Advanced Materials and Systems for Biomedical applications

Photoresponsive textiles for textiles self-cleaning and disinfection

KEYWORDS: Clothing industry, healthcare industry, photocatalysis, bleaching, antimicrobial activity, self-cleaning, electromagnetic protection, metal oxides, lead-free,

Photosensitive nanoparticles, led by titanium dioxide (TiO_2), revolutionize cotton textile cleaning, replacing harsh industrial bleaching methods. Graphitic carbon nitride (GCN-T), a metal-free photocatalyst, introduces eco-friendly self-cleaning and antimicrobial qualities through budget-friendly LED setups in textiles. TiO_2, Fe_2O_3, and PEDOT:PSS enhance EMI shield development due to their unique properties, seen in innovative clothing designs achieving over 30 dB shielding effectiveness (SE). Textiles coated with 70 wt.% Bi_2O_3 dispersed in a polymeric matrix surpassed heavy lead-based solutions in flexibility and efficacy for high-frequency radiation protection.

Introduction

Functional textiles possess a range of properties like electromagnetic protection, anti-odour, wrinkle recovery, flame retardancy, self-cleaning, and antimicrobial qualities, finding application across industries like clothing, personal protective equipment, and healthcare. Antimicrobial and self-cleaning functionalities in these textiles significantly diminish the biological load in healthcare settings, mitigating the risk of infection transmission among patients, visitors, and healthcare workers by hindering the spread of harmful pathogens. Regarding electromagnetic protection, the healthcare textile sector collaborates with scientists due to concerns over human exposure to electromagnetic radiation. Growing networking and wireless technologies raise concerns about increased low-frequency electromagnetic radiation. Developing electromagnetic interference (EMI) shields using absorbing materials emerges as a solution to mitigate direct exposure to the human body or electronic devices. The textile industry prioritizes wellness-driven products, emphasizing the creation of fabrics integrated with EMI shielding properties. In terms of high-frequency (ionizing radiation) radiation exposure, functional fabrics have been designed due to the surge in radiological procedures in recent decades. Protecting medical staff and patients from the adverse effects of X-ray exposure remains a constant concern. Moreover, the toxicity and environmental hazards linked to current solutions, notably metallic lead, underscore the urgency to find safer alternatives for health and the environment.

The materials with active properties are integrated into various applications through diverse techniques. Antimicrobial and self-cleaning textiles, for instance, are achieved by immobilizing photosensitive nanoparticles like TiO_2 and GCN-T. Under specific wavelengths, these nanoparticles generate electron-hole pairs that can degrade contaminants directly or produce reactive oxygen species (ROS). ROS contribute to breaking down organic compounds and induce oxidative stress in bacteria, effectively inhibiting bacterial growth. EMI shielding in functional textiles involves a two-step process: first, formulating materials with the desired properties, then applying these formulations using diverse textile finishing techniques. Among these, the coating process stands out as simple yet highly effective. It allows for precise control over shielding thickness, a critical factor influencing the shielding effectiveness (SE) of the textile. Factors like the loading of active materials in the formulations and ensuring a uniform coating surface are crucial considerations. These elements impact how radiation is attenuated—whether through reflection, absorption, multiple reflections, and ultimately, the amount of radiation attenuated by the textile. There are several commercial and patented lead-free solutions on the market for protection against X-rays, but with effective results. As such, the objective is to contribute to developing sustainable textile solutions by incorporating metals/metal oxides such as Bi, W, Sb, Sn or their combinations.

Current Development

Sustainable bleaching of raw cotton

Raw cotton was coated with TiO_2 using a pad-dry method to study its bleaching by photocatalysis, in collaboration with the Center for Nanotechnology and Smart Materials (CeNTI). This catalyst proved to be efficient in the photocatalytic degradation of hydrophobic impurities of cotton, such as pectins and waxes, but also in the degradation of the natural pigments that give cotton its yellowish colour. Thus, using an ultraviolet-visible (UV-Vis) lamp, it was possible to bleach and clean cotton without the use of toxic chemicals, and the water and energy resources required by traditional techniques. TiO_2 is a metallic semiconductor that essentially absorbs ultraviolet radiation.

Self-cleaning and antimicrobial textiles

GCN-T began to receive greater attention as it is active under visible light. GCN-T was immobilized on raw cotton by a simple exhaustion method and its self-cleaning properties were tested for the degradation of a reference dye, Rhodamine B (RhB), using a visible LED system. The antimicrobial properties of the coated cotton were tested against three Gram-positive bacteria (*S. aureus*, *S. epidermidis*, and *S. hominis*) and two Gram-negative bacteria (*P. aeruginosa* and *E. coli*), in collaboration with the Faculty of Sciences of the University of Porto (FCUP) and the Associated Laboratory for Green Chemistry (LAQV) of the Network of Chemistry and Technology (REQUIMTE). These functional textiles were also tested for their cytotoxicity to two skin cell lines, L929 fibroblasts and HaCaT keratinocytes, in collaboration with the Faculty of Pharmacy of the University of Porto (FFUP) and LAQV REQUIMTE. Carbon-nitride-coated cotton demonstrated effective photocatalytic self-cleaning, totally degrading RhB after 60 min of visible light irradiation. These properties were reproducible and recyclable, which indicates the high stability of the photocatalyst in cotton (Fig 1).

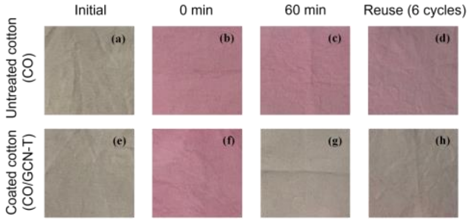

Fig. 1 Uncoated textiles CO (a, b, c, d) and coated CO/GCN-T (e, f, g, h) textiles. Control textiles without RhB (a, e). In the presence of RhB in dark conditions (b, f), after 60 min of visible irradiation (c, g) and after 6 cycles of reuse (60 min of irradiation with visible LED) (d, h).

The coated cotton also demonstrated high antimicrobial activity, eliminating Gram-negative bacteria after irradiation with visible light. Furthermore, these functional textiles do not affect the growth of fibroblast and keratinocyte cell lines, which means they are non-cytotoxic to skin cell lines.

Functional textiles for low-frequency radiation protection

The I&D of electromagnetic shielding materials, the development of coating formulations and the lab-scale developed functional textiles were performed in collaboration with the FCUP and the LAQV-REQUIMTE. After, approximately, 800 developed functional textiles, the most promising formulation for pilot-scale tests was found, which was then applied at the pilot scale in the Technological Center for the Textile and Clothing Industries of Portugal (CITEVE). Knitted fabric, supplied by Cottonanswer company, was modified through a coating finishing process using the best formulation, which contained 5 wt.% TiO_2 anatase and 5 wt.% Fe_2O_3 that were dispersed in PEDOT:PSS, which acted as polymeric matrix for both metal oxides incorporation. The obtained modified textile was submitted to a lamination process, which permitted the development of pockets inserted in jackets, trousers and sweatshirts, as shown in Fig 2.

Fig 2. Prototype clothes with pockets created using functional textiles with EMI shielding properties for low-frequency radiation attenuation.

Functional textiles for high-frequency radiation protection

Formulations focused on using elements with a lower degree of toxicity than lead were developed. In this context, Bi, W and Sb and Bi_2O_3, WO_3, SnO, Sb_2O_3, TiO_2 dispersed in polymeric matrices based on polyurethane and PVC were used. The most promising formulations (attenuation values greater than 97% at 45 kV) were sent to the Institute of Welding and Quality (ISQ) to determine the attenuation properties of 100 kV X-rays. After analyzing several samples with different formulations, different thicknesses, and different binders, it was concluded that the formulation with 70 wt.% Bi_2O_3 with EDOLAN CT and the formulation with 70 wt.% Bi_2O_3 with DeckBlack showed the best attenuation results.

These samples were evaluated for washing fastness by subjecting them to 25 washing cycles. The results showed that coated textiles with Bi_2O_3 dispersed in DeckBlack obtained washing resistance (Fig 3.). These coatings were analyzed by a German certification laboratory (LMG), validating them, considering the protection required by standards. This work was carried out in collaboration with the CITEVE, FCUP, ICETA, Lemar, Onwork and Polyanswer.

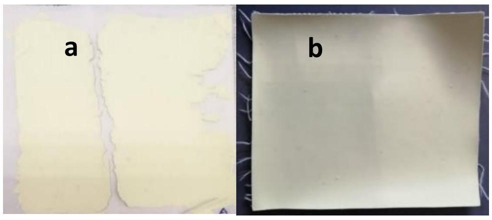

Fig. 3 Wash fastness: Edolan CT with 70 wt.% Bi_2O_3 – 10 cycles (a) and DeckBlack with 70 wt.% Bi_2O_3 – 25 cycles (b).

Future Work

Functional textiles with photosensitive nanoparticles could be an important technological advance in the clothing industry. Nevertheless, some barriers still need to be overcome before these fabrics can be used on a large scale. Scale-up evaluation of the catalyst and leaching phenomena are some of the possible studies to carry out.

Regarding self-cleaning and antimicrobial functional textiles, functional textiles have been shown to be safe for skin cells, which means these materials could be used in direct contact with the skin in the future. These photosensitive nanoparticles can be applied in hospital facilities to prevent the spread of harmful pathogenic bacteria. Despite these encouraging results, further research into the antibacterial mechanisms of these nanoparticles is required to broaden their activity spectrum against Gram-positive bacteria.

The creation of fabrics modified with materials possessing EMI shielding properties has been achieved, resulting in prototypes of clothing suitable for everyday use. Attenuation values above 30 dB, classified as excellent for general use, were achieved for low-frequency radiation. However, the prospect of developing a stable, breathable, and flexible modified fabric capable of achieving attenuation values equal to or greater than 60 dB is a challenge and a potential focus for future work. This could allow for the introduction of such materials into a sector of the textile industry to meet the needs of professional use.

Regarding new materials for high-frequency radiation-protective clothing, it is necessary to develop materials with advanced functionalities/performances that have lead-free X-ray protective characteristics and are lighter and more flexible to develop medical protective clothing. To increase user comfort, this solution must also feature multifunctional waterproofing, breathability, dirt repellence, tear-resistance, anti-odour, and antimicrobial characteristics.

Related Sustainable Development Goals

3 GOOD HEALTH AND WELL-BEING

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Outputs

Master Dissertations

Maria A. Barros, Limpeza e branqueamento de têxteis de algodão em cru usando nanopartículas fotossensíveis, MIEQ, FEUP, 2018

Ana Luísa Poças, Estudo e desenvolvimento de novos materiais e estruturas para vestuário de proteçao, MIEQ, FEUP, 2018.

Patents

G.M.M. Santos, R. Marques, J.A. Morgado, M.A.S. Marinho, J.Santos, C.I.B.R. Pereira, T.V.O. Pinto, J.A.P.F. Almeida, J.F.M. Sousa, S.C.A. Teixeira, A.C.M. Freire, M.F.R. Pereira, O.S.G.P. Soares, P.S.F. Ramalho, I.A.V. Ribeiro, B.A.C. Oliveira, M.P.L. Pinto, G.M.V.S Araújo, A.J.S.S. Araújo, A.J.S.S. Araújo, J.M.A. Pinto , Formulações para artigos de proteção radiológica, artigos de proteção radiológica, e seus usos. Portuguese Patent, PT 117219, 10 may 2021.

Selected Publications

[1] M.A. Barros et al., U.Porto Journal of Engineering, 6, 2183 (2020)
[2] M.A. Barros et al., Applied Surface Science, 629, 157311 (2023)
[3] Ana Sousa, Renata Matos, Jose R. M. Barbosa et al., Solid State Phenomena, 333, 161-169 (2022)
[4] Ana Sousa, Renata Matos, Jose R. M. Barbosa et al., Physica Status Solidi (A) Applications and Materials, 219, 2100516 (2022)

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