mL Itobinder AG are added dropwise for 30 minutes and ultrasonicated. The cotton knit is immersed in the resulted milky homogeneous solution and maintained for 10 minutes in the ultrasonic bath at 30°C. Then, the cotton fabric was removed, squeezed and dried in an oven at 100°C. Knit notation: *T_1S_2-2ITO*.

Method c: cotton knits were immersed into the graphene/TiO_2 solutions prepared according to experiments 2 and 3 and maintained for 10 minutes in an ultrasonic bath at 30°C and then, another 20 minutes without ultrasound at 20°C, stirring occasionally.

The cotton knits were removed from the bath and dried at 100°C.

Knits notations:

T_2S_2: knit treated with the solution prepared according to experiment 2;

T_3S_2: knit treated with the solution prepared according to experiment 3.

Method d: cotton knits were introduced in 200mL Itobinder AG solution and stirred mechanically for 10 minutes; after that the fabrics are removed from the bath, squeezed and immersed in 200mL solution containing 0.1g graphene (0.5% wt.)/TiO_2, 140mL distilled water and 60mL ethanol (experiments 4-6); the fabrics are maintained in the ultrasonic bath for 10 minutes at 30°C and, then removed from the bath, squeezed and dried in an oven at 90-100°C.

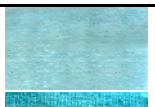
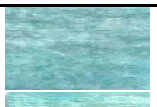
Knits notations: *T_4S_2*: knit treated with the solution prepared according to experiment 4; *T_5S_2*: knit treated with the solution prepared according to experiment 5; *T_6S_2*: knit treated with the solution prepared according to experiment 6.

RESULTS

Photocatalytic Effect Assessment

In the following, we evaluated the photocatalytic effect of graphene (0.5%)/TiO_2, stained with MB and exposed to UV and Vis light. Also, the photocatalytic effect was evaluated in terms of treatment durability to washing. Aspect of the fabrics and color changes of methylene blue (MB), the dye used for staining the treated and untreated fabrics are presented in Tables 1-6.

Table 1. Aspect of cotton knits treated with graphene (0.5%)/TiO_2, stained with MB and exposed to UV light

Time, Sample	**0h**	**11h**	**15h**	**21h**	**28h**
Cotton blank					
T_1S_2-2					

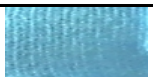
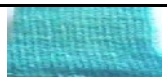
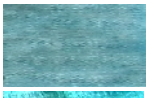
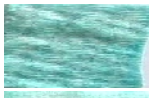
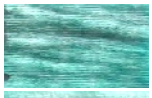
Time, Sample	0h	11h	15h	21h	28h
T_1S_2-2 ITO					
T_2S_2					
T_3S_2					

Table 2. Trichromatic coordinates of cotton knits treated with graphene (0.5%)/TiO_2, stained with methylene blue and exposed to UV light for 28 hours

Sample	L*	a*	b*	dL*	da*	db*	dE*	dC*	dH*	dL	Note
Blank	84.55	-11.7	-7.22	0.07	4.01	2.34	4.64	-4.64	0.1	0.08	2.5
T_1S_2-2	83.97	-12.31	-8.03	1.53	3.72	3.34	5.23	-4.96	-0.66	1.83	2.5
T_1S_2-2 ITO	72.08	-19.79	-18.9	**2.84**	1.66	6	**6.85**	-5.5	-2.92	3.17	2.5
T_2S_2	82.35	-13.52	-8.94	-0.03	4.1	2.98	5.07	-5.07	-0.2	-0.04	2.5
T_3S_2	85.43	-12.82	-5.91	0.17	3.99	3.13	5.07	-4.97	-1.01	0.21	2.5

By exposure to UV light, the higher brightness (dL*) and color (dE*) differences are presented by sample T_1S_2-2 ITO followed by the same sample but untreated, with polyacrylic binder (T_1S_2-2). The other samples were similar to the untreated cotton knit. The pronounced photocatalytic effect of sample T_1S_2-2 ITO is due to both relatively large amount of photocatalyst present on the material surface and to the carboxylic groups of polyacrylic binder, which due to attraction of a greater amount of water from the atmosphere facilitates photooxidation.

Table 3. Aspect of cotton knits treated with graphene (0.5%)/TiO_2, stained with 0.0064 g/L MB and exposed 60 hours to UV light

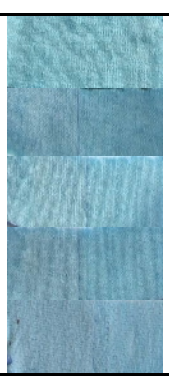
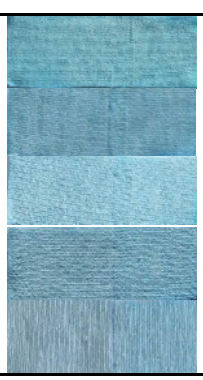
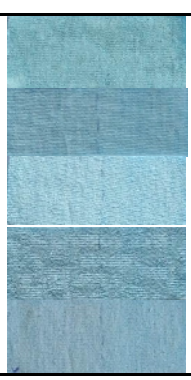
Time (h)	Blank	T_4S_2	T_5S_2	T_6S_2
0				
12				
24				
46				
62				

Table 4. Trichromatic coordinates of cotton knits treated with graphene (0.5%)/TiO_2, stained with methylene blue and exposed to UV light for 62 hours

Sample	L*	a*	b*	dL*	da*	db*	dE*	dC*	dH*	Note
Blank	83.87	-10.33	-6.45	1.16	5.24	4.53	7.02	-6.88	-0.85	**2**
T_4S_2	82.44	-11.76	-9.12	-0.34	2.21	1.79	2.86	-2.84	-0.06	3.5
T_5S_2	83.71	-11.02	-7.57	0.65	2.74	2.18	3.56	-3.5	-0.22	3
T_6S_2	82.8	-12.12	-9	0.51	1.96	2.02	2.86	-2.78	-0.42	3.5

Even after a long time exposure to UV radiation, the treated materials shows a less intense fading compared to the control sample. It can be noted that the biggest change in color is found on T_5S_2 material, treated with the small amount of graphene/TiO_2.

Table 5. Aspect of cotton knits treated with graphene (0.5%)/TiO_2, stained with 0.0064g / L MB and exposed to visible light 8 hours

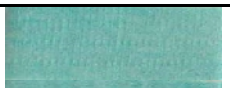
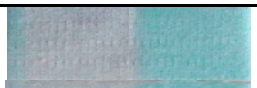
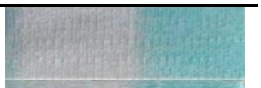
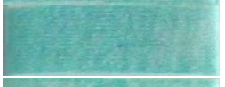
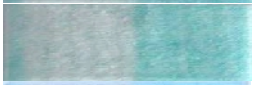
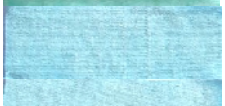
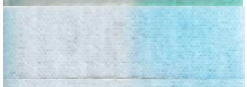
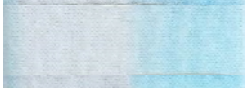
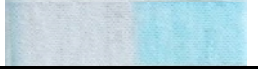
Sample/ Time (h)	0	2 hours	8 hours
Blank			
T_1S_2-2			
T_2S_2			
T_3S_2			
T_4			
T_5			
T_6			

Table 6. Trichromatic coordinates of cotton knits treated with graphene/0.5% TiO_2, stained with MB and exposed to visible light for 8 h

Sample	L*	a*	b*	dL*	da*	db*	dE*	dC*	dH*	Note
Blank	87.15	-1.54	-2.12	4.15	13.36	8.7	16.47	-15.79	2.19	1
T_1S_2-2	87.07	-2.22	-2.68	3.92	12.76	7.9	15.51	-14.86	2.1	1
T_2 S_2	87.82	-2.89	-1.94	5.52	12.91	9.79	17.11	-16.19	-0.39	1
T_3 S_2	91.32	-2.42	0.52	**7.08**	14.48	10.46	19.21	-17.13	-5.06	1
T4S2	84.57	-2.07	-3.03	4.05	12.99	10.12	16.96	-16.32	2.17	1
T5S2	87.2	-1.77	-1.89	4.2	11.4	7.95	14.52	-13.85	1.15	1
T6S2	85.75	-2.25	-2.94	2.82	12.99	7.56	15.29	-14.8	2.58	1

Under visible light, the results demonstrate an increase in the brightness (dL*) and color (dE*) difference as the amount of TiO_2 present on the surface of the material decreases. Surprisingly is the more intense discoloration of methylene blue in case of blank sample when compared to samples T_4S_2-T_6S_2. It is assumed that due to the high

amount of graphene/TiO_2 these samples absorb a much larger amount of dye compared to untreated fabric cotton. Dye photo-discoloration is more intense under visible light than under UV light. It can be observed a growing prevalence of fading with increasing concentration of acrylic polymer binder. Dye photo-discoloration is more intense than under visible light under UV light.

The treatments Durability to Washing

Morphological aspect and TiO_2 existing on the materials surface after washing were evaluated by scanning electron microscopy and energy dispersive analysis, results being shown in Figures 1 and 2 and Table 7.

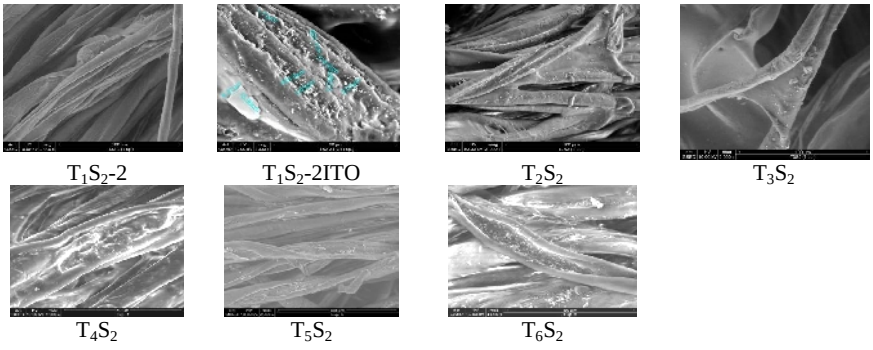


Figure 1. SEM analysis of cotton fabric treated with graphene/0.5% TiO_2 after washing

A relatively high number of particles are present on the materials surface after washing. Thick layers of acrylic polymer show a high adhesion after washing, the composite particles being firmly fixed on the surface.

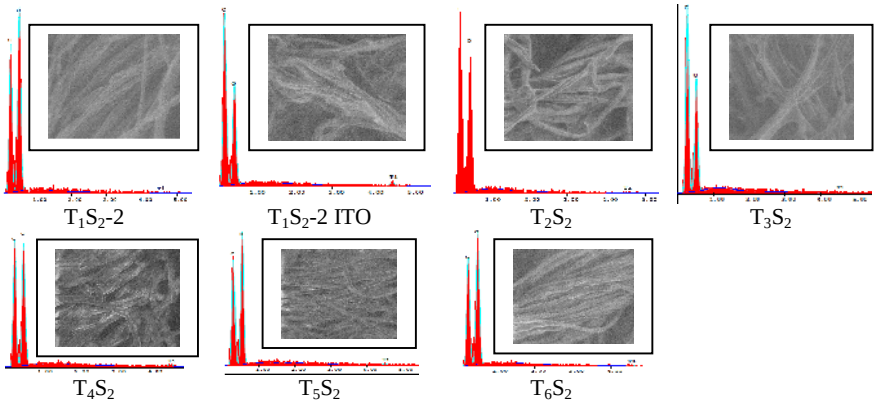


Figure 2. SEM/EDAX analysis of cotton knit treated with graphene/0.5% TiO_2 after washing

Table 7. EDAX quantification of %wt Ti on the cotton knit surface treated with graphene (0.5%)/TiO_2 after washing

Element,%Wt.	**T_1S_2-2**	**T_1S_2-2 ITO**	**T_2S_2**	**T_3S_2**	**T_4S_2**	**T_5S_2**	**T_6S_2**
TiK_i	7.36	4.48-5.35	1.02	0.57	19.62	12.99	13.12
TiK_s	1.21	6.03	1.81	1.07-1.71	3.81	3.89	5.21
$\Delta(TiK_s - iK_i)$*, %	- 83.56	+ 12.71	+ 77.45	+ 200	- 80.58	-70	- 60.3

* TiK_i – initial; TiKs – after washing

It can be observed an entirely different washing behavior depending on the method of treatment. Thus, after washing, the fabric T_1S_2-2 treated only with graphene/TiO_2 gives approximately 83.56% of the initial amount of TiO_2. Subsequent treatment with polyacrylic binder and usage of mixture binder/composite contributes decisively to fixation of composite particles on the surface of the fabric. The high concentration of TiO_2 found on washed cotton knits T_1S_2-2 ITO, T_2S_2 washed T_3S_2 is due to a slight exfoliation of the polymer layer which allows re-dispersing TiO_2 particles on the surface of the fabric. The largest amount of TiO_2 left on the material after washing is found on the fabric T_1S_2-2 ITO treated twice, followed by T_2S_2 treated with the highest concentration of polyacrylic binder. Instead, knits treated by method d, although initially had high amount of titanium deposited on the surface, after washing the amount of TiO_2 removed from the material has a rate of 60-80%. It is assumed that, using a concentration below 5mL/L polyacrylic binder does not provide a high adhesion of the particles onto the substrate.

CONCLUSIONS

From the four methods used to deposit the composite graphene/TiO2 that have been used, both double impregnation (method a) and pre-treatment with polyacrylic binder (method d) facilitates the deposition of greater amounts of composite compared to simple impregnation. Subsequent treatment with polyacrylic binder and usage of binder/composite mixture increase the treatment durability at washing.

Cotton fabric treated by method b has the most pronounced photocatalytic effect under UV light, probably because of carboxylic groups of polyacrylic binder that facilitates photooxidation. Under visible light photocatalytic efficiency decreases as the quantity of graphene/TiO_2 present on the material surface increases.

Acknowledgements

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