

Article

The Photocatalytical Properties of RGO/TiO₂ Coated Fabrics

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Abstract: The aim of this work was to immobilize reduced graphene oxide (RGO) and titanium dioxide (TiO₂) on the surface of selected fibrous structures. Textile fabrics made of cotton (CO) and polyamide (PA) were used as a carrier. The following modification methods were applied: coating for modification of PA and dip-coating for modification of CO. In the dip-coating method, no auxiliaries were used, which is a huge advantage. The RGO/TiO₂ coated fabrics were characterized using several techniques: ultraviolet–visible (UV–VIS) spectroscopy, scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The obtained results showed the immobilization of RGO and TiO₂ on the fabrics. Raw fabrics absorb much less radiation than coated ones, which is associated with strong absorption of radiation by applied modifiers (RGO and TiO₂). Photocatalytic activity of functionalized textiles was determined using aqueous phenol solutions. Phenol removal efficiency obtained for RGO/TiO₂ coated CO and RGO/TiO₂ coated PA was 51% and 46%, respectively. The hydroxyl radicals play a major role in the phenol photocatalytic degradation. The phenol removal efficiency in the fifth cycle was higher (about 14% and 8% for RGO/TiO₂ coated CO and RGO/TiO₂ coated PA, respectively) compared to the first cycle.

Keywords: RGO/TiO₂ coated fabrics; functionalized polyamide fabric; functionalized cotton fabric; photocatalysis; photocatalytic textiles; photodegradation of phenol

1. Introduction

In recent years, surface modification, including surface modification of various textile structures, has attracted the attention of scientists. Surface modification of textiles usually leads to changes in their properties. Mention should be made of multifunctional fabrics that have electroconductive properties [1–4], antibacterial properties [5–9], self-cleaning [10], flame retardant properties [11], ultraviolet blocking properties [3,4,9] and also photocatalytic properties [5,6,12]. The development of photocatalytic textiles is mainly associated with their covering with photocatalyst coatings. Due to the immobilization of photocatalysts on a proper carrier, the problem of their removal from the reaction solution after the photocatalytic process can be solved. One of the best known and most studied photocatalysts is titanium dioxide (TiO₂) which is characterized by relatively low toxicity, chemical stability and low cost [13–27]. Easy and fast recombination of photogenerated electron–hole pairs and limited photoactivity in the visible light range, which leads to lower photocatalytic performance, are the disadvantages of this catalyst. To increase the photocatalytic activity of TiO₂, doping with

various noble metals [13–17], as well as modification with nonmetallic chemical elements [18–20], including graphene and its derivatives (graphene oxide (GO), reduced graphene oxide (RGO)), can be done [21–26]. Graphene, defined as a single layer of carbon atoms densely packed in a benzene-ring structure, has a large specific surface area, high adsorption capacity and electrical conductivity [28]. Due to its unique properties, graphene and its derivatives can act as a conductive carrier, adsorbent, photosensitizer, photostabilizer, photocatalyst and co-catalyst in nanocomposites [28]. Pedrosa et al. applied GO materials, prepared by Hummers' and Brodie's method, as photocatalysts for phenol degradation under UV/VIS and visible irradiation [29]. These experiments showed that GO prepared by Brodie's method has a much higher photocatalytic activity compared to GO prepared by Hummers' method [29]. Moreover, GO prepared by Brodie's method is active in visible light and stable in re-use cycles [29]. Hybrid graphene/TiO₂ nanocomposites have been used for photodegradation of pollutants and microorganisms, for the production of hydrogen, as well as in photoanodes of dye-sensitized solar cells [13–16,18–21,23–26,30–34].

The immobilization of the photocatalyst is a widely studied process [24,31,35–41]. Lin and coworkers synthesized the TiO₂-RGO coated side-glowing optical fibers and applied them for photocatalytic oxidation of pharmaceuticals [24]. Analysis of UV–VIS absorption spectra of the above nanocomposites indicated that mixing RGO into TiO₂ particles could reduce band gap energy, thereby enhancing utilization efficiency of visible light [24]. The sandwich structured GO-based membrane intercalated by TiO₂ was used in nanofiltration process [31]. Such a membrane showed a high water flux and maintained high organic dye rejection (99.36% and 99.85% for methyl orange and methylene blue, respectively) [31].

Gracic et al. used four series of supported photocatalysts based on TiO₂-chitosan composite (with or without the addition of triarylmethane dye) for photocatalytic treatment of a model solution of bisphenol A under visible irradiation, and household greywater effluent under sunlight [42]. As a carrier for the immobilization of photocatalysts, a polyester/wool blend fabric pre-treated with atmospheric and low pressure oxygen plasma was used. The authors observed the sensitizing effect of the dye during the first 180 min of photocatalytic treatment of greywater under solar irradiation. Whereas in the case of photocatalytic degradation of bisphenol A under visible light, the addition of dye caused a lower degradation rate [42]. Karimi and co-workers applied cotton fabric coated with graphene/TiO₂ nanocomposite for dye photodegradation [7]. The efficiency of photodegradation of methylene blue using of the above-mentioned photoactive cellulose textiles reached over 99% and 92% under UV irradiation and sunlight, respectively [7]. In addition, the cotton-coated nanocomposite had excellent antibacterial and antifungal properties and low cytotoxicity to human fibroblasts [7]. Research conducted by Molina et al. showed that photocatalytic potential of polyester fabrics based on RGO and TiO₂ coatings increased with the number of RGO coatings, due to the increased light absorption and better electrical properties [6]. A similar relationship occurred in the case of photocatalytic degradation of rhodamine B by using RGO and TiO₂ immobilized on cotton textile—the increase in the number of applied RGO layers caused an increase in photodegradation efficiency [43]. Touhid et al. used a semi-continuous dyeing process to immobilize RGO and TiO₂ on polyester fabric [41]. The functionalized fabric showed antibacterial properties. Overall efficiency of TiO₂-RGO against Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria was 99.5 and 98.0%, respectively [41]. Cao et al. showed that the use of neoprene as a binder in the production of TiO₂-coated fabrics improves the rate of photodegradation of dyes by the fabrics [44]. This binder simultaneously modifies the surface of the TiO₂ particles with Cl and dopes TiO₂ with Cl. The TiO₂ coated fabric exhibits excellent adsorption for two cationic dyes (rhodamine B and methylene blue), while the anionic dye (methyl orange) is very weakly adsorbed on the coated fabric [44]. After 50 min of photodegradation using TiO₂ coated fabric, the removal efficiency for rhodamine B and methylene blue was 95.2 and 96.0%, respectively. In the case of methyl orange, the photodegradation rate reached 95.4% after 180 min [44]. In addition, it should be noted that the photocatalyst-coated fabric has

good recycling properties—the performance of this fabric has not been reduced after eight cycles of photodegradation of rhodamine B [44].

This paper describes research on the immobilization of RGO and TiO₂ on the surface of selected fibrous structures. The following modification methods were used: coating and dip-coating. As a result of the conducted experiments, RGO/TiO₂ coated fabrics were obtained. The RGO/TiO₂ coated fabrics were characterized by UV–VIS spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). Photocatalytic activity of functionalized fabrics was determined using aqueous phenol solutions.

2. Materials and Methods

2.1. Materials

GO (water-based GO solution, oxygen content 45–52%) and RGO were purchased from Łukasiewicz Research Network—Institute of Electronic Materials Technology. TiO₂ (Aeroxide® P25, 21 nm primary particle size), hydrochloric acid (37%), acetonitrile (hypergrade for LC-MS LiChrosolv®, Supelco), phenol (≥99.0%) and *tert*-butyl alcohol (*t*-BuOH) (≥99.7%) were from Sigma-Aldrich (Taufkirchen, Germany). Binders (Helizarin® Binder TX 4738, Helizarin® Fixing Agent TX 4737) and thickeners (Lutexal TX 4733) were purchased from BASF (Berlin, Germany).

Woven fabrics made of cotton (CO) (surface mass of 150 g·m⁻², Andropol S.A., Poland) and polyamide (PA) (surface mass of 294 g·m⁻², Pabiantex Wojtas Tomaszewski Sp. J., Poland) were used as a carrier.

2.2. Methods

The applied modification methods included coating and dip-coating. Modification of CO was made by dip-coating method using a water dispersion containing GO (5 cm⁻³ water-based GO solution at the concentration of 10 g·dm⁻³) and TiO₂ (10 g). The dispersion was acidified with hydrochloric acid (0.2 cm⁻³ HCl solution with concentration of 37%), next mechanically mixed (60 min) and sonicated (60–90 min). The fabric samples were placed in the water dispersion, and then were squeezed (automatic padding machine, Ernst Benz Textilmaschinen, Rumlang-Zurich, Switzerland) at a nip pressure of 30 kg·cm⁻². Three padding cycles were applied. Then the samples were dried (20 min, 60 °C) and heated (3 h, 200 °C) in a KTF-350 S coating-heating machine (Mathis) which caused a thermal reduction of GO. The deposition of the TiO₂ and GO on CO by using the dip-coating method gave satisfactory results (data presented in the results and discussion), therefore the coating method was not applied for CO. As the melting point of polyamide is in the range 200–230 °C [45,46], it makes the application of the above described dip-coating method followed by thermal reduction of GO for PA modification difficult. Therefore, for modification of PA only coating method was applied.

The PA was modified by the coating method using a KTF-350 S coating-heating machine (Mathis, Oberhasli, Switzerland). The water-based paste (100 cm⁻³) consisting of TiO₂ (5 g), RGO (0.025 g), binding agents (12 g of Helizarin® Binder TX 4738, 2 g of Helizarin® Fixing Agent TX 4737) and a thickener (5 g of Lutexal TX 4733) was used. The coated PA samples were dried (4 min, 100 °C) and heated (30 s, 160 °C) in a KTF-350 S coating-heating machine (Mathis).

XPS/AES Microlab 350 spectrometer (Thermo Electron, Waltham, MA, USA) was used to analyze the chemical composition of the surface of the obtained materials. Non-monochromated X-ray source (Al K_α) with excitation energy at 1486.6 eV and 300 W of power was used for XPS analysis. For determination of the chemical state of the individual elements and quantitative chemical composition, the high-resolution XPS spectra were recorded in narrow binding energy ranges with a resolution of 0.1 eV. For deconvolution of the recorded XPS spectra, an Avantage software (ver. 5.9911, Thermo Fisher Scientific, Waltham, MA, USA) was used.

SEM-EDX analyses were performed using a scanning electron microscope equipped with a BSE detector (backscattered electrons signal detection) (LEO Electron Microscopy Ltd., Cambridge, UK)

(model 1430 VP, 2001) and an energy dispersive X-ray spectrometer (EDX) Quantax 200 with an XFlash 4010 detector (Bruker AXS, Karlsruhe, Germany 2008).

FTIR spectra were obtained using Fourier-transform infrared spectrophotometer (Jasco 4200 series) equipped with an ATR attachment (Pike Gladi ATR, Fitchburg, WI, USA). The study was carried out in the range of 400–4000 cm^{-1} .

UV–VIS spectra were assessed using a double beam Jasco V-550 UV/VIS spectrophotometer (Tokyo, Japan) with integrating sphere attachment in the range of 200–800 nm.

The photocatalytic efficiency of the prepared fabric-based composites was investigated by phenol degradation. The experiments were carried out in a 400 cm^{-3} quartz photoreactor placed in a merry-go-round device located between UV lamps. Three UV A (11 W, Philips, Eindhoven, The Netherlands) and one UV ABC (125 W, Philips, Eindhoven, The Netherlands) lamps were used as a source of ultraviolet light. A roll of rectangular RGO/TiO₂ coated fabric (dimensions 14 cm $\times$ 22 cm) was immersed in a photoreactor filled with an aqueous phenol solution. The content of the photoreactor was irradiated for 6 h and 2 cm^{-3} samples were taken continuously. The photolysis experiment was carried out in a similar way, but without a coated fabric placed in the photoreactor. The adsorption experiment was also carried out in the above-mentioned equipment, but without irradiation. In case of scavenger test, *t*-BuOH in concentration of 0.1 mol dm^{−3} was added to the aqueous phenol solution. After the experiments, the coated fabrics were rinsed with demineralized water and dried at ambient temperature.

The progress of phenol degradation was monitored by liquid chromatographic analysis using a chromatograph (Nexera-I LC-2040C, 3D Plus, LCMS-8045, Shimadzu, Kyoto, Japan) equipped with a Kinetex C18 column (100 mm $\times$ 3.0 mm, 1.7 μm) (Phenomenex, Aschaffenburg, Germany). A linear H₂O/acetonitrile gradient (10% acetonitrile at 1 min to 100% at 4 min) was used during the analysis. The analyses were performed at a constant temperature of 30 °C. The injection volume of the samples was 20 μL . Phenol was detected at 272 nm.

3. Results and Discussion

3.1. Physicochemical Properties of Coated Fabrics

3.1.1. UV–VIS Analysis

At the beginning, the light-absorbance properties of the raw and coated fabrics were analyzed by UV–VIS spectroscopy. The results of this analysis are presented in Figure 1. It can be clearly seen that both coated and raw fabrics absorb UV–VIS radiation. Raw fabrics, however, absorb much less radiation than coated ones, which is associated with strong absorption of radiation by the applied modifiers (RGO and TiO₂). In general, TiO₂ absorbs radiation in the UV region, what can be assigned to the intrinsic band gap absorption of this photocatalyst resulting from the electron transitions from the valence band to the conduction band ($\text{O}2\text{p} \rightarrow \text{Ti}3\text{d}$) [22]. GO absorbs the UV and VIS radiation, which leads to changing of its physicochemical properties and the toxicity [47]. GO shows characteristic absorbance peaks at 230 and 300 nm due to $\pi\text{-}\pi^*$ transitions of $\text{C}=\text{C}$ and $\text{n-}\pi^*$ transitions of $\text{C}=\text{O}$, $\text{O}-\text{C}=\text{O}$ and $\text{C}-\text{OH}$, respectively [47]. According to the studies performed by Chen et al., the transmittance of the RGO/water nanofluids is quite less than of the GO/water one, what indicate that the change from GO to RGO enhanced optical absorption [48]. UV–VIS diffuse reflectance spectra measurement performed by Landi Jr. et al. [43] showed that the addition of more RGO coatings onto the cotton fabric induce the increase of absorbance in the UV region. Moreover, the above studies confirmed the strong absorption of radiation in the visible region by RGO [43].

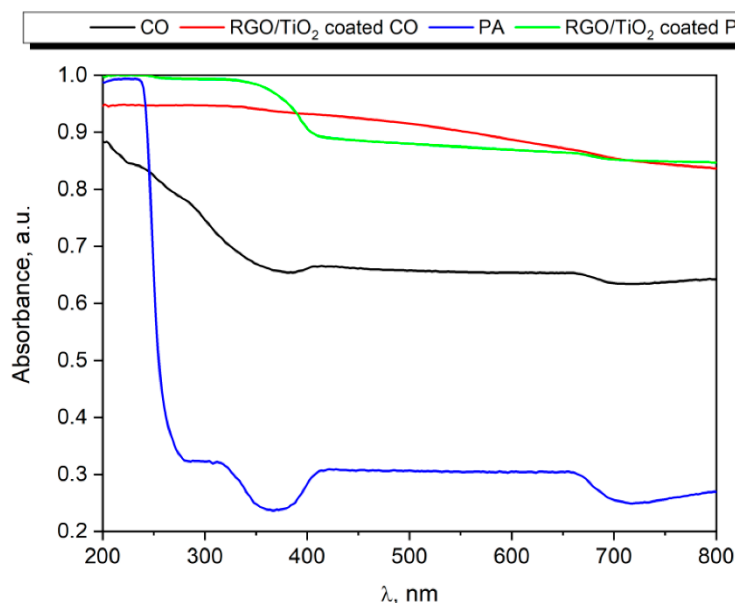


Figure 1. Absorption spectra of raw and reduced graphene oxide (RGO)/TiO₂ coated fabrics.

3.1.2. SEM-EDX Analysis

RGO/TiO₂ coated fabrics were examined using SEM. This analysis confirmed the immobilization of RGO/TiO₂ onto fabrics (Figure 2). The energy-dispersive X-ray spectroscopy (EDX) mapping showed the aggregation of TiO₂ (Figures 3 and 4), which is particularly evident in RGO/TiO₂ coated PA (Figure 4). The aggregation of TiO₂ nanoparticles on the RGO coatings was also noticed by Molina et al. during the modification of polyester fabrics [6]. Cai et al. observed the laminar GO layers on the SEM image of the cotton fabric treated with GO [4]. These laminar structures were also seen on the cotton fabrics surface coated with GO after thermal treatment [4]. SEM analysis performed by Zulan et al. showed that the morphology of RGO coated silk fabric was similar to the morphology of GO coated silk fabric, what suggests that the thermal GO reduction did not change the surface conformation [49]. The modification of cotton fabric by graphene and TiO₂ performed by Karimi et al. lead to achieving the cotton surface completely coated by graphene/TiO₂ nanocomposite layer [7]. The similar observation was made by Landi Jr. et al. [43].

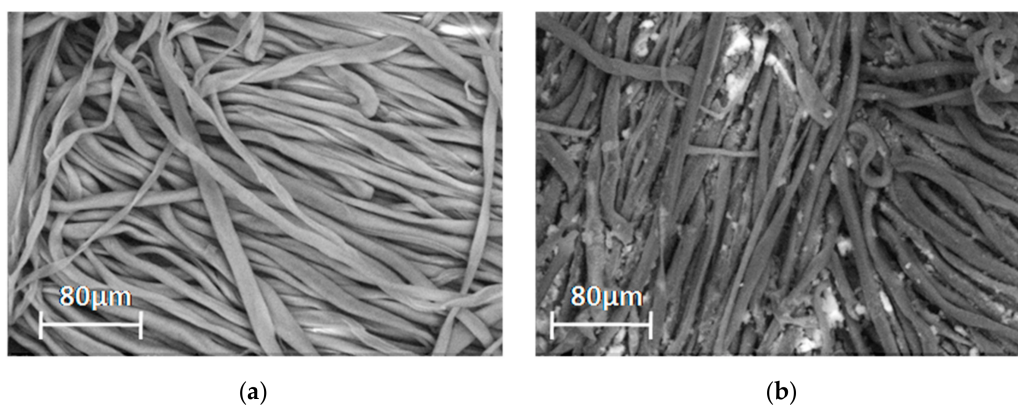


Figure 2. *Cont.*

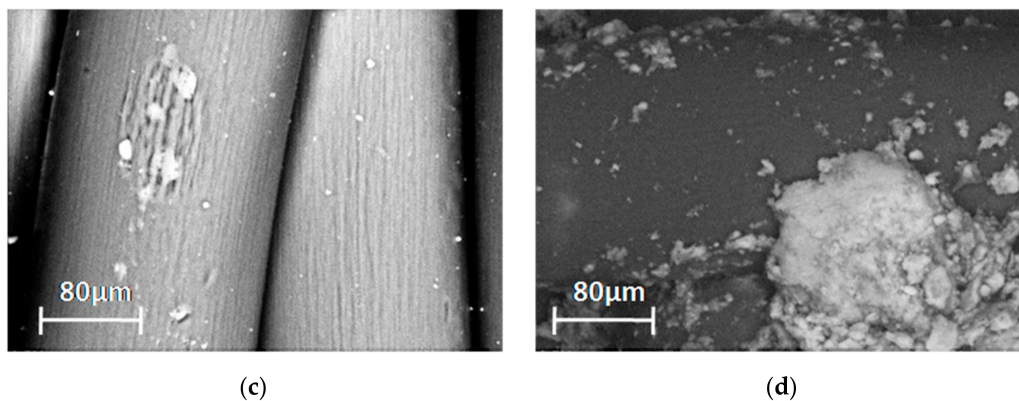


Figure 2. SEM images of (a) raw CO, (c) raw PA, (b) RGO/TiO₂ coated CO and (d) RGO/TiO₂ coated PA fibrous structures.

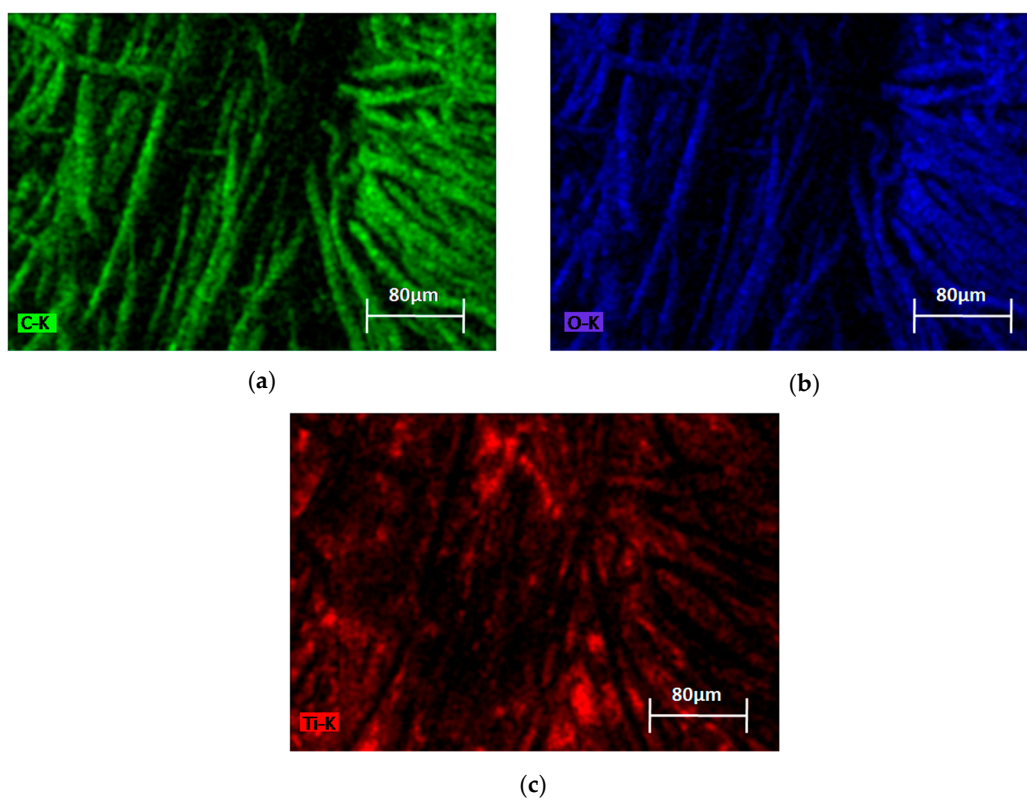


Figure 3. EDX mapping of RGO/TiO₂ coated CO ((a)- map of the C element, (b)- map of the O element, (c)- map of the Ti element).

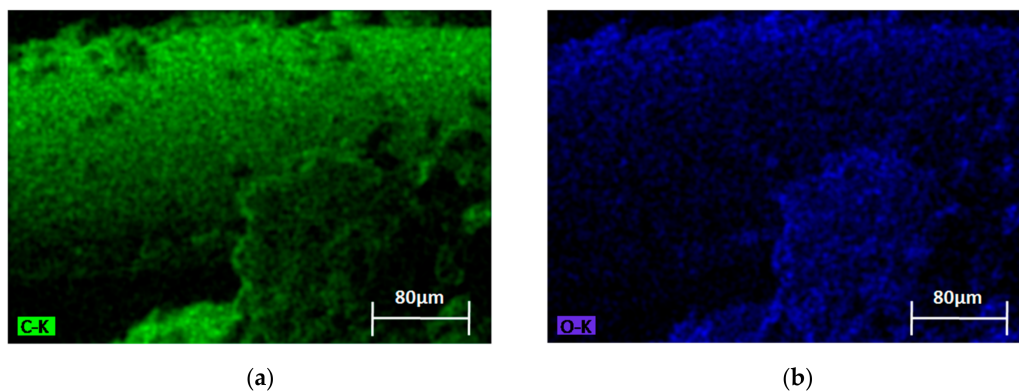


Figure 4. Cont.

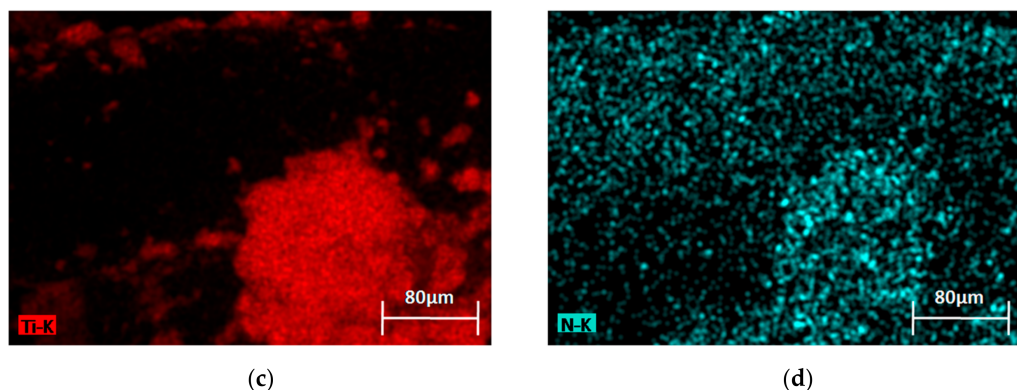


Figure 4. EDX mapping of RGO/TiO₂ coated PA ((a)- map of the C element, (b)- map of the O element, (c)- map of the Ti element, (d)- map of the N element).

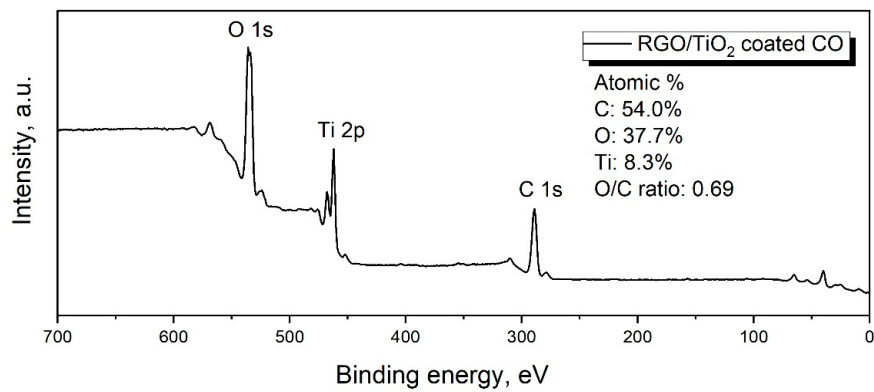
Table 1 provides the results of the EDX analysis. Raw fibrous structures consisted mainly of C, O and in the case of PA also of the N element, while coated fabrics additionally contained Ti with mass percentages of 50.27% and 72.67% (Table 1) for RGO/TiO₂ coated CO and RGO/TiO₂ coated PA, respectively.

Table 1. Results of EDX analysis.

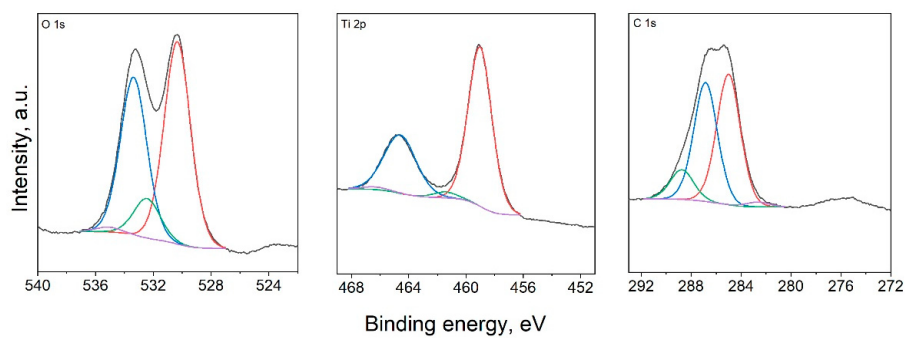
Sample	Mass Percentage, %			
	C	O	Ti	N
CO	46.15	53.85	-	-
RGO/TiO ₂ coated CO	19.84	29.88	50.27	-
PA	74.49	13.42	0.36	11.73
RGO/TiO ₂ coated PA	19.96	7.19	72.67	0.19

3.1.3. XPS Analysis

Figures 5 and 6 show the results of the XPS analysis of RGO/TiO₂ coated fabrics. The XPS wide scans revealed the presence of C 1s and O 1s peaks, which are related to RGO deposits and fabrics. Whereas the presence of Ti 2p signals was associated with the TiO₂ nanoparticles deposits. Additionally, in case of RGO/TiO₂ coated PA the N 1s peak appears, what is associated with nitrogen functional groups being part of this fabric. In Figures 5b and 6b it can be observed that C 1s, O 1s and Ti 2p spectra can be deconvoluted respectively into few peaks, which correspond to characteristics bonds of analyzed materials like: C–C, C–O, C=O, C–N, C–F, Ti–O (TiO₂). The XPS results are summarized in Table 2, which show the most probable origin of the peaks with their binding energies and atomic percentage of each group. Our XPS results are consistent with the literature data [4,6,32]. The reduction of GO should be indicated by the decrease in oxygen to carbon (O/C) ratio of XPS spectra. Gao et al. obtained the O/C ratio equal to 0.4 and 0.59 for GO irradiated under UV and Vis light, respectively [47]. Chen et al. performed the reduction of GO under UV irradiation [48]. After irradiation of GO by UV light, they observed the decrease in area percentage of C=O group and the increase in area percentage of the C–C group [48]. The calculated O/C ratio for RGO/TiO₂ coated CO is higher (0.69) than O/C ratio for RGO/TiO₂ coated PA (0.44) which may suggest that the RGO/TiO₂ coated CO contains more oxygen functional groups than RGO/TiO₂ coated PA.

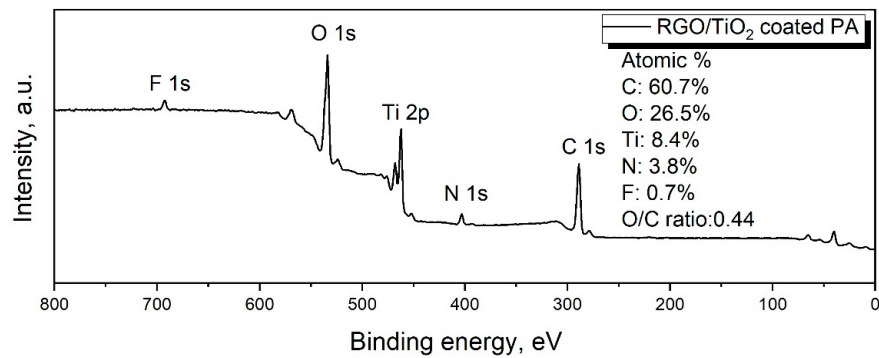


(a)

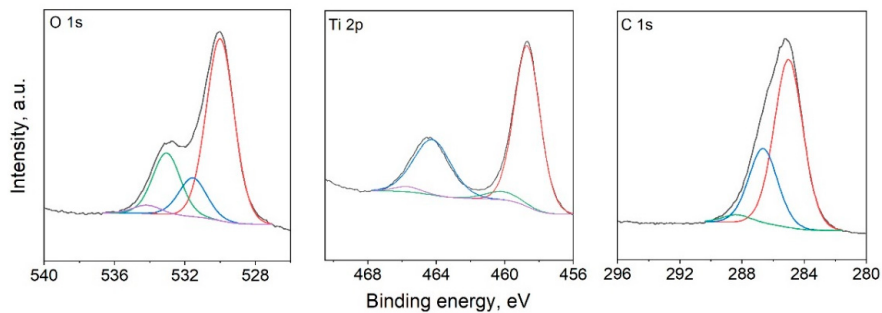


(b)

Figure 5. XPS (a) and C 1s, O 1s and Ti 2p XPS (b) spectra of RGO/TiO₂ coated CO.



(a)



(b)

Figure 6. XPS (a) and C 1s, O 1s and Ti 2p XPS (b) spectra of RGO/TiO₂ coated PA.

Table 2. Deconvoluted XPS data of coated fabrics (A smart-type background subtraction model was used to obtain the XPS signal intensity of each individual peaks. Subsequently, an asymmetric Gaussian/Lorentzian function at a constant ratio G/L = 0.35 was used for the deconvolution procedure. All measured BEs were calibrated to the position of C 1s peak at 285.0 eV).

RGO/TiO ₂ Coated CO			
Name	Peak BE	Atomic %	Bond
Ti2p3	459	8	Ti–O (TiO ₂)
Ti2p3	461.4	0.3	Ti–O (TiO _x)
O1s	530.3	18.8	Ti–O (oxide)
O1s	533.4	14.7	C–O
O1s	532.4	3.7	C=O
O1s	535.1	0.5	CO ads or H ₂ O
C1s	285	24.9	C–C/C–H
C1s	286.8	22.6	C–OH, C–O, C–N
C1s	288.7	5.7	O–C–O, O=C–OH
C1s	282.7	0.9	carbide
RGO/TiO ₂ Coated PA			
Name	Peak BE	Atomic %	Bond
Ti2p3	458.7	7.9	Ti–O (TiO ₂)
Ti2p3	460.2	0.5	Ti–O (TiO _x)
O1s	530	16.6	Ti–O (oxide)
O1s	531.6	3.5	C=O
O1s	533	5.6	C–O
O1s	534.2	0.8	CO ads or H ₂ O
C1s	285	40.7	C–C
C1s	286.6	18.2	C–O/C–N
C1s	288.4	1.8	C=O/C–F
F1s	689	0.7	C–F
N1s	399.6	3.8	C–N

3.1.4. FTIR Analysis

Figure 7 presents FTIR spectra of modifiers as well as raw and coated fabrics. The FTIR spectra of raw and coated fabrics displayed a broad absorption band of around 3280 cm^{-1} , which is attributed to the O–H stretching vibration of C–OH groups [4]. The presence of peaks at 1640 and at 1514 cm^{-1} is related to C=O stretching of COOH groups and C=C groups, respectively [4,43]. The broad absorption band in the range of $100\text{--}400\text{ cm}^{-1}$ is attributed to Ti–O and Ti–O–Ti vibrations [42,50]. In addition, for cotton fabrics there is a peak of around 1057 cm^{-1} corresponding to C–O stretching [4]. For coated fabrics, a decrease in the intensity of characteristic peaks can be observed compared to the raw fabrics. Cai et al. did not observe any significant changes in the FTIR spectrum of GO coated CO fabric. However, in the case of CO fabric coated with RGO, in the FTIR spectrum the peak related to C=O stretching was absent and the peaks associated with O–H stretching and asymmetrical C–H stretching became relatively weak [4].

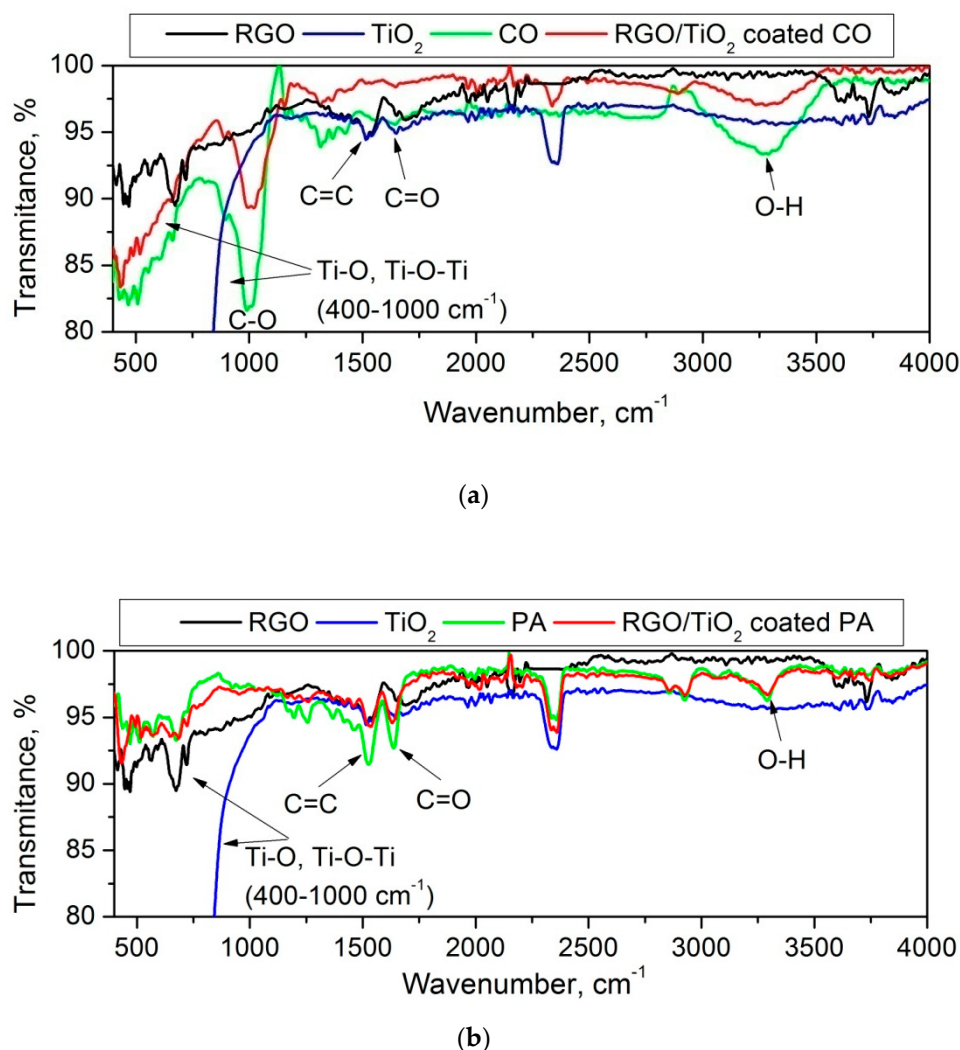


Figure 7. FTIR spectra of modifiers, raw and RGO/TiO₂ coated CO (a) and RGO/TiO₂ coated PA fabrics (b).

3.1.5. Photocatalytic Activity

The photocatalytic activity of RGO/TiO₂ coated fabric was evaluated for the photodegradation of phenol under UV light irradiation. Figure 8a shows the results of phenol degradation using various processes: photocatalytic degradation as well as adsorption and photolysis. In the case of RGO/TiO₂ coated CO, after 6 h of degradation process, the removal efficiency reached 4% and 51% for adsorption and photocatalysis, respectively. The application of RGO/TiO₂ coated PA leads to the phenol removal efficiency of 8% and 46% for adsorption and photocatalysis, respectively. The photolysis efficiency after the same time was 30% which indicates that this process plays an important role in phenol degradation during photocatalytic degradation using RGO/TiO₂ coated fabrics, while the adsorption process has a small effect. The studies of photocatalytic degradation of phenol under visible light irradiation and using AgBr/BiOBr/graphene as a photocatalyst showed that photolysis had no effect on phenol removal, and the adsorption process remarkably influenced degradation of this compound. In these studies, simultaneous adsorption and photocatalysis led to complete mineralization of phenol within 6 h [51].

In order to better understand the mechanism of the phenol photodegradation, the scavenger tests were performed. In these studies, the well-known hydroxyl radical scavenger—*t*-BuOH [52] was applied. The obtained results (Figure 8a) suggested that hydroxyl radicals (OH•) play a major role in the phenol photocatalytic degradation. The phenol removal efficiencies in the presence of *t*-BuOH

(about 25% and 29%, respectively for CO and PA) were slightly lower than efficiency of the photolysis process, which indicates that radicals take part in the phenol photolysis process. According to the literature, absorption of UV radiation by phenol leads to its excitation [53]. The excited state of phenol can undergo relaxation to the ground state or transformation to the phenoxyl radicals and solvated electrons. Then, the phenoxyl radicals can react with oxygen leading to the formation of benzoquinone. While solvated electrons can undergo a few reactions leading to the hydroxyl radicals formation, which can then react with phenol [53].

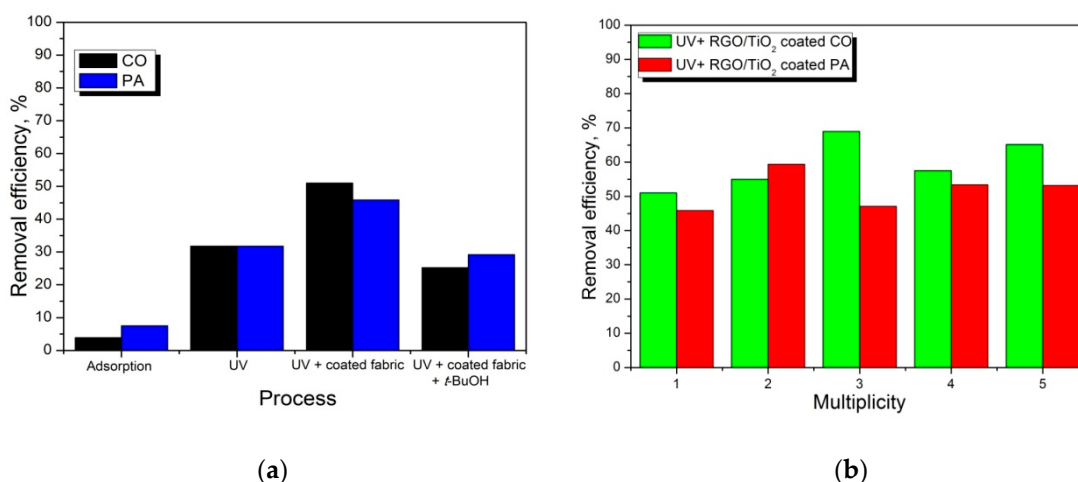


Figure 8. Phenol removal from aqueous solution by various methods (a) and multiple applications of RGO/TiO₂ coated fabrics (b) in photocatalytic degradation of phenol.

Figure 8b shows the results of re-use tests of coated fabrics for photocatalytic degradation of phenol. After each photocatalytic experiment the coated fabric was washed with deionized water and dried at ambient temperature before re-use. As can be seen, the phenol removal efficiency in the fifth cycle was higher (about 14% and 8% for RGO/TiO₂ coated CO and RGO/TiO₂ coated PA, respectively) compared to the first cycle. On the surface of coated fabrics probably a small amount of GO is present (especially in the case of RGO/TiO₂ coated CO fabric) which has not been reduced during the thermal reduction process. The performed XPS analysis suggests that RGO/TiO₂ coated CO contains more oxygen functional groups than RGO/TiO₂ coated PA (the calculated O/C atomic ratio for RGO/TiO₂ coated CO is higher than O/C ratio for RGO/TiO₂ coated PA). According to the literature, GO can undergo the photoreduction process under UV radiation [28]. Therefore, the amount of RGO on coated fabrics may change, which can lead to changes in phenol removal efficiency. This phenomenon can be associated with the photoreduction of GO under UV irradiation, but this requires further experimentation studies.

The disadvantage of this work is low phenol removal efficiency; therefore, our future work will be focused on the improvement and optimization of the photodegradation efficiency. The removal efficiency can be improved by the addition of a higher amount of TiO₂ to the dispersion or paste used in the dip-coating and coating process, respectively, which may increase the absorption of the UV light by this photocatalyst. According to the Chun et al. studies, an appropriate catalyst dosage can avoid direct photolysis of phenol and possibly other compounds, as well as increase the mineralization rate of phenol [54]. On the other hand, the amount of RGO can also influence the photodegradation. The experiments performed by Lin et al. indicated that the photocatalytic activity increased with increasing concentration of RGO in composites from 0% to 2.7%, but the degradation was inhibited when the RGO concentration was larger than 2.7% [24]. The increasing of RGO amount in the composite may be achieved by application of another GO reduction method after dip-coating process. There are several methods of GO reduction: thermal reduction applied in this and other works [4,49,55], hydrothermal [32,56], UV photoreduction [28,48,57], chemical reduction [1,6,7,43],

electrochemical reduction [58,59]. Moreover, the application of GO prepared by Brodie's method instead of the GO prepared by Hummers' method can increase the photodegradation efficiency. According to the literature, GO prepared by Brodie's method has a much higher photocatalytic activity compared to GO prepared by Hummers' method [29].

4. Conclusions

Textile fabrics made of cotton and polyamide have been modified by RGO and TiO₂. The following two methods were used for modification: coating for modification of PA and dip-coating for modification of CO. In the dip-coating method, no auxiliaries were used, which is a huge advantage. The physicochemical studies (UV-VIS, SEM, XPS, FTIR) confirmed immobilization of RGO/TiO₂ on fibrous structures. The raw fabrics absorb much less radiation than coated ones, which is associated with strong absorption of radiation by the applied modifiers (RGO and TiO₂). The photocatalytic activity of functionalized textiles using aqueous solutions of phenol was determined. The 51% and 46% efficiency of phenol removal was obtained for RGO/TiO₂ coated CO and RGO/TiO₂ coated PA, respectively. The hydroxyl radicals play a major role in the phenol photocatalytic degradation. Phenol removal efficiency in the fifth cycle was higher (about 14 and 8% for RGO/TiO₂ coated CO and RGO/TiO₂ coated PA, respectively) compared to the first cycle. In summary, very promising results have been obtained, but more research is needed, particularly related to improvement of the photodegradation efficiency.

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References

- Shateri-Khalilabad, M.; Yazdanshenas, M.E. Fabricating electroconductive cotton textiles using graphene. *Carbohydr. Polym.* **2013**, *96*, 190–195. [\[CrossRef\]](#) [\[PubMed\]](#)
- Sahito, I.A.; Sun, K.C.; Arbab, A.A.; Qadir, M.B.; Jeong, S.H. Integrating high electrical conductivity and photocatalytic activity in cotton fabric by cationizing for enriched coating of negatively charged graphene oxide. *Carbohydr. Polym.* **2015**, *130*, 299–306. [\[CrossRef\]](#) [\[PubMed\]](#)
- Hu, X.; Tian, M.; Qu, L.; Zhu, S.; Han, G. Multifunctional cotton fabrics with graphene/polyurethane coatings with far infrared emission, electrical conductivity, and ultraviolet blocking properties. *Carbon* **2015**, *95*, 625–633. [\[CrossRef\]](#)
- Cai, G.; Xu, Z.; Yang, M.; Tang, B.; Wang, X. Functionalization of cotton fabrics through thermal reduction of graphene oxide. *Appl. Surf. Sci.* **2017**, *393*, 441–448. [\[CrossRef\]](#)
- Krishnamoorthy, K.; Navaneethaiyer, U.; Mohan, R.; Lee, J.; Kim, S.-J. Graphene oxide nanostructures modified multifunctional cotton fabrics. *Appl. Nanosci.* **2012**, *2*, 119–126. [\[CrossRef\]](#)
- Molina, J.; Fernandes, F.; Fernández, J.; Pastor, M.; Correia, A.; Souto, A.P.; Carneiro, J.O.; Teixeira, V.; Cases, F. Photocatalytic fabrics based on reduced graphene oxide and TiO₂ coatings. *Mater. Sci. Eng. B* **2015**, *199*, 62–76. [\[CrossRef\]](#)
- Karimi, L.; Yazdanshenas, M.E.; Khajavi, R.; Rashidi, A.; Mirjalili, M. Optimizing the photocatalytic properties and the synergistic effects of graphene and nano titanium dioxide immobilized on cotton fabric. *Appl. Surf. Sci.* **2015**, *332*, 665–673. [\[CrossRef\]](#)
- Hegab, H.M.; El Mekawy, A.; Zou, L.; Mulcahy, D.; Saint, C.P.; Ginic-Markovic, M. The controversial antibacterial activity of graphene-based materials. *Carbon* **2016**, *105*, 362–376. [\[CrossRef\]](#)
- Berendjchi, A.; Khajavi, R.; Yousefi, A.A.; Yazdanshenas, M.E. Improved continuity of reduced graphene oxide on polyester fabric by use of polypyrrole to achieve a highly electro-conductive and flexible substrate. *Appl. Surf. Sci.* **2016**, *363*, 264–272. [\[CrossRef\]](#)

10. Yu, M.; Wang, Z.Q.; Liu, H.Z.; Xie, S.Y.; Wu, J.X.; Jiang, H.Q.; Zhang, J.; Li, L.; Li, J. Laundering durability of photocatalyzed self-cleaning cotton fabric with TiO₂ nanoparticles covalently immobilized. *ACS Appl. Mater. Interfaces* **2013**, *5*, 3697–3703. [\[CrossRef\]](#)
11. Some, S.; Shackery, I.; Kim, S.J.; Jun, S.C. Phosphorus-Doped Graphene Oxide Layer as a Highly Efficient Flame Retardant. *Chem. Eur. J.* **2015**, *21*, 15480–15485. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Pakdel, E.; Wang, J.; Kashi, S.; Sun, L.; Wang, X. Advances in photocatalytic self-cleaning, superhydrophobic and electromagnetic interference shielding textile treatments. *Adv. Colloid Interfac. Sci.* **2020**, *277*, 102116. [\[CrossRef\]](#)
13. Li, M.; Yu, Z.; Liu, Q.; Su, L.; Huang, W. Photocatalytic decomposition of perfluorooctanoic acid by noble metallic nanoparticles modified TiO₂. *Chem. Eng. J.* **2016**, *286*, 232–238. [\[CrossRef\]](#)
14. Ran, H.; Fan, J.; Zhang, X.; Mao, J.; Shao, G. Enhanced performances of dye-sensitized solar cells based on Au-TiO₂ and Ag-TiO₂ plasmonic hybrid nanocomposites. *Appl. Surf. Sci.* **2018**, *430*, 415–423. [\[CrossRef\]](#)
15. Ribao, P.; Rivero, M.J.; Ortiz, I. TiO₂ structures doped with noble metals and/or graphene oxide to improve the photocatalytic degradation of dichloroacetic acid. *Environ. Sci. Pollut. Res.* **2017**, *24*, 12628–12637. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Iliev, V.; Tomova, D.; Bilyarska, L. Promoting the oxidative removal rate of 2,4-dichlorophenoxyacetic acid on gold-doped WO₃/TiO₂/reduced graphene oxide photocatalysts under UV light irradiation. *J. Photochem. Photobiol. A Chem.* **2018**, *351*, 69–77. [\[CrossRef\]](#)
17. Moslah, C.; Kandyla, M.; Mousdis, G.A.; Petropoulou, G.; Ksibi, M. Photocatalytic Properties of Titanium Dioxide Thin Films Doped with Noble Metals (Ag, Au, Pd, and Pt). *Phys. Status. Solidi. A* **2018**, *215*, 1800023. [\[CrossRef\]](#)
18. Guan, R.; Zhai, H.; Li, J.; Qi, Y.; Li, M.; Song, M.; Zhao, Z.; Zhang, J.; Wang, D.; Tan, H. Reduced mesoporous TiO₂ with Cu₂S heterojunction and enhanced hydrogen production without noble metal cocatalyst. *Appl. Surf. Sci.* **2020**, *507*, 144772. [\[CrossRef\]](#)
19. Kumar, P.; Kar, P.; Manuel, A.P.; Zeng, S.; Thakur, U.K.; Alam, K.M.; Zhang, Y.; Kisslinger, R.; Cui, K.; Bernard, G.M. Noble metal free, visible light driven photocatalysis using TiO₂ nanotube arrays sensitized by P-doped C₃N₄ quantum dots. *Adv. Optical. Mater.* **2020**, *8*, 1901275. [\[CrossRef\]](#)
20. Basavarajappa, P.S.; Patil, S.B.; Ganganagappa, N.; Raghava Reddy, K.; Raghu, A.V.; Venkata Reddy, C.H. Recent progress in metal-doped TiO₂, non-metal doped/codoped TiO₂ and TiO₂ nanostructured hybrids for enhanced photocatalysis. *Int. J. Hydrog. Energy.* **2020**, *45*, 7764–7778. [\[CrossRef\]](#)
21. Faraldos, M.; Bahamonde, A. Environmental applications of titania-graphene photocatalysts. *Catal. Today* **2017**, *285*, 13–28. [\[CrossRef\]](#)
22. Morawski, A.W.; Kusiak-Nejman, E.; Wanag, A.; Kapica-Kozar, J.; Wróbel, R.J.; Ohtani, B.; Aksienionek, M.; Lipińska, L. Photocatalytic degradation of acetic acid in the presence of visible light-active TiO₂-reduced graphene oxide photocatalysts. *Catal. Today* **2017**, *280*, 108–113. [\[CrossRef\]](#)
23. Morales-Torres, S.; Pastrana-Martínez, L.M.; Figueiredo, J.L.; Faria, J.L.; Silva, A.M.T. Design of graphene-based TiO₂ photocatalysts-a review. *Environ. Sci. Pollut. Res.* **2012**, *19*, 3676–3687. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Lin, L.; Wang, H.; Xu, P. Immobilized TiO₂-reduced graphene oxide nanocomposites on optical fibers as high performance photocatalysts for degradation of pharmaceuticals. *Chem. Eng. J.* **2017**, *310*, 389–398. [\[CrossRef\]](#)
25. Wu, Y.; Mu, H.; Cao, X.; He, X. Polymer-supported graphene-TiO₂ doped with nonmetallic elements with enhanced photocatalytic reaction under visible light. *J. Mater. Sci.* **2020**, *55*, 1577–1591. [\[CrossRef\]](#)
26. Chi Hieu, N.; Mai Lien, T.; Thi Tuong Van, T.; Juang, R.-S. Enhanced removal of various dyes from aqueous solutions by UV and simulated solar photocatalysis over TiO₂/ZnO/rGO composites. *Sep. Purif. Technol.* **2020**, *232*, 115962.
27. Kanan, S.; Moyet, M.A.; Arthur, R.B.; Patterson, H.H. Recent advances on TiO₂-based photocatalysts toward the degradation of pesticides and major organic pollutants from water bodies. *Catal. Rev.* **2020**, *62*, 1–65. [\[CrossRef\]](#)
28. Li, X.; Yu, J.; Wageh, S.; Al-Ghamdi, A.A.; Xie, J. Graphene in Photocatalysis: A Review. *Small* **2016**, *12*, 6640–6696. [\[CrossRef\]](#)
29. Pedrosa, M.; Da Silva, E.S.; Pastrana-Martínez, L.M.; Drazic, G.; Falaras, P.; Faria, J.L.; Figueiredo, J.L.; Silva, A.M.T. Hummers' and Brodie's graphene oxides as photocatalysts for phenol degradation. *J. Colloid. Interface Sci.* **2020**, *567*, 243–255. [\[CrossRef\]](#)

30. Kusiak-Nejman, E.; Morawski, A.W. TiO₂/graphene-based nanocomposites for water treatment: A brief overview of charge carrier transfer, antimicrobial and photocatalytic performance. *Appl. Catal. B Environ.* **2019**, *253*, 179–186. [[CrossRef](#)]
31. Chen, L.; Li, N.; Wen, Z.; Zhang, L.; Chen, Q.; Chen, L.; Si, P.; Feng, J.; Li, Y.; Lou, J.; et al. Graphene oxide based membrane intercalated by nanoparticles for high performance nanofiltration application. *Chem. Eng. J.* **2018**, *347*, 12–18. [[CrossRef](#)]
32. Zhang, Y.; Hou, X.; Sun, T.; Zhao, X. Calcination of reduced graphene oxide decorated TiO₂ composites for recovery and reuse in photocatalytic applications. *Ceram. Int.* **2017**, *43*, 1150–1159. [[CrossRef](#)]
33. Ren, H.; Koshy, P.; Chen, W.F.; Qi, S.; Sorrell, C.C. Photocatalytic materials and technologies for air purification. *J. Hazard. Mater.* **2017**, *325*, 340–366. [[CrossRef](#)]
34. Xu, D.; Li, L.; He, R.; Qi, L.; Zhang, L.; Cheng, B. Noble metal-free RGO/TiO₂ composite nanofiber with enhanced photocatalytic H₂-production performance. *Appl. Surf. Sci.* **2018**, *434*, 620–625. [[CrossRef](#)]
35. Yaparathne, S.; Tripp, C.P.; Amirbahman, A. Photodegradation of taste and odor compounds in water in the presence of immobilized TiO₂-SiO₂ photocatalysts. *J. Hazard. Mater.* **2018**, *346*, 208–217. [[CrossRef](#)] [[PubMed](#)]
36. Padoin, N.; Soares, C. An explicit correlation for optimal TiO₂ film thickness in immobilized photocatalytic reaction systems. *Chem. Eng. J.* **2017**, *310*, 381–388. [[CrossRef](#)]
37. Lin, L.; Wang, H.; Jiang, W.; Mkaouar, A.R.; Xu, P. Comparison study on photocatalytic oxidation of pharmaceuticals by TiO₂-Fe and TiO₂-reduced graphene oxide nanocomposites immobilized on optical fibers. *J. Hazard. Mater.* **2017**, *333*, 162–168. [[CrossRef](#)]
38. EL-Mekkawi, D.M.; Abdelwahab, N.A.; Mohamed, W.A.A.; Taha, N.A.; Abdel-Mottaleb, M.S.A. Solar photocatalytic treatment of industrial wastewater utilizing recycled polymeric disposals as TiO₂ supports. *J. Clean. Prod.* **2020**, *249*, 119430. [[CrossRef](#)]
39. Islam, M.T.; Dominguez, A.; Turley, R.S.; Kim, H.; Sultana, K.A.; Shuvo, M.A.I.; Alvarado-Tenorio, B.; Montes, M.O.; Lin, Y.; Gardea-Torresdey, J.; et al. Development of photocatalytic paint based on TiO₂ and photopolymer resin for the degradation of organic pollutants in water. *Sci. Total. Environ.* **2020**, *704*, 135406. [[CrossRef](#)]
40. De Araujo Scharnberg, A.R.; de Loreto, A.C.; Bender Wermuth, T.; Kopp Alves, A.; Arcaro, S.; Mantey dos Santos, P.A.; de Assis Lawisch Rodriguez, A. Porous ceramic supported TiO₂ nanoparticles: Enhanced photocatalytic activity for Rhodamine Biodegradation. *Bol. Soc. Esp. Cerám. Vidr.* **2020**, in press. [[CrossRef](#)]
41. Touhid, S.S.B.; Shawon, M.R.K.; Deb, H.; Khoso, N.A.; Ahmed, A.; Fu, F.; Liu, X.D. Nature inspired rGO-TiO₂ micro-flowers on polyester fabric using semicontinuous dyeing method: A binder-free approach towards durable antibacterial performance. *Synth. Met.* **2020**, *261*, 116298. [[CrossRef](#)]
42. Grcic, I.; Erjavec, B.; Vrsaljko, D.; Guyon, C.; Tatoulian, M. Influence of plasma surface pretreatment and triaryl methane dye on the photocatalytic performance of TiO₂-chitosan coating on textile. *Prog. Org. Coat.* **2017**, *105*, 277–285. [[CrossRef](#)]
43. Landi, S., Jr.; Carneiro, J.O.; Fernandes, F.; Parpot, P.; Molina, J.; Cases, F.; Fernández, J.; Santos, J.G.; Soares, G.M.B.; Teixeira, V.; et al. Functionalization of cotton by RGO/TiO₂ to enhance photodegradation of Rhodamine B under simulated solar irradiation. *Water Air Soil Pollut.* **2017**, *228*, 335. [[CrossRef](#)]
44. Cao, Z.; Zhang, T.; Ren, P.; Cao, D.; Lin, Y.; Wang, L.; Zhang, B.; Xiang, X. Doping of chlorine from a neoprene adhesive enhances degradation efficiency of dyes by structured TiO₂-coated photocatalytic fabrics. *Catal* **2020**, *10*, 69. [[CrossRef](#)]
45. Kiziltas, A.; Nazari, B.; Gardner, D.J.; Bousfield, D.W. Polyamide 6–Cellulose Composites: Effect of cellulose composition on melt rheology and crystallization behavior. *Polym. Eng. Sci.* **2014**, *54*, 739–746. [[CrossRef](#)]
46. Freluche, M.; Iliopoulos, I.; Flat, J.J.; Ruzette, A.V.; Leibler, L. Self-organized materials and graft copolymers of polymethyl methacrylate and polyamide-6 obtained by reactive blending. *Polym.* **2005**, *46*, 6554–6562. [[CrossRef](#)]
47. Gao, Y.; Ren, X.; Zhang, X.; Chen, C. Environmental fate and risk of ultraviolet- and visible-light transformed graphene oxide: A comparative study. *Environ. Pollut.* **2019**, *251*, 821–829. [[CrossRef](#)]
48. Chen, L.; Liu, J.; Fang, X.; Zhang, Z. Reduced graphene oxide dispersed nanofluids with improved photothermal conversion performance for direct absorption solar collectors. *Solar Energy Mater. Solar Cells* **2017**, *163*, 125–133. [[CrossRef](#)]

49. Zulan, L.; Zhi, L.; Lan, C.; Sihao, C.; Dayang, W.; Fangyin, D. Reduced Graphene Oxide Coated Silk Fabrics with conductive property for wearable electronic textiles application. *Adv. Electron. Mater.* **2019**, *5*, 1800648. [CrossRef]
50. Abdel-Messih, M.F.; Ahmed, M.A.; El-Sayed, A.S. Photocatalytic decolorization of rhodamine B dye using novel mesoporous SnO₂-TiO₂ nano mixed oxides prepared by sol-gel method. *J. Photochem. Photobiol. A Chem.* **2013**, *260*, 1–8. [CrossRef]
51. Singh, P.; Sonu Raizada, P.; Sudhaik, A.; Shandilya, P.; Thakur, P.; Agarwal, S.; Kumar Gupta, V. Enhanced photocatalytic activity and stability of AgBr/BiOBr/graphene heterojunction for phenol degradation under visible light. *J. Saudi Chem. Soc.* **2019**, *23*, 546–560. [CrossRef]
52. Staehelin, J.; Hoigne, J. Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. *Environ. Sci. Technol.* **1985**, *19*, 1206–1213. [CrossRef]
53. Wu, C.; Liu, X.; Wei, D.; Fan, J.; Wang, L. Photocatalytic degradation of phenol in water. *Wat. Res.* **2001**, *35*, 3927–3933. [CrossRef]
54. Chun, H.; Yizhong, W.; Hongxiao, T. Destruction of phenol aqueous solution by photocatalysis or direct photolysis. *Chemosphere* **2000**, *41*, 1205–1209. [CrossRef]
55. Kim, T.; Parale, V.G.; Jung, H.; Kim, Y.; Driss, Z.; Driss, D.; Bouabidi, A.; Euchy, S.; Park, H. Facile Synthesis of SnO₂ Aerogel/Reduced Graphene Oxide Nanocomposites via in Situ Annealing for the Photocatalytic Degradation of Methyl Orange. *Nanomaterials* **2019**, *9*, 358. [CrossRef] [PubMed]
56. Nawaz, M.; Miran, W.; Jang, J.; Sung Lee, D. One-step hydrothermal synthesis of porous 3D reduced graphene oxide/TiO₂ aerogel for carbamazepine photodegradation in aqueous solution. *Appl. Catal. B Environ.* **2017**, *203*, 85–95. [CrossRef]
57. Lu, Z.; Zhai, X.; Yi, R.; Li, Z.; Zhang, R.; Wei, Q.; Xing, G.; Lu, G.; Huang, W. Photoluminescence Emission during Photoreduction of Graphene Oxide Sheets as Investigated with Single-Molecule Microscopy. *J. Phys. Chem. C* **2020**, *124*, 7914–7921. [CrossRef]
58. Quezada-Renteria, J.A.; Ania, C.O.; Chazaro-Ruiz, L.F.; Rangel-Mendez, J.R. Influence of protons on reduction degree and defect formation in electrochemically reduced graphene oxide. *Carbon* **2019**, *149*, 722–732. [CrossRef]
59. Hung, Y.; Cheng, C.; Kai Huang, C.; Yang, C. A facile method for batch preparation of electrochemically reduced graphene oxide. *Nanomaterials* **2019**, *9*, 376. [CrossRef]

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