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Durable Multifunctional Properties on Polyester Fabric by Applying Nanocoating

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Abstract This work is done to prepare multifunctional fabric by coating with nano composite made of reduced graphene oxide and TiO_2 on polyester fabric. The influence of the RGO coatings on polyester fabrics imparts properties such as light absorption, conductivity, electroactivity and photocatalytic properties. With the increased number of RGO layers the properties also developed. RGO treated polyester fabric was then treated with TiO_2 to enhance the multifunctional properties of the fabric. The photo-catalytic properties of the fabrics were tested with Rhodamine B dye solutions. Photocatalytic efficiency increased with the number of RGO coatings, due to the increased light absorption, and better electrical properties. Moreover, the nanocomposite finished polyester fabric demonstrated proper antimicrobial properties and UV blocking activity.

Keywords Polyester fabric, Graphene Oxide, TiO_2, Multifunctional properties, Cationic Modification

1. Introduction

Now a days functional fabrics with different kind of properties are being so much popular and an interesting topic to researchers. Various kinds of properties are being applied on textiles like photocatalytic, fire retardant, water proof, UV absorbent etc. An innovative strategy for functional finishing of textile fabrics is nano coating. Nowadays, the variety of nanomaterials used for textile finishing includes nano photocatalysts like TiO_2, ZnO, $SrTiO_3$ and ZrO_2. Among them, nanoTiO_2 applications has great promise due to its fascinating properties, such as optical and electronic properties, abilities to purify pollutions, chemical stability, and nontoxicity. Titanium dioxide photocatalyst has received significant interest in recent years due to its fascinating properties, such as optical and electronic properties, low cost, abilities to purify pollutions, long term stability and nontoxicity [1, 2]. Deposition of titanium dioxide nanoparticles on textiles provides new properties such as self-cleaning, super hydrophilic, antibacterial, UV-protection, flame retardancy, etc [3-10].

Graphene, one-atom-thick planar sheets of sp2-bonded carbon atoms that are densely packed into a 2-D honeycomb crystal lattice, has become one of the most attractive materials due its unique chemical and physical properties as well as its diverse potential applications [11, 12]. Moreover, graphene oxide, an atomic sheet of graphite with a wide range of functional groups (epoxy, hydroxyl, and carboxyl), is one of the most important derivatives of graphene.

One obvious way to exploit the properties of either graphene or nano titanium dioxide is to combine them. This allows the properties of each constituent to be conserved or modified. The poor solubility of graphene in water or polar organic solvents makes it difficult to deposit nanoparticles on its surface. The presence of oxygen containing functional groups in graphene oxide makes it as excellent supporters to anchor TiO_2 nanocrystals in liquid phase [13].

Graphene can serve as a conductor and electrons are transferred from the conduction band of TiO_2 to graphene sheets, this difficulties the recombination of the pair electron/hole and increases the lifetime of the pair. Moreover, the efficiency of the system is increased by a greater generation of radicals. Other benefit of employing graphene and its derivatives is the great adsorption capacity of organic molecules, which allows a better contact between the pollutants and the catalytic surface area. Another plus that has been observed is an increased absorption in the spectral range due to an increased band-gap of TiO_2 arising from the interaction with graphene derivatives. Several studies have focused on the employment of graphene and TiO_2 in heterogeneous photocatalysis [14-18].

In this paper, the combination of TiO_2 and RGO to produce photocatalytic fabrics is studied. A Bovine serum albumin coating were applied to increase the fixation and homogeneity of the RGO coatings. GO was reduced to RGO and different number of RGO coatings was applied to improve the conductivity of the fabrics. Thereafter, TiO_2 nanoparticles were deposited by immersion of the RGO-coated fabrics in a TiO_2 solution. An electrochemical

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approach has been employed to study the influence of the conductivity and the electrochemical properties of the graphene coated fabrics on the photocatalytic properties of the fabrics. The photocatalytic properties of the fabrics were tested with the degradation of Rhodamine B solutions.

2. Experimental

Materials: Bovine serum albumin (BSA), Commercial TiO_2 nanoparticles, Polyester (PES) fabrics characteristics with surface den-sity, 100 g m^{-2}; warp threads per cm, 60; weft threads per cm, 23. sulphuric acid (H_2SO_4) and potassiumchloride (KCl), $K_4Fe(CN)_6$ 99%.

Synthesis of Graphene Oxide: GO was synthesized from graphite powder by the modified Hummer's (Hummers & Offeman, 1958) method in two distinct oxidation and filtering phases. During the oxidation phase, 5 g of graphite powder was added to 200 mL of concentrated H_2SO_4 in an ice bath with continuous stirring for 30 min. $KMnO_4$ (25 g) was added slowly at temperature no higher than 10°C and was left stirring for next 30 min. Later, the mixture was allowed to react at 35°C for about 6 h with vigorous stirring. To stop the reaction, the temperature was dropped to 10°C with the use of ice, and 250 mL of D.I water was added very slowly. During the addition of water, the temperature was kept less than 55°C. Afterwards, 5 mL of H_2O_2 (30%) was added and then, the mixture was stirred for 30 more min. Then, this mixture was kept for 2 h followed by rinsing the supernatant during the filtering phase, with 0.5 L of 10% HCl and then 0.5 L water. At that time, 250 mL of water was added to the resulting product to form dispersion. The GO was bath sonicated for 30 min. Removal of unexfoliated GO sheets was done by centrifugation of the solution for 5 min at 10,000 rpm. Finally, dialysis of the solution was realized to remove the inorganic ions in the suspension.

Application of GO on Polyester surface: GO presents negative charges so the deposition of GO on the fabrics is not possible in these conditions since electrostatic repulsion does not allow it. This is why bovine serum albumin(BSA) was employed as an intermediate coating that acquired positive charge and allowed the deposition of GO on the surface of the fabrics. It can attach both negative and positive charged surfaces depending on the pH. A 0.5% weight BSA solution was employed to coat fabrics [19]. Fabrics were put in contact with the BSA solution during 10 min to allow its adsorption, after this time fabrics were rinsed with water the remove the BSA's excess.

The pH of GO solution have to be 2.0. Fabric would be soaked in that solution for 30 min at 110°C, making it easier for GO to coated on fabric. At this stage thermal reduction of GO takes place. After this time, fabrics with RGO were dried under room conditions.

Dispersion of TiO_2 on the RGO fabrics: A solution of 5 g L^{-1} (500 mL) of TiO_2 nanoparticles was prepared in water. An anionic surfactant was added (Setamol BL) (1 mL) to increase the fixation of TiO_2 nanoparticles on the fabrics. The solution was stirred during 5 min. After this time, the RGO fabrics were put in contact and stirred with the solution during 2 min. After this, the fabrics were padded two times at 1 bar pressure and finally dried in an oven at 80°C.

3. Result and Discussion

Photocatalytic activity: The photocatalytic activity of all samples was calculated by measuring the degradation of Rhodamine B (Rh-B) aqueous solutions (4 mg L^{-1}) under UV light irradiation. Rh-B was selected for its good resistance to light degradation (the dye sensitization).

Here, the polyester-RGO/TiO_2 samples (5 cm × 5 cm) were dipped into a flask with 300 ml of Rh-B aqueous solution. Then it was stirred for 40 min in dark to reach the adsorption desorption equilibrium and then fitted in an UV simulation chamber. Then, the samples were irradiated with a 300 W UV lamp from a distance of around 20 cm. The average irradiance was around 40 W/m^2.

Absorbance of the Rh-B solution was monitored during 420 min (at time intervals of 40 min up to 120 min) and then at intervals of 60 min up to 420 using a spectrophotometer in the range of 300-700 nm. For this, some aliquots of Rh-B solution (3.5 mL) were taken out and then analyzed by monitoring the magnitude variation of its main absorption peak (around 564 nm). The rate of Rh-B consumed in a chemical reaction can be written as:

$$-\frac{dC}{dt} = KCn$$

Where C is the concentration of the Rh-B aqueous solution, n is the kinetics order of the chemical reaction, and k is the rate constant of the photo degradation process.

A_t low concentrations and for a specific time instant, the absorbance of the solution, At is related to the solution's concentration through the Beer–Lambert law, that is, At= $\varepsilon \cdot l \cdot Ct$, where ε is the molar extinction coefficient, l is the light path length, and Ct is the solution concentration. For a first order kinetics reaction, the photo degradation efficiency, η, of Rh-B can be calculated according to the following equation:

$$\eta(\%) = [1 - (\frac{\mathrm{At}}{\mathrm{A0}})] \times 100$$

Where A_0 is the absorbance at zero time. Therefore, the change of Rh-B concentration can be evaluated by measuring the change in the intensity of its main absorption peak.

The photocatalytic activity of RGO and TiO_2 coated fabrics was evaluated in terms of degradation of Rh-B under UV light irradiation.

Fig.1 shows the control experiment where Rh-B solution is irradiated in the presence of polyester fabric in the same conditions applied to the catalytic fabrics. During the first 40 min a slight adsorption was observed. Thereafter, absorbance increased with the increasing due to the evaporation of part of the water due to the heat generated by the UV lamp. The

final absorbance of the solution was higher than the initial one, this discards degradation of Rh-B by UV irradiation. Adsorption was also minimal as explained.

Fig. 2 shows, for different irradiation times in the presence of polyester-RGO + TiO_2 fabric, the evolution of the absorption spectra of Rh-B solutions.

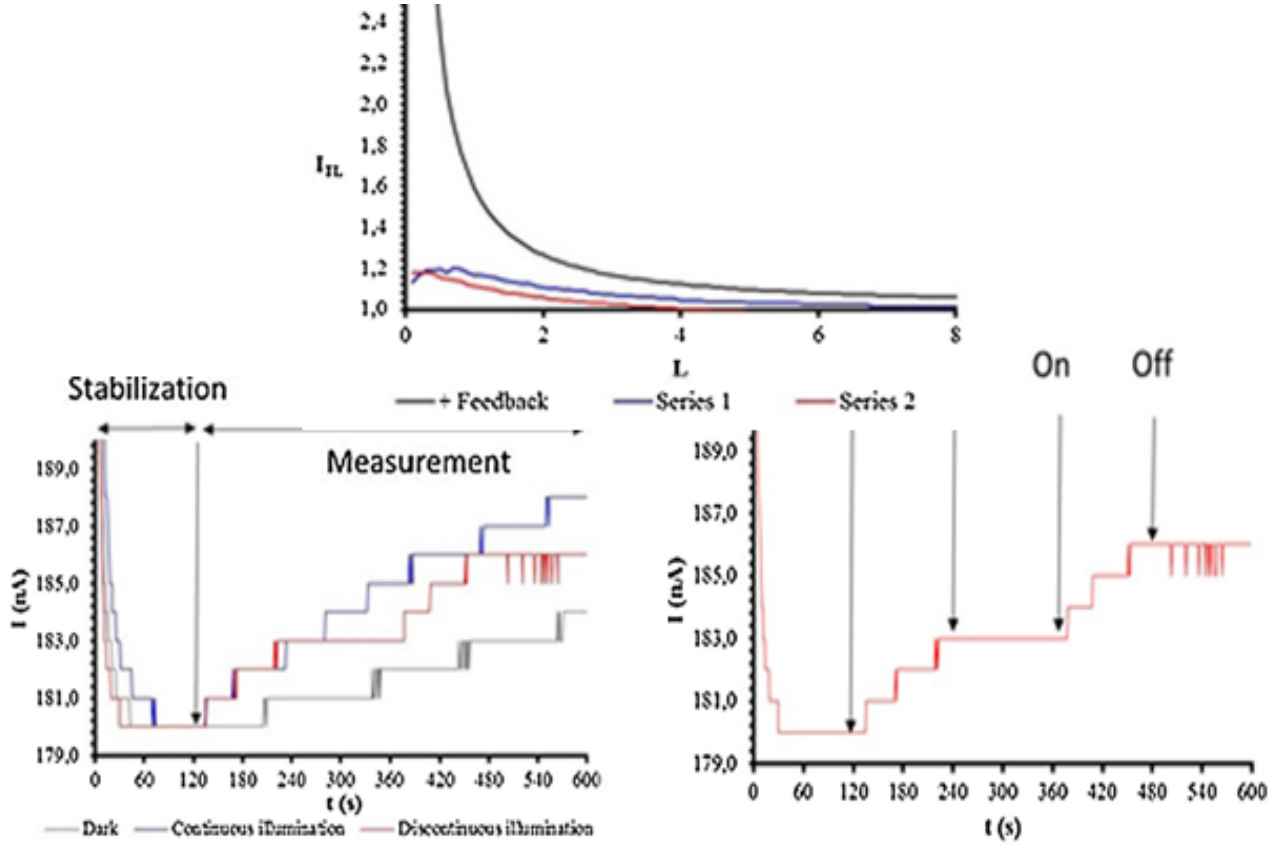

Figure 1. a) Approach curves for polyester-4RGO + TiO_2 sample. b) Chroamperometries obtained for a sample of polyester-4RGO + TiO_2 in different conditions of irradiation. During the first 120 s the current was allowed to stabilize, after this time an experiment was performed in darkness, another with continuous illumination and another with discontinuous illumination. c) Experiment performed with discontinuous illumination. Conditions applied for SECM measurements: 100- m-diameter-Pt tip, working potential +0.4 V, 0.01 M Fe (CN) 64−/0.1 M KCl. The approach rate employed to obtain approach curves was 10 m s^{-1}. Applied power radiation: 300 W

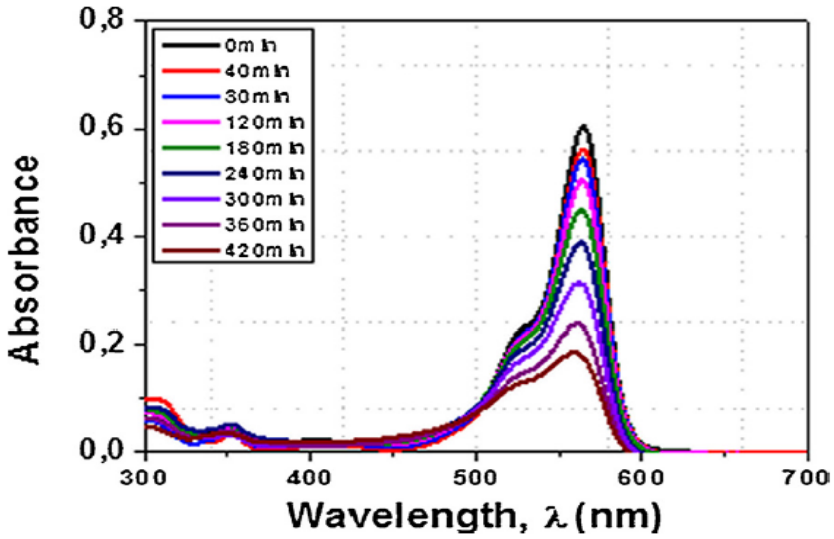

Figure 2. Absorption spectra of Rh-B aqueous solution at different irradiation times. The absorption data refer to the photocatalytic activity of polyester RGO + TiO_2 inserted in a flask filled with Rh-B (4 mg/L) aqueous solution

As can be observed, the maximum absorption peak, at around 564 nm, gradually decreased during UV irradiation. For this sample, the initial absorbance decreased about 70% after 420 min. In fact, the color of the dye changed from dark red to light red. Itis important to refer that under similar UV irradiation conditions, the absence of the photocatalyst did not affect the Rh-B absorption curves.

Using the absorption spectra of all the analyzed samples, it was possible to calculate the corresponding photocatalytic efficiencies by applying Eq. (2). By using the UV–vis spectroscopy data from all the polyester-RGO + TiO_2 fabric samples, it was possible to determine for each fabric the photo degradation rate constant, K for the Rh-B dye. Assuming pseudo-first-order reaction kinetics the calculated K values are presented in Table 1.

Table 1. Parameters of photocatalytic degradation of Rh-B solutions by PES-RGO + TiO_2

Number of rGO layers	Photocatalytic Efficiency %	Rate constant K (min^{-1})
1	70.2	9.04×10^{-2}
2	72.3	9.13×10^{-2}
3	74.9	9.25×10^{-2}
4	78.1	9.70×10^{-2}

The results presented in Table 3 show that there is a gradual increase of photocatalytic efficiency with the number of RGO layers. The sample with 4 RGO layers presented the highest η. The gradual increase in the η could be attributed to a higher light absorption. In addition, the reduced charge transfer resistance and lower time constants promote the electron/hole separation and increase its lifetime.

Stability of the photocatalytic fabrics:

Fig. 3 shows the micrographs of the catalytic fabrics (4G + TiO_2 fabrics) prior (a, b) and after (c, d) performing the photocatalytic experiments. It can be seen that the major part of the TiO_2 nanoparticles remain linked to the RGO structure. The formation of a bidentate carboxylate ligand was responsible for such stability. The same trend was observed for the rest of the fabrics (1G, 2G and 3G). The advantage of employing fabrics as supports for catalysis is that the catalyst can be deposited on the fabric and can be easily recovered from solution. Traditional photo-catalysts that are dispersed in solution have the disadvantage that after reaction, the catalyst has to be recovered through centrifugation. The catalytic activity is affected by the recycling due to aggregation or incomplete separation from the solution [20]. In this way, the nanoparticle content and contact between the components would be increased.

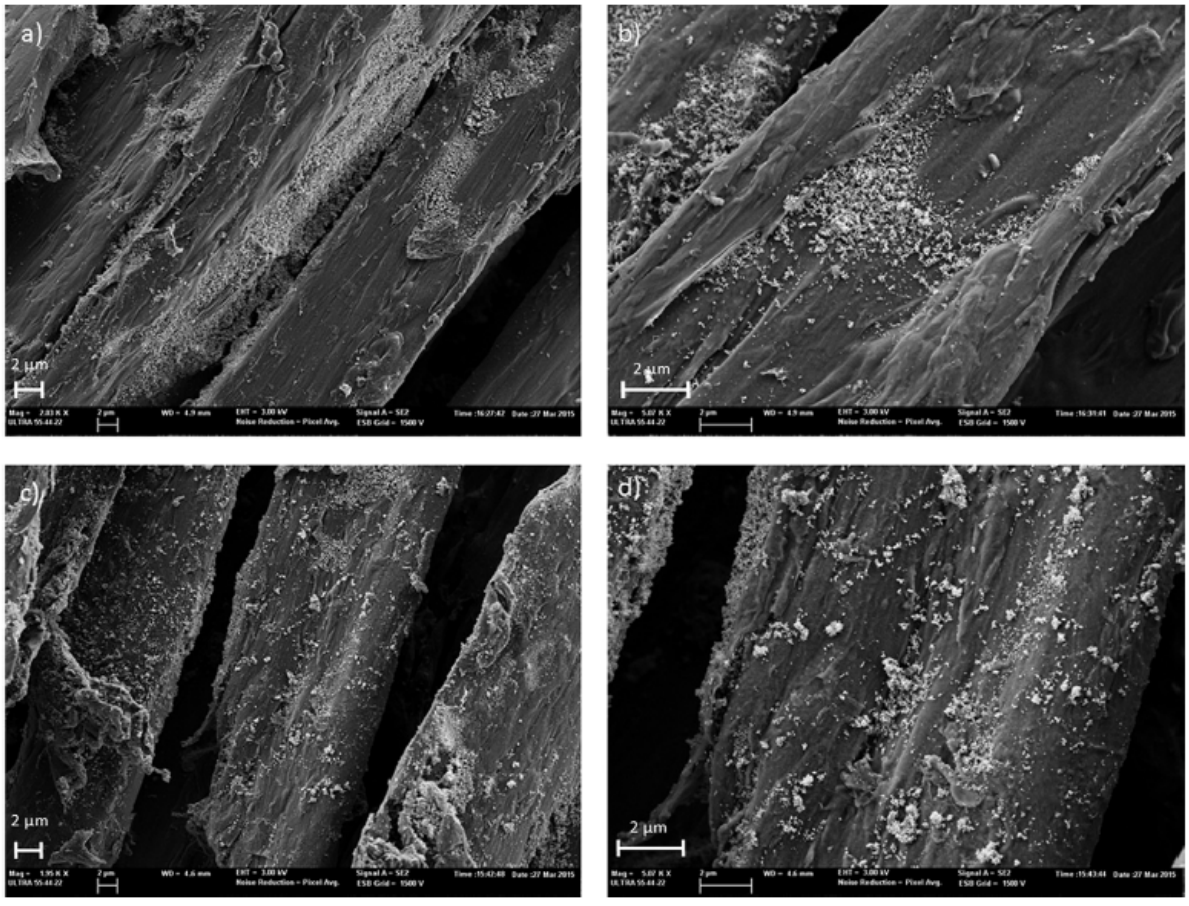

Figure 3. FESEM micrographs of polyester-4G + TiO_2 prior (a, b) and after performing the photocatalytic tests (c, d)

UV blocking: The UV transmittance spectra treated polyester fabric with RGO/TiO_2 nanocomposite were illustrated in Figure 4.

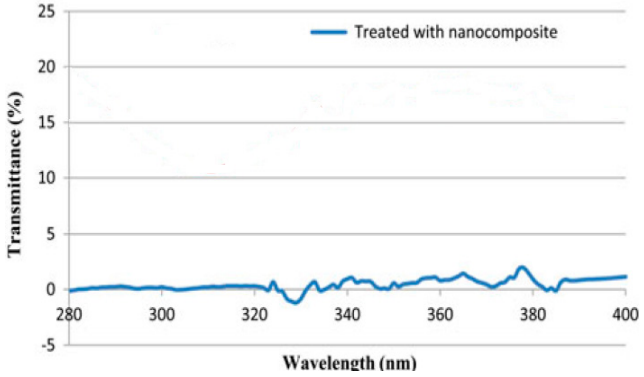

Figure 4. UV transmittance spectra of treated polyester fabric with RGO/TiO_2 nanocomposite

The graphene oxide/TiO_2 nanocomposite treated polyester fabric had lower UV transmittance. Consequently, the treated polyester fabrics with RGO/TiO_2 nanocomposite have good UV blocking property due to the synergetic UV absorption of titanium dioxide and graphene oxide.

Anti-microbiological tests: The antimicrobial activity of the samples was evaluated against Escherichia coli (E. coli, ATCC 25922, Gram negative bacterium) and Staphylococcus aureus (S. aureus, ATCC 25923, Gram-positive bacterium) using two different methods, i.e. agar diffusion plate method (qualitative method) and suspension method (quantitative method).

The agar diffusion plate method was carried out according to ISO 20645:2004 (E). In this method, bacterial cells were cultured on a plate containing Triptic soy broth culture medium. Circular samples of fabric with 10-mm diameter were prepared and placed on the plate. The samples were incubated for 24 h in an oven at 37°C. Subsequently, the samples were studied visually, and the presence of bacteria was observed underneath as well as around the fabric.

The suspension tests were performed according to an AATCC test method 100-2004. This method is specially designed for specimens treated with non-releasing antibacterial agents under dynamic contact conditions. Antimicrobial activity was expressed in terms of the percentage reduction of the micro-organisms and calculated as:

$$\text{Percentage reduction of microorganisms (R)\%} = (A - B)/A \times 100$$

Where A and B are the number of micro-organisms colonies on untreated and treated fabrics, respectively.

There was 3.4 × 105 colony forming units (cfu) of bacteria in the primary inoculum. Saline solution 8.5 g/L sodium chloride to 1000 ml distilled water was used as the neutralizing solution. Serial dilution of 10–10,000 was made for incubation on agar plate. Tryptic soy agar was applied as the agar.

Table 2. Formulations and numbers of sam*ples investigated in this study*

Sample Number	Graphene oxide %	TiO_2 %	Under sunlight E %
1	0	0	2.8
2	0	1	40.53
3	0.4	0.1	16.82
4	0.4	0.5	52.87
5	0.4	1	63.46
6	0.8	0.1	20.13
7	0.8	0.5	60.35
8	0.8	1	71.59
9	0.12	0.1	20.18
10	0.12	0.5	68.87
11	0.12	1	80.24
12	0.2	0.1	26.73
13	0.2	0.5	78.07
14	0.2	1	84.21
15	0.4	0.1	31.54
16	0.4	0.5	81.28
17	0.4	1	87.94

Antimicrobial activity of the samples was evaluated against both Gram-positive (S. aureus) and Gram-negative (E. coli) bacteria. The S. aureus bacterium is a pathogenic micro-organism causing many diseases such as toxic shock, purulence, abscess, fibrin coagulation, and endocarditic. Moreover, it is resistant to common antimicrobial agents. Furthermore, E. coli bacterium which causes urinary tract and wound infections is a popular test organism [21].

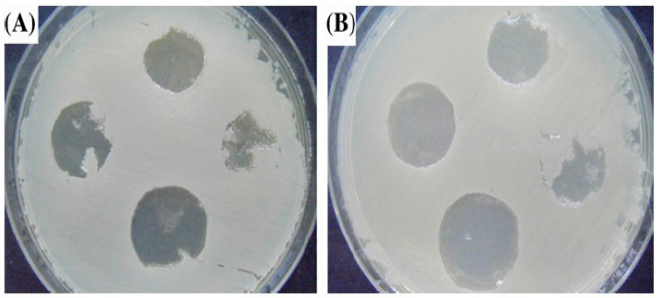

Figure 5. Antimicrobial activities of the fabrics placed on the agar plate inoculated with (A) S. aureus and (B) E. coli: (top) the TiO_2-coated polyester, (right) the raw polyester, (left) the graphene oxide-coated polyester, and (bottom) the graphene oxide/TiO_2-coated polyester

The results of the qualitative test are shown in Figure 5. For RGO/TiO_2 nanocomposite treated samples (sample 14) tested no growth is observed where the samples were in contact with the culture media, in contrast to the raw sample where bacterial growth seems unrestricted. However, no clear zone of inhibition was found around the composite treated fabric due to good fixation of graphene oxide/ TiO_2 nanocomposite on the fibers, which prevents its diffusion into the agar.

Table 3. Antimicrobial properties of treated fabrics according to AATCC 100-2004 test method

Sample	Anti-Microbial activity %	
	Staphylococcus aureus	Escherichia coli
Raw sample-1	00	00
TiO_2 coated sample-2	16	27
RGO/TiO_2 coated sample-14	84	91

For a quantitative determination of the samples' antimicrobial effect, the results of the second test method are summarized in Table 3. As expected, no reduction of the bacteria was found on the raw cotton fabric. Moreover, the graphene oxide/TiO_2 nanocomposite treated samples exhibit a strong antimicrobial activity against both S. aureus and E. coli bacteria as can be seen in Figure 9. Therefore, adding graphene oxide to nano-TiO_2 particles can also facilitate effective bacterial decomposition by increasing the contact between the catalyst nanoparticles and the bacteria. This could be a result of the high surface area of graphene oxide.

4. Conclusions

As showed, a simple method based on polyester fabric coated with reduced graphene oxide/titanium dioxide nanocomposite was developed to produce multifunctional cellulose textiles. Coating graphene oxide/titanium dioxide nanocomposite on the polyester fabrics created functional characteristics including photocatalytic self-cleaning, antimicrobial, electrical conductivity, and UV blocking. Different numbers of RGO coatings were applied (1–4) to see the influence of this parameter on photocatalytic properties. FESEM showed the formation of the RGO/TiO_2 coatings on the fabrics. No significant variations were observed between the fabrics with different number of RGO layers. It was difficult to characterize the surface TiO_2 content due to the irregularity of the fabrics and the uneven distribution of the TiO_2 nanoparticles.

An increase in the photocatalytic degradation efficiency (η) of Rhodamine B was observed with the increasing number of RGO layers. This increase can be attributed to a higher light absorption, better conductivity, the decrease in the charge transfer resistance and the decrease of the time constant, which allows a better electron transfer between TiO_2 nanoparticles and RGO-coated fabrics. It is expected that the graphene oxide/TiO_2 nanocomposite might be used to produce high-performance fabrics and smart textiles.

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