ANTIBACTERIAL AND SELF-CLEANING COTTON FABRIC BY NANO TiO_2-CELLULOSE COATING

KALE Bandu Madhukar[1], WIENER Jakub[1], RWAWIIRE Samson[1], MILITKY Jiri[1]

[1]*Technical University of Liberec, Liberec, Czech Republic, EU*

Abstract

Antibacterial and self-cleaning cotton fabric was prepared by coating TiO_2 nanoparticles with cellulose on the surface of cotton fabric. TiO_2 nanoparticles were dispersed in cellulose solution (10% cellulose in 60% sulphuric acid solution) by mechanical stirring in order to coat. Appeared white particles on the surface of fabric in Scanning Electron Microscope (SEM) pictures proves that TiO_2 was coated successfully on the surface of cotton fabric. Significant degradation of wine stain was observed after 60 minutes of UV irradiation on TiO_2-cellulose coated cotton fabric. Maximum 98.2% reduction of S.aureus bacteria was observed on TiO_2-cellulose coated cotton fabric whereas 81.6% reduction of Methicillin-resistant Staphylococcus aureus (MRSA) bacteria was observed.

Keywords: Cellulose, TiO_2, Antibacterial activity, Self-cleaning, Cotton

1. INTRODUCTION

Antibacterial and self-cleaning properties of textile are very interesting and demanding properties of cotton fabrics [1-4]. In this report, we describe the coating of cellulose and TiO_2 on the cotton fabric and its characterization for antibacterial and self-cleaning properties. In recent years, researchers have been trying to make cotton fabric self-cleaning and antibacterial in different ways such as: antibacterial finishing of cotton by microencapsulation [3], by synthesizing Photo bactericidal porphyrin-cellulose nanocrystals [5], Treating cotton fabric by SBA-15-NH_2/polysiloxane hybrid containing tetracycline [6], Plasma treatment and ZnO/Carboxymethyl chitosan composite finishing [7], self-cleaning by copper (II)porphyrin/TiO_2 visible-light photocatalytic systém [8], coating with nano TiO_2-acrylate copolymer [9], Nano TiO2 coating after treatment of cotton fabric with carboxylic acids such as oxalic, succinic, and adipic acids [10], functionalizing cotton fabric with p-BiOI/n-TiO_2 heterojunction [11], bleaching and cationized cotton using nanoTiO_2 [1] etc. Nano particles like TiO_2, ZnO, CuO, Ag, SWCNTs, MWCNTs etc. show excellent antibacterial activity. TiO_2 is the most environment-friendly among all other nano particles [12]. Titanium dioxide has the ability to oxidize various organic pollutants as well as to kill microbial cells [13].

TiO_2 can be applied on different substrates such as activated carbon, stainless steel and glass[14]. TiO_2 shows extraordinary photocatalytic activity since it has a high sensitivity to light [8]. Nano TiO_2 has the ability to decompose dye pollutant such as Acid Orange [15], Methylene Blue[16], C.I. Acid Blue 9[17], Methyl Orange [18, 19], Ethyl violet dye[20], C.I. Reactive Red 2[21] and photocatalytic decomposition of some air pollutants [22]. Recently some researches have coated TiO_2 on cotton fabric by in-situ suspension polymerization with nano TiO_2-acrylate copolymer [9] and functionalizing cotton fabric with nano sized TiO_2 [23]. However, they do not claim that fabric is stable against washing. Here we present new method to coat cotton fabric with TiO_2 by roller padding, which will be stable against washing.

2. MATERIALS AND METHODS

2.1. Materials

Viscose fiber was used as a source of cellulose for coating and it was provided by Tepna Nachod, Czech Republic. Cotton fabric was also obtained from Tepna Nachod, Czech Republic. TiO_2 nanoparticles with

average size of 50nm was obtained from Sigma Aldrich. Sulfuric acid and sodium carbonate were purchased from Lach-ner, Czech Republic.

2.2. Cellulose-TiO_2 coating on cotton fabric

Cellulose (Viscose fibers) was dissolved in 60% H2SO4 in order to prepare 10% cellulose solution at 20°C. TiO_2-cellulose dispersions with different concentrations (1,3,5,10%) of TiO_2 nanoparticles were prepared by mechanical stirring at 20°C and 150rpm for 5min. Dispersion of cellulose-TiO_2 was coated by using roller padding on the surface of cotton fabric at 20°C quickly in 20 sec. After padding fabrics were washed with 100gm/l aq.(aqueous) sodium carbonate solution and water until neutralization. The washed fabric was dried in an oven at 70°C for 25 min.

2.3. Morphological observation

Morphology of TiO_2-cellulose coated cotton fabric was observed by SEM (Scanning Electron Microscope). Coated samples were cut and placed on SEM stubs by two sided tape and then morphology observed using TS5130 Vega-Tescan at voltage of 30 KV acceleration.

2.4. Quantitative Evaluation of Anti-Bacterial Activity (AATCC-100)

Two different kinds of bacteria Staphylococcus aureus (Gram positive CCM 226) and Methicillin-resistant Staphylococcus aureus (MRSA) (Gram positive CCM 4223) were used. Wet sample swatches of dimensions 18X18mm were placed on a wet filter paper and placed in a petri dish and covered. A sterile container was placed under UV radiation for 15min thereafter 50µl of inoculums was placed on top of the swatch and allowed to wick through the sample stack.

The inoculated swatches incubated for 24 hours at 37oC; thereafter a neutralizing broth composed of 50ml of saline was added and containers were shaken so as to release the inoculums from the test swatches and into the neutralizing broth. The bacterium present in this liquid was obtained as the percentage reduction. Anti-bacterial activity of the fabric samples was quantitatively analyzed using the AATCC 100 method29.

The percentage reduction of bacteria was calculated using the following formula:

$$(B - A)\frac{100}{B} = R$$

Where R is the percentage reduction; A and B are the number of bacteria recovered from the inoculated treated and untreated fabrics.

2.5. Photocatalytic self-cleaning

Red wine stain was used to evaluate the self-cleaning ability of TiO_2-cellulose coated samples fabrics in order to understand the effect of TiO_2 on stain degradation; samples were irradiated with UV light as a function of time. For irradiation stain Philips TL 6W/05 CE UV tube (400-320nm) was used. Irradiated samples were scanned at 300dpi by scanner and afterwards images were analysed by using 'Image J' software [24].

3. RESULTS AND DISCUSSIONS

3.1. Morphology of coated fabric

Morphological characterization ofTiO_2-cellulose coated fabric was done by using scanning electron microscope. Only cellulose coated cotton fabric was characterized to prove TiO_2 nanoparticles coated with cellulose. **Figure 1a, b** and **c** shows control, only cellulose coated, and TiO_2-cellulose coated cotton fabric respectively. **Figure 1c** shows white particles on the surface of the cotton fabric and that confirms TiO_2 particles were coated successfully. **Figure 1b** shows that cellulose is attached to the fabric surface. In our previous

study, 5 it was proved that coated cellulose stays with cotton fabric permanently. The coated cellulose does not get washed away unlike starch because it forms an interchain linkage with cotton cellulose during coating. Since solvent is strong the solvent molecules try to interact with the surface of the cotton fabric and during interaction coated cellulose forms hydrogen bonding with cotton cellulose. It is not easy to prove hydrogen bonding by spectroscopic method because both are same molecule and it has hydrogen bonding.

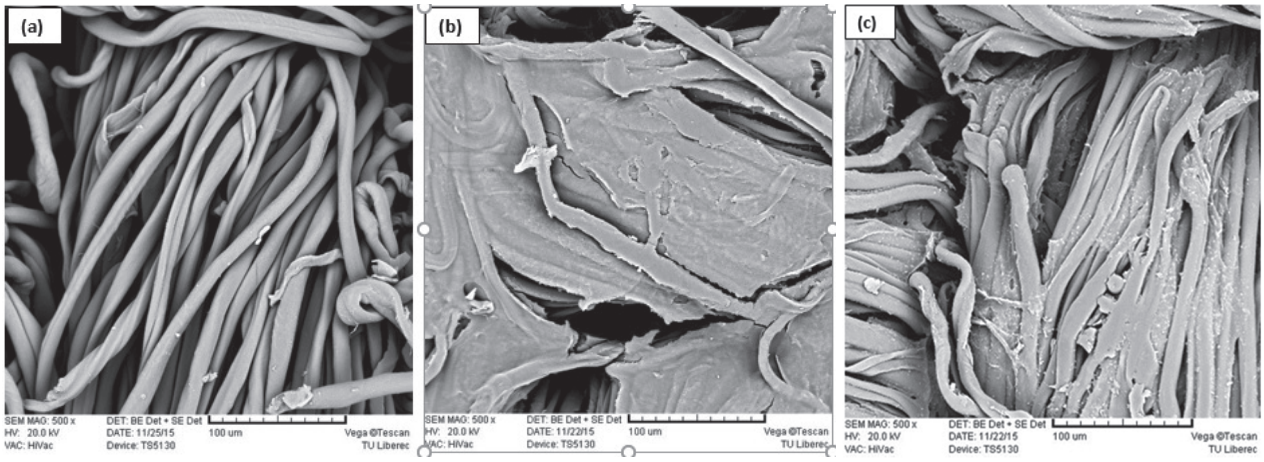

Figure 1 SEM micrographs of (a) Control (b) Cellulose coated and (c) TiO_2-cellulose coated cotton fabric

3.2. Degradation of wine stain

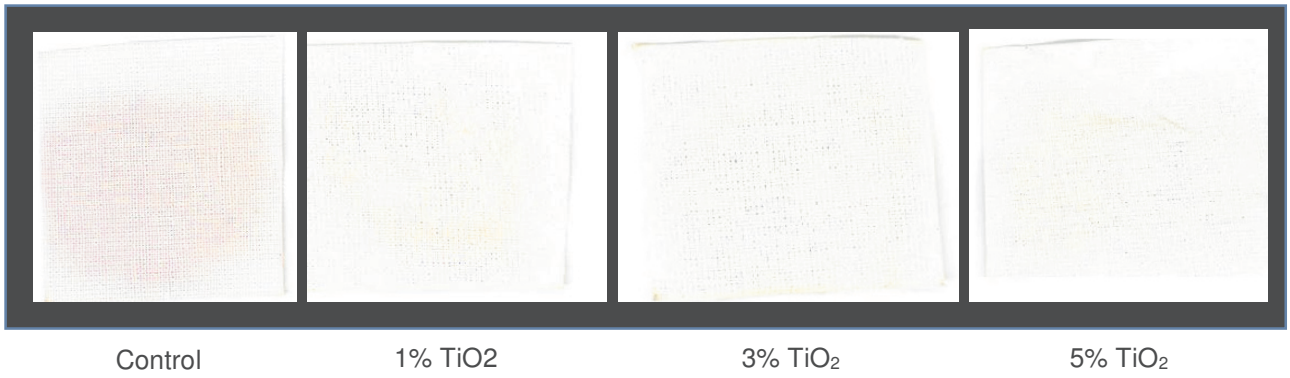

Figure 2 Wine stain degradation

Red wine was used as a stain to understand the self-cleaning ability of TiO_2-cellulose coated cotton fabric. Samples were irradiated under UV light for 60 min. The irradiated samples were scanned on the scanner and then evaluated by using imageJ software. ImageJ software measures the colour intensity and here white colour intensity was measured to see the self-cleaning ability.

Figure 2 shows the scanned images of control, 1%, 3% and 5% TiO_2 coated cotton fabric after 30 min irradiation under UV light. It is clear from **Figure 2** that wine stain of TiO_2-cellulose coated sample was degraded after irradiation under UV light whereas uncoated sample remained unaffected. **Figure 3** shows the effect of TiO_2 concentration on wine stain decolourization after exposing to UV light. It is apparent from the **Figure 3** that wine colour degradation increases with increasing TiO_2 concentration.

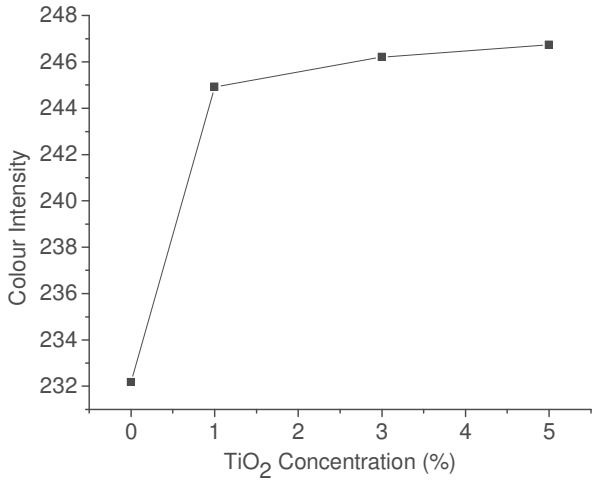

Figure 3 Effect of TiO_2 concentration on wine stain degradation

3.3. Antibacterial activity

Effect of TiO_2 coating on the growth of bacteria Staphylococcus aureus and Methicillin-resistant Staphylococcus aureus (MRSA) were investigated. **Table 1** shows the percentage reduction/multiplication of the test bacteria (S. aureus and MRSA) confirmed quantitatively utilizing the AATCC100 method. It's observed that the coating of fabrics with TiO_2-cellulose had a positive reduction of S. aureus bacteria and MRSA bacteria. The effectiveness of the anti-microbial activity increased with increase in the concentration of the TiO_2 coating. Fabrics treated with 1% TiO_2 had the lowest S. aureus bacterial reduction, however with an increase in the concentration of TiO_2, there was a high jump from 6.3% to 96.7% reduction of S.aureus bacteria on 3% TiO_2 treated fabrics. These results prove that TiO_2-cellulose coated cotton fabric shows excellent antimicrobial activity.

Table 1 Antimicrobial analysis (AATCC 100) of the fabric samples

Test Sample	Bacterial Reduction/Multiplication	
	Staphylococcus aureus	Methicillin-resistant Staphylococcus aureus (MRSA)
Control	-	-
1% TiO_2	6.3	13.3
3% TiO_2	96.7	65.0
5% TiO_2	97.7	68.3
10% TiO_2	98.2	81.6

4. CONCLUSION

TiO_2-cellulose was coated successfully on cotton fabric by using roller padding for antibacterial and self-cleaning properties. Surface morphology by SEM proved that TiO2 was coated successfully coated on the surface of cotton fabric along with cellulose. Cellulose plays a carrier role in this TiO_2 coating. Samples coated TiO_2 shows significant reduction 98.2% of Staphylococcus aureus and 81.6% Methicillin-resistant Staphylococcus aureus bacteria under UV light. Significant discoloration was observed for Cellulose-TiO_2 coated cotton fabric. Degradation of wine stain and reduction in bacteria were increased with increasing TiO_2 concentration. Therefore, we claim that Antibacterial and Self-cleaning cotton fabric could be achieved by coating Cellulose-TiO_2.

ACKNOWLEDGEMENTS

Authors would like to acknowledge Ing. Jana Grabmüllerová for providing SEM micrographs. This study was supported by SGS project of Technical University of Liberec.

REFERENCES

[1] NAZARI, A., MONTAZER, M., MOGHADAM, M.B., ANARY-ABBASINEJAD, M. Self-cleaning properties of bleached and cationized cotton using nanoTiO2: A statistical approach, *Carbohydrate Polymers*, 2011, vol. 83 pp. 1119-1127.

[2] XU, B., DING, J., FENG, L., DING, Y., GE, F., CAI, Z. Self-cleaning cotton fabrics via combination of photocatalytic TiO2 and superhydrophobic SiO2, *Surface and Coatings Technology*, 2015, vol. 262 pp. 70-76.

[3] EL-RAFIE, H.M., EL-RAFIE, M.H., ABDELSALAM, H.M., EL-SAYED, W.A. Antibacterial and anti-inflammatory finishing of cotton by microencapsulation using three marine organisms, *International Journal of Biological Macromolecules*, 2016, vol.86, pp. 59-64.

[4] SHAHEEN, T.I., EL-NAGGAR, M.E., ABDELGAWAD, A.M., HEBEISH, A. Durable antibacterial and UV protections of in situ synthesized zinc oxide nanoparticles onto cotton fabrics, *International Journal of Biological Macromolecules,* 2016, vol. 83 pp. 426-432.

[5] FEESE, E., SADEGHIFAR, H., GRACZ, H.S., ARGYROPOULOS, D.S., GHILADI, R.A. Photobactericidal Porphyrin-Cellulose Nanocrystals: Synthesis, Characterization, and Antimicrobial Properties, *Biomacromolecules*, 2011, vol. 12, pp. 3528-3539.

[6] HASHEMIKIA, S., HEMMATINEJAD, N., AHMADI, E., MONTAZER, M. A. novel cotton fabric with anti-bacterial and drug delivery properties using SBA-15-NH2/polysiloxane hybrid containing tetracycline, *Materials Science and Engineering: C*, 2016, vol. 59, pp. 429-437.

[7] WANG, C., LV, J., REN, Y., ZHOU, Q., CHEN, J., ZHI, T., LU, Z., GAO, D., MA, Z., JIN, L. Cotton fabric with plasma pretreatment and ZnO/Carboxymethyl chitosan composite finishing for durable UV resistance and antibacterial property, *Carbohydrate Polymers*, 2016, vol. 138, pp. 106-113.

[8] AFZAL, S., DAOUD, W.A., LANGFORD, S.J. Photostable self-cleaning cotton by a copper(II) porphyrin/TiO2 visible-light photocatalytic system, *ACS applied materials & interfaces*, 2013, vol. 5, pp. 4753-4759.

[9] JIANG, X., TIAN, X., GU, J., HUANG, D., YANG, Y. Cotton fabric coated with nano TiO2-acrylate copolymer for photocatalytic self-cleaning by in-situ suspension polymerization, *Applied Surface Science*, 2011, vol. 257 pp. 8451-8456.

[10] KHAJAVI, R., BERENDJCHI, A. Effect of dicarboxylic acid chain length on the self-cleaning property of Nano-TiO2-coated cotton fabrics, *ACS applied materials & interfaces*, 2014, vol. 6 pp. 18795-18799.

[11] WU, D., WANG, H., LI, C., XIA, J., SONG, X., HUANG, W. Photocatalytic self-cleaning properties of cotton fabrics functionalized with p-BiOI/n-TiO2 heterojunction, *Surface and Coatings Technology*, 2014, vol. 258, pp. 672-676.

[12] JOOST, U., JUGANSON, K., VISNAPUU, M., MORTIMER, M., KAHRU, A., NOMMISTE, E., JOOST, U., KISAND, V., IVASK, A. Photocatalytic antibacterial activity of nano-TiO2 (anatase)-based thin films: effects on Escherichia coli cells and fatty acids, *Journal of photochemistry and photobiology. B, Biology*, 2015, vol. 142 pp. 178-185.

[13] HONG, K.H., SUN, G. Photoactive antibacterial cotton fabrics treated by 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, *Carbohydrate Polymers*, 2011 vol. 84 pp. 1027-1032.

[14] SHAN, A.Y., GHAZI, T.I.M., RASHID, S.A. Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: A review, *Applied Catalysis A: General*, 2010, vol. 389 pp. 1-8.

[15] STYLIDI, M. Visible light-induced photocatalytic degradation of Acid Orange 7 in aqueous TiO2 suspensions, *Applied Catalysis B: Environmental, 2004, vol.* 47 pp. 189-201.

[16] RYU, J., KIM, K., HAHN, B., CHOI, J., YOON, W., LEE, B., PARK, D., PARK, C. Photocatalytic nanocomposite thin films of TiO2-β-calcium phosphate by aerosol-deposition, *Catalysis Communications*, 2009, vol. 10 pp. 596-599.

[17] A.R. KHATAEE, V. VATANPOUR, A.R. AMANI GHADIM, Decolorization of C.I. Acid Blue 9 solution by UV/Nano-TiO(2), Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: a comparative study, J Hazard Mater, 161 (2009) 1225-1233.

[18] ANDRONIC, L., DUTA, A. The influence of TiO2 powder and film on the photodegradation of methyl orange, *Materials Chemistry and Physics*, 2008, vol. 112, pp.1078-1082.

[19] HE, H.Y. Comparison Study of Photocatalytic Properties of $SrTiO_3$ and TiO_2 Powders in Decomposition of Methyl Orange, *International Journal of Environmental Research,* 2009, vol. 3, pp. 57-60.

[20] MAI, F.D., LEE, W.L., CHANG, J.L., LIU, S.C., WU, C.W., CHEN, C.C. Fabrication of porous TiO2 film on Ti foil by hydrothermal process and its photocatalytic efficiency and mechanisms with ethyl violet dye, *J Hazard Mater*, 2010, vol. 177 pp. 864-875.

[21] WU, C.H. Photodegradation of C.I. Reactive Red 2 in UV/TiO2-based systems: effects of ultrasound irradiation, *J Hazard Mater*, 2009, vol. 167 pp. 434-439.

[22] CAPPELLETTI, G., ARDIZZONE, S., BIANCHI, C.L., GIALANELLA, S., NALDONI, A., PIROLA, C., RAGAINI, V. Photodegradation of Pollutants in Air: Enhanced Properties of Nano-TiO(2) Prepared by Ultrasound, *Nanoscale Res Lett,* 2008, vol. 4 pp. 97-105.

[23] DOGANLI, G., YUZER, B., AYDIN, I., GULTEKIN, T., CON, A.H., SELCUK, H., PALAMUTCU, S. Functionalization of cotton fabric with nanosized TiO2 coating for self-cleaning and antibacterial property enhancement, *Journal of Coatings Technology and Research,* 2015, vol. 15 pp. 9743-7.

[24] TANG, X.N., BERMAN, A.E., SWANSON, R.A., YENARI, M.A. Digitally quantifying cerebral hemorrhage using Photoshop and Image J, *Journal of neuroscience methods*, 2010, vol. 190, pp. 240-243.