COTTON FABRICS COATED WITH AG-TiO₂ AND AG-TiO₂/REDUCED GRAPHENE OXIDE NANOCOMPOSITES

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Ag-TiO₂ and Ag-TiO₂/reduced graphene oxide nanopowders were deposited onto 100% cotton fabrics via electrostatic spraying method. The surface of cotton fabrics was pre-treated by plasma at atmospheric pressure using argon and nitrogen mixture. The as-prepared cotton fabrics were characterized in terms of structural and optical properties by X-ray diffraction (XRD) and optical reflectance measurements. The photocatalytic self-cleaning ability of Ag-TiO₂ and Ag-TiO₂/reduced graphene oxide coated cotton fabrics was evaluated by the photo-discoloration of methylene blue and berries juice stains, under 6 h simulated visible light irradiation. The combined functionalized coating on cotton fabrics demonstrated an improved photocatalytic effect compared with untreated cotton fabrics. The antimicrobial activity of Ag-TiO₂ and Ag-TiO₂/reduced graphene oxide coated cotton fabrics was tested against the *Staphylococcus aureus* and *Candida albicans* test strains as model microorganism of skin bacteria and fungi, respectively. An antimicrobial effect against the *Staphylococcus aureus* is observed even if the inhibition zone is not present. Untreated fabrics showed no antibacterial activity. No inhibitory effect on fungi colony growth was observed.

Keywords: Ag-TiO₂, Ag-TiO₂/reduced graphene oxide, self-cleaning properties, antimicrobial activity

INTRODUCTION

Cotton is an important natural renewable cellulose fiber, widely used in textile industry due to its good hygroscopicity and breath ability. Cotton fabric coatings with nanoparticles exhibit antimicrobial properties, ultraviolet (UV) protection, superhydrophobicity, self-cleaning and flame retardancy (Zhang *et al.*, 2019; Li *et al.*, 2017). As one of the most important nanomaterial, TiO₂ nanoparticles demonstrated efficient photocatalytic activity, chemical stability, biocompatibility, being used in a wide range of applications such as photocatalysis, nanomedicine, textiles, electronic devices, water sanitization (Ahmad Barudin *et al.*, 2013).

The main goal of the presented research work was to examine the self-cleaning properties and antimicrobial activity of cotton fabric samples pre-treated with plasma and coated with Ag-TiO₂ and Ag-TiO₂/reduced graphene oxide nanopowders.

EXPERIMENTAL PART

Materials

Bleached 100% cotton woven fabric with the weight of 168 g/m² has been used for all experiments. One percent of Ag-TiO₂ nanoparticles was prepared by liquid

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impregnation method using TiO₂ P25 powder from Degussa, silver nitrate from Alfa-Aesar as source of silver and distilled water, followed by a simple thermal treatment under argon atmosphere at 450°C. Ag-TiO₂/reduced graphene oxide (Ag-TiO₂/RGO) nanopowder was obtained by mixing Ag-TiO₂ nanoparticles with graphene oxide (GO) (10:1 mass ratio) followed by thermal reduction of GO under argon atmosphere at 300°C. GO was prepared according to the previously described procedure (Pogacean *et al.*, 2015). Methylene blue (MB) was purchased from Aldrich Sigma. Natural berries juice has been freshly prepared by freeze-thaw method of berries and then filtered.

Functionalization Treatments

A homemade model of Portable plasma generator from INCDTIM was used for pre-treatment of cotton fabric samples (25 cm x 60 cm), under specified experimental conditions (process gas: Ar:N₂/air, gas flow rate: 6 l/min, input power: 200 W, plasma treatment time: 9 min) for an increased adhesion of nanopowders onto cotton fabrics. The deposition of 0.1% dispersions based on Ag-TiO₂ and Ag-TiO₂/RGO nanopowders on the textile materials was performed by electrostatic spraying method using a Microbecide®TC-320 Electrostatic Sprayer equipment (Singapore). The cotton coating experiments were conducted at ambient conditions on average spraying distance from samples of 80 cm, with an flow rate adjustable of 20 – 240 ml/min, average droplet size of 40 microns; negative electrostatic charge polarity, 1.0 bar (15 psi) liquid line pressure, 2.1 bar (30 psi) air line pressure and 0.6 – 1.2 kV electrostatic charging voltage.

Methods

X-ray Diffraction

The structural characterization of cotton fabric pre-treated with plasma and coated with nanopowders was performed using a BRUKER D8 Advance X-ray diffractometer using CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$) in order to identify the phase of a crystalline material.

Optical Reflectance Measurements

The optical properties of cotton fabric samples were investigated by UV-Vis spectroscopy using an UV-VIS Jasco Spectrophotometer (Japan).

Assessment of Self-Cleaning Activity

The self-cleaning properties of cotton samples pre-treated with plasma and coated with nanopowders were evaluated by photo-discoloration of methylene blue and berries juice stains on their surface. The cotton fabrics were cut into 3 x 3 cm pieces. Some of them were dipped in 20 ppm MB solution and others were stained with 10 μ l of berries juice, then all cotton samples were freely dried for 24 h in the dark. Subsequently, the stained cotton samples were exposed to visible light irradiation for 6 h by using the Xenotest equipment (Apolo James Heal). Evaluation of the self-cleaning ability of cotton samples pre-treated with plasma and coated with nanopowders was performed by measuring the color difference of the irradiated samples compared to non-irradiated samples (reference). Color measurements were performed according to ISO 105 J03:2001, using the

Datacolor™ 650 Spectrophotometer (Datacolor, Switzerland) and the light source was the standard illuminant D65/10. The obtained values of the lightness difference (DL*) are the average of 5 individual measurements carried out in different points on the same sample. DL* indicates a lighter color if positive and darker if negative.

Antimicrobial Activity

The antimicrobial activity of cotton samples pre-treated with plasma and coated with nanopowders was qualitatively assessed by Agar diffusion method according with the SR EN ISO 20645:2004 standard, by using of cultures in liquid medium replicated at 24 hours of ATCC 25923 *Staphylococcus aureus* (Gram-positive) and ATCC 10231 *Candida albicans* test strains. The cotton samples were cut in circular shape with a diameter of 2 cm and subsequently disposed on the culture medium in the middle of Petri plates, and then were incubated at 37°C (*S. aureus*) and 30°C (*C. albicans*) for 48h. After incubation, the diameter of the clear zone (mm) that indicates the microbial growth inhibition was measured and antimicrobial activity was evaluated.

RESULTS AND DISCUSSIONS

The compared XRD patterns of pristine cotton and selected cotton sample pre-treated with plasma and coated with Ag-TiO₂/RGO were presented in Figure 1. The diffraction peaks at 2θ values of $2\theta = 14.8^\circ$, 16.5° , 22.8° and 34.5° are assigned to the (101), (101), (002) and (040) planes of cellulose fiber (Abdelhameed *et al.*, 2017; Ahmad *et al.*, 2019). The reflection peak at $2\theta = 25.19$ is indexed to the (101) plane of the TiO₂ anatase phase (PDF Sheet no. 21-1276). No reflection peaks related to the crystalline silver are shown, possible to its reduced amount. A slightly changed profile of broad XRD peak centered at $2\theta \approx 15.5^\circ$ was observed by contribution of (002) reduced graphene oxide that has a characteristic peak at $2\theta = 25^\circ$ (Dey *et al.*, 2016).

The reflectance of cotton samples (Figure 2) is almost overlapped in the entire UV-Vis region, implying no superior UV-rays blocking properties and absorption to the visible light of the nanopowder-coated cotton samples (Chaudhari *et al.*, 2012; Ojstršek and Fakin, 2019), probably due to the penetration of these nanoparticles into the cotton fabric material. All cotton samples show high reflectance values (>75%) across the full visible spectrum, in accordance with their white-light grey color.

Figure 1. Comparative XRD pattern of cotton samples

Figure 2. Comparative UV-VIS spectra of cotton samples

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Self-Cleaning Activity

The self-cleaning abilities of cotton samples pre-treated with plasma and coated with Ag-TiO₂ and Ag-TiO₂/RGO nanopowders were evaluated by monitoring the color changes due to the photocatalytic degradation of MB and berries juice stains. Color lightness difference (DL*) was determined considering the non-irradiated cotton samples as reference and their values are presented in Table 1.

Table 1. DL* values and digital photo of stained cotton fabric samples, before and after 6 h of simulated visible light irradiation

Sample	DL*	Sample	DL*	Sample	DL*	Sample	DL*
Cotton/ Ag-TiO ₂		Cotton/ Ag-TiO ₂ /RGO		Cotton/ Ag-TiO ₂		Cotton/ Ag-TiO ₂ /RGO
3.80		2.29		7.10		3.6
Methylene blue				Berries juice			

Note: DL* = difference in lightness/darkness value (+ = lighter - = darker)

The obtained data revealed that the cotton samples pre-treated with plasma and coated with Ag-TiO₂ and Ag-TiO₂/RGO nanopowders showed great photodegradation efficiency of MB and berries juice stains. The best self-cleaning activity was obtained for cotton sample coated with Ag-TiO₂ nanopowder and stained with berries juice. However, the photocatalytic activity depends on the various parameters, such as nature and amount of the nanopowder as photocatalysts, light source, time exposure, type and concentration of contaminants etc.

Antimicrobial Activity

The antimicrobial and antifungal properties of textiles treated with TiO₂-Ag nanoparticles (Li *et al.*, 2017; Saraswati *et al.*, 2019) and also RGO/TiO₂ nanoparticles (Karimi *et al.*, 2014; Stan *et al.*, 2019) are already reported.

The evaluation of the antimicrobial activity consisted in highlighting the presence or absence of the inhibition zone around the samples and the colonies formed or not on the contact surface with the environment, the results obtained being presented in Table 2.

Table 2. Antimicrobial activity of cotton fabric samples

Sample	<i>S. aureus</i>		<i>C. albicans</i>	
	Inhibition zone [mm]	Evaluation	Inhibition zone [mm]	Evaluation
Untreated cotton	0	Satisfactory effect	0	Unsatisfactory effect
Cotton/Ag-TiO ₂	0	Satisfactory effect	1	Unsatisfactory effect
Cotton/Ag-TiO ₂ /RGO	0	Satisfactory effect	0	Unsatisfactory effect

Table 3. Criteria for inhibition zones according to the standard SR EN ISO 20645:2005

Inhibition zone[mm]	Growth	Evaluation
>1		
1-0	Absence	Satisfactory effect
0		
0	little	Efficiency limit
0	moderate	
0	important	Unsatisfactory effect

An antimicrobial effect against the *Staphylococcus aureus* is observed even if the inhibition zone is not present. Untreated fabrics showed no antibacterial activity. No inhibitory effect on fungi colony growth was observed.

Various factors, such as phase composition, mass loading and dispersion uniformity of nanopowders on cotton fabric, the surface modification of cotton have to be considered in order to provide antimicrobial efficacy.

CONCLUSIONS

Ag-TiO₂ and Ag-TiO₂/RGO nanopowders were successfully prepared by impregnation method. The cotton fabric samples were pre-treated with plasma and coated with Ag-TiO₂ and Ag-TiO₂/RGO nanopowders. XRD patterns confirmed the presence of nanopowders on the cotton fabric samples. UV-Vis spectral data showed a high reflectance values (>75%) across the full visible spectrum, proving their white-light grey appearance. The self-cleaning ability to degrade methylene blue and berries juice stains is demonstrated. An antibacterial effect against *Staphylococcus aureus* is observed, but no inhibitory effect on fungi colony growth of *Candida albicans* was present. Further strategies include the variation of different experimental parameters to increase the antimicrobial activity of cotton fabrics coated with Ag-TiO₂ and Ag-TiO₂/RGO nanopowders.

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REFERENCES

- Abdelhameed, R.M., Kamel, O.M.H.M., Amr, A., Rocha, J. and Silva, A.M.S. (2017), "Antimosquito activity of a titanium-organic framework supported on fabrics", *ACS Appl Mater Interfaces*, 9(27), 22112–22120, <https://doi.org/10.1021/acsami.7b03164>.
- Ahmad Barudin, N.H., Sreekantan, S., Thong, O.M. and Sahgal, G. (2013), "Antibacterial activity of Ag-TiO₂ nanoparticles with various silver contents", *Materials Science Forum*, 756, 238–245, <https://doi.org/10.4028/www.scientific.net/MSF.756.238>.
- Ahmad, I., Kan, C. and Yao, Z. (2019), "Photoactive cotton fabric for UV protection and self-cleaning", *RSC Adv*, 9, 18106–18114, <https://doi.org/10.1039/C9RA02023C>.
- Chaudhari, S.B., Mandot, A.A. and Patel, B.H. (2012), "Effect of nano TiO₂ pretreatment on functional properties of cotton fabric", *International Journal of Engineering Research and Development*, 1(9), 24–29.
- Dey, M.K., Reddy, A.V.R. and Satpati, A.K. (2016), "Determination of melamine by a reduced graphene oxide-gold nanoparticle composite carbon paste electrode", *Anal Lett*, 49(17), 2703–2715, <https://doi.org/10.1080/00032719.2016.1154065>.

<https://doi.org/10.24264/icams-2020.I.6>

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- Karimi, L., Yazdanshenas, M.E., Khajavi, R., Rashidi, A. and Mirjalili, M. (2014), "Using graphene/TiO₂ nanocomposite as a new route for preparation of electroconductive, self-cleaning, antibacterial and antifungal cotton fabric without toxicity", *Cellulose*, 21(5), 3813-3827, <https://doi.org/10.1007/s10570-014-0385-1>
- Li, S., Zhu, T., Huang, J., Guo, Q., Chen, G. and Lai Y. (2017), "Durable antibacterial and UV-protective Ag/TiO₂@fabrics for sustainable biomedical application", *Int J Nanomedicine*, 12, 2593-2606, <https://doi.org/10.2147/IJN.S132035>.
- Ojstršek, A. and Fakin, D. (2019), "Washing durability and photo-stability of nanoTiO₂-SiO₂ coatings exhausted onto cotton and cotton/polyester fabrics", *Coatings*, 9, 545-557, <https://doi.org/10.3390/coatings9090545>.
- Pogacean, F., Socaci, C., Pruneanu, S., Biris, A.R., Coros, M., Magerusan, L., Katona, G., Turcu, R. and Borodi, G. (2015), "Graphene based nanomaterials as chemical sensors for hydrogen peroxide - A comparison study of their intrinsic peroxidase catalytic behavior", *Sensors Actuators, B Chem*, 213, 474-483, <https://doi.org/10.1016/j.snb.2015.02.124>.
- Saraswati, M., Permadani, R.L. and Slamet A. (2019), "The innovation of antimicrobial and self-cleaning using Ag/TiO₂ nanocomposite coated on cotton fabric for footwear application", *IOP Conf. Series: Mat Sci Eng*, 509, 012091, <https://doi.org/10.1088/1757-899X/509/1/012091>.
- Stan, M.S., Nica, I.C., Popa, M., Chifiriuc, M., Iordache, O., Dumitrescu, I., Diamandescu, L. and Dinischiotu, A. (2019), "Reduced graphene oxide/TiO₂ nanocomposites coating of cotton fabrics with antibacterial and self-cleaning properties", *J Ind Text*, 49, 277-293, <https://doi.org/10.1177/1528083718779447>.
- Zhang, G., Wang, D., Yan, J., Xiao, Y., Gu, W. and Zang, C. (2019), "Study on the photocatalytic and antibacterial properties of TiO₂ nanoparticles-coated cotton fabrics", *Materials (Basel, Switzerland)*, 12(12), 2010-2019, <https://doi.org/10.3390/ma12122010>.