PHOTOCATALYTIC PERFORMANCES OF TEXTILES COATED WITH GRAPHENE OXIDE/TIO$_2$ NANOCOMPOSITES – PART 1

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The objective of this research 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 of composite/polyacrylic binder (c), and treatment of the materials in adhesive polymer followed by immersion in composite dispersion (d). The surface, morphology and distribution of nanoparticles covering the textile materials and also the elemental composition were investigated by scanning electron microscopy coupled with X-ray energy dispersive spectroscopy (EDAX). The modifications of chemical and physical properties (surface morphology, hidrophily, electrical resistivity, and elemental composition) have been analysed. The obtained values after determination of electrical resistivity demonstrate that method of treating cotton knits with graphene/TiO$_2$ cause a very slight decrease of surface resistivity and a 10 times increase of volume resistivity compared to the blank sample. The results have demonstrated that the applied coatings induce minor modifications of the initial untreated materials.

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). An intimate interfacial contact between graphene and TiO$_2$ is necessary to increase the electron-hole pair production and avoid their recombination. Unfortunately, TiO$_2$ nanoparticles are highly agglomerated onto graphene nanosheets, diminishing the ability to create holes and oxidize the contaminants. More than that, when deposited on irregular textile surfaces, the nanoparticles are not uniformly distributed and the photocatalytic efficiency is much lowered (Karimi *et al.*, 2015). New methods to prepare better graphene/TiO$_2$ composites and to more uniformly coat the textiles are required for developing enhanced applications. Our work was directed to the methods development to coat cotton knit with large amount of graphene/TiO$_2$ and to the evaluation of the textiles properties (surface morphology, hydrophilicity, electrical resistivity, elemental composition) modifications. 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).

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/m^2, 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 (exp. 2-6). The parameters of the prepared solutions are presented in Table 1.

Table 1. The parameters of the graphene (0.5% wt)-TiO$_2$ solutions

No.	Graph. - TiO$_2$, [g/L]	Graph.- TiO$_2$, g	Dist. water mL	EtOH mL	Itobinder AG		Sol. vol. mL	Stirring time, min	Aspect
					mL	%			
1	0.5	0.05	67.7	32.3	-	-	100	60	Milky White dispersion
1*	0.23	0.05	117.7	32.3	60	28.57	210	30	Homogeneous solution
2	0.5	0.05	47	23	30	30	100	60	Milky White dispersion
3	0.26	0.05	94	46	50	26.31	190	60	Homogeneous solution
4	0.5	0.1	140	60	10	5	200	60	Milky White dispersion
5	0.5	0.1	140	60	6	3	200	10	Milky White dispersion
6	0.5	0.1	140	60	4	2	200	10	Milky White dispersion

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.

Characterization of Coated Textiles

The morphology and chemical composition of treated and untreated fabrics were investigated by scanning electron microscopy (SEM, Quanta 200, FEI, Holland) equipped with energy dispersive X-ray (EDX) microanalyzer. The hydrophilicity was investigated by measuring the contact angle on VCA Optima equipment, and electrical resistivity with concentric rings (PRS-801) device according to SR EN 1149: 2006.

RESULTS

Surface Morphology of Cotton Knits Treated with Graphene (0.5%)/TiO_2

SEM images of the cotton knits surfaces treated with graphene (0.5%)/TiO_2 are shown in Figure 1.

| Blank | T_1S_2-2 | T_1S_2-2ITO | T_2S_2 |

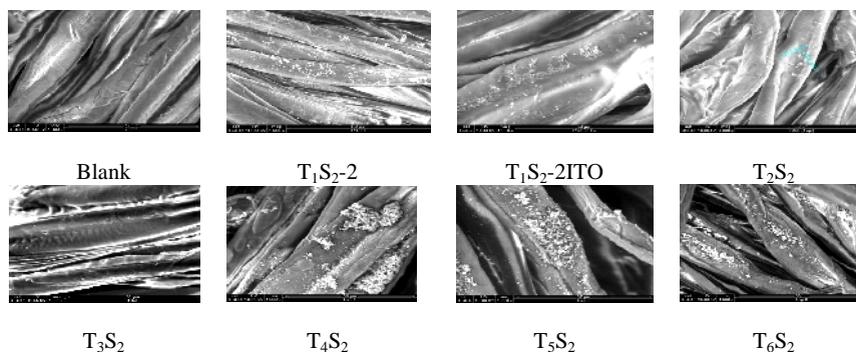| T_3S_2 | T_4S_2 | T_5S_2 | T_6S_2 |

Figure 1. SEM Images of cotton knits treated with graphene/0.5% TiO_2

SEM images show particle deposition on the surface of cotton fibers. The addition of polyacrylic binder (method b, the sample T_1S_2-ITO) leads to the deposition of relatively large quantities of particles on the fibers surface. This method has beneficial effects on reducing both environmental pollution due to the high degree of treatment bath exhaustion and on process total cost reduction because is no longer necessary to change the treatment bath, the consumption of water, energy and labor being highly reduced. T_2S_2 and T_3S_2 materials, treated by method c are covered with thick layers of polymer that includes most of the particles graphene/TiO_2. Pretreatment of knitted fabric with polyacrylic binder and subsequently with graphene/TiO_2 (d method, samples

T$_4$S$_2$, T$_5$S$_2$, T$_6$S$_2$) favors the deposition of large quantities of particles compared to using a binder/composite mixture (method c). Apparently, the binder forms a uniform film on the fibers surface, increasing the adherence of particles onto the substrate.

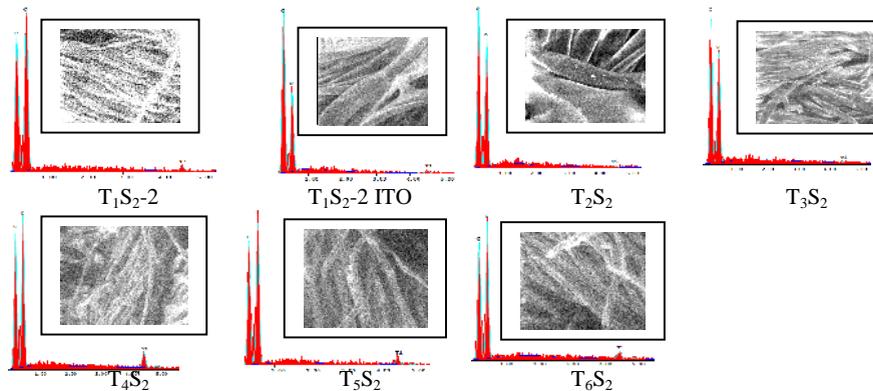**Elements Quantification by SEM/EDAX on the Cotton Knit Surface Treated with Graphene (0.5%)/TiO$_2$**

Figure 2. EDAX spectra of cotton knits treated with graphene (0.5%)/TiO$_2$

Table 2. Elements quantification by EDX on the knit treated with graphene (0.5%)/TiO$_2$

Element	Knit blank	T$_1$S$_2$-2	T$_1$S$_2$-2 ITO	T$_1$S$_2$-2 ITO – sample 2	T$_2$S$_2$	T$_3$S$_2$	T$_4$S$_2$	T$_5$S$_2$	T$_6$S$_2$
C K	45.99	40.76	57.23	58.07	51.46	51.69	34.4	38.1	37.53
O K	54.01	51.88	38.29	36.58	47.52	47.74	45.9	48.9	49.34
TiK	0	7.36	4.48	5.35	1.02	0.57	19.6	12.9	13.12
Total	100	100	100	100	100	100	100	100	100

The amount of particles deposited on the fabrics depends on the concentration of composite graphene/TiO$_2$ and the acrylic binder, the number of immersions, and the method of material treatment. Thus, lowering the concentration of graphene/TiO$_2$ from 0.5 to 0.25g/L (experiments 1-1 and 3-4 *) lowers to about half the amount of TiO$_2$ deposited on the material. Doubling the number of immersion increases the amount of TiO$_2$ deposited on the material. On textiles treated once (sample T$_1$S$_2$-ITO, 5.35% Ti K) a small amount of TiO$_2$ (5.35% Ti K) is found compared to those treated by double impregnation (sample T$_1$S$_2$-2; 7.36% TIK). This decrease is even more dramatic if the cotton fabric is treated once with preformed mixtures of graphene-TiO$_2$-polyacrylic binder. Thus, in the case of knitted fabrics treated with the same concentration of TiO$_2$, TiK concentration decreases from 7.36% (sample T$_1$S$_2$-2) if treated with 0.5g/mL graphene/TiO$_2$ to 1.02% (sample T$_2$S$_2$) if treated with binder/graphene-TiO$_2$ mixture.

In the case of textiles treated initially with polyacrylic binder (method d, samples T$_4$S$_2$, T$_5$S$_2$, T$_6$S$_2$) significant increases of the quantities of TiO$_2$ deposited is observed. Increasing the concentration of binder from 2-3% to 5% lead to increase by 33.2 - 33.8% of the amount of TiO$_2$ deposited. But if the concentration of binder greatly increase (exp. 2, 3) it was observed a massive decline in the number of particles deposited on the surface of

knitted fabrics due to the formation of clusters of large dimensions remaining in the fleet of treatment, no longer having the ability to migrate to the surface of the fibers.
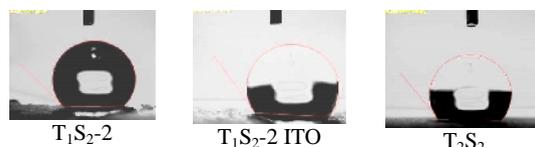
Determination of the Contact Angle

T_1S_2-2 T_1S_2-2 ITO T_2S_2

Figure 3. Contact angle of cotton knit treated with graphene (0.5% wt)/TiO_2

Table 3. Mean values of knits contact angle treated with graphene (0.5%wt)/TiO_2

Sample	Left angle	Right angle	Wetting time, s
T_1S_2-2	0	0	< 2
T_1S_2-2 ITO	131.16	131.44	> 300
T_2S_2	126.762	127.04	> 300
T_3S_2	133.76	131.30	300
T_4S_2	135.32	136.06	56
T_5S_2	136.72	137.11	27
T_6S_2	132.27	132.33	16.6

Contact angle values and short wetting time demonstrates that treatment with 0.5g/L graphene-TiO_2 (T_1S_2-2) does not modify the hydrophilic properties of cotton. Adding of acrylic binder in high concentrations induces a pronounced hydrophobic character of the materials (T_1S_2-2 ITO, T_2S_2) and a harsh handle due to thick polymer layer formed on the surface.

Determination of Electrical Resistivity

Electrical resistivity was calculated according to the equation:
Surface resistivity: = Rs x [2   / ln (R2 / R1)] = R x k [   ]   (1)
where: - surface resistivity; R_S - resistance surface; R_1: the outer electrode radius; R_2: inner electrode radius; k: geometric coefficient.
Volume resistivity: $_v$ = (A / L) x R_s, μ   · cm.   (2)
where: $_v$ = volume resistivity; A = transversal area; L = length (material thickness)

Table 4. Electrical resistivity of knit cotton treated with graphene (0.5%)/TiO_2

No.	Sample	Surface resistivity, x10[12]	Vol. resistivity, xcm x10[13]	Thickness, mm
1	Blank Cotton knit	5.03	3.13	1.22
2	T_1S_2-2	4.43	33	1.19
3	T_1S_2-2 ITO	4.86	3.69	1.12
4	T_2S_2	41.8	48.9	1.19
5	T_3S_2	71.8	73.7	1.20

In principle graphene, because of its conjugated structure should determine an increase in conductivity, knowing that it has a mobility of 15 000 $cm^2 \cdot V^{-1} \cdot s^{-1}$ and a resistivity of 10^{-6} ·cm^{-1} (Geim and Novoselov, 2007; Chen *et al*., 2008). Also, graphene is a zero band gap material and working function of -4.42eV – less than anatase TiO_2 (-4.40 eV) (Czerw *et al*., 2002; Ocak *et al*., 2009). This makes graphene to be a good acceptor of TiO_2 donated electrons, thus avoiding recombination with gaps that remain on TiO_2. The

obtained values demonstrate that treating cotton knits with graphene/TiO$_2$ cause a very slight decrease of surface resistivity and a 10 times increase of volume resistivity compared to the blank sample. The polyacrylic acid treatment determines the resistivity of both types increases, in particular when treated with the graphene-TiO$_2$ and polyacrylate mixtures (method c). Increased resistivity can be attributed to the small amount of graphene, to its covering with layers of polyacrylate and uneven deposition without providing continuous contact between small plates of graphene coating the cotton fabric.

CONCLUSIONS

Four methods to deposit the composite graphene/TiO$_2$ have been used: double treatment only with composite material (a) to deposit a large quantity of graphene, treatment with graphene/TiO$_2$ followed by reprocessing in the same bath in which a polyacrylic binder was added so as to provide both an high exhaustion of the bath and a better fixation of the particles (method b), treatment with graphene/TiO$_2$/polyacrylic binder mixture (method c) to lower the cost of energy, water, labor and initial treatment with polyacrylic binder followed by double immersion in graphene/TiO$_2$ dispersion to increase particles adhesion to the substrate and to deposit a larger quantity of particles on the material. 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. Increasing the amount of binder cause, on one hand good hydrophobization of materials, an increase of electrical resistivity, increase of particles adherence and on the other hand decrease of the number of particles deposited on the material because of the formation of large clusters that remain in solution, no longer having the ability to migrate on the material surface and because of the thick polymer layer that coats uniform both cotton fibers and graphene/TiO$_2$ particles.

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