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Designing cotton fibers impregnated with photocatalytic graphene oxide/Fe, N-doped TiO_2 particles as prospective industrial self-cleaning and biocompatible textiles

Miruna Silvia Stan[a,b,*], Madalina Andreea Badea[a], Gratiela G. Pircalabioru[b,c], Mariana Carmen Chifiriuc[b,c], Lucian Diamandescu[d], Iuliana Dumitrescu[e], Bogdan Trica[f], Claude Lambert[g], Anca Dinischiotu[a]

[a] Department of Biochemistry and Molecular Biology, Faculty of Biology, University of Bucharest, 91–95 Splaiul Independentei, 050095 Bucharest, Romania
[b] Research Institute of the University of Bucharest–ICUB, University of Bucharest, 91–95 Splaiul Independentei, 050095 Bucharest, Romania
[c] Department of Botanic-Microbiology, Faculty of Biology, University of Bucharest, 1-3 Aleea Portocalelor, 60101 Bucharest, Romania
[d] National Institute of Materials Physics (NIMP), Atomistilor 405A, 077125 Bucharest-Magurele, Romania
[e] National R&D Institute for Textiles and Leather Bucharest (INCDTP), 16 Lucretiu Patrascanu, 030508 Bucharest, Romania
[f] The National Institute for Research & Development in Chemistry and Petrochemistry (INCDCP-ICECHIM), 202 Splaiul Independentei, 060021 Bucharest, Romania
[g] Immunology Laboratory, University Hospital of Saint-Étienne, 42055 Saint-Étienne, France

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ABSTRACT

Our study reports the fabrication and characterization (surface morphology, hydrophobicity/hydrophilicity, photocatalytic efficiency) of cotton fibers treated by various methods with graphene oxide decorated with Fe, N-doped TiO_2 nanoparticles. Designed as prospective industrial self-cleaning, antimicrobial and biocompatible textiles, microbiological and cytotoxicity tests were performed on these particles-treated fibers to validate their qualities. The photocatalytic effect was dependent on chemicals used to disperse the nanoparticles, the parameters of the treatment, the fiber structure and composition of the material. The double and triple treatment of the textiles with the same particle dispersion resulted in a relatively uniform coverage of cotton fibers with relatively large amounts of particles. A larger amount of doped TiO_2 particles demonstrated a better photocatalytic effect under visible light. The material's hydrophobicity increased with the number of treatments due to the deposition of successive layers of reduced graphene, ensuring self-cleaning properties. The photocatalyst-treated cotton fabrics exhibited an increased resistance to *Enterococcus faecalis* and *Escherichia coli* colonization, and also high biocompatibility, as they did not affect the cell viability, membrane integrity and morphology, nor induce inflammation. All these data confirm the improved properties of cotton fibers treated with graphene oxide decorated with Fe, N-doped TiO_2 particles in order to be used as industrial self-cleaning and biocompatible textiles.

1. Introduction

The photocatalytic activity of titanium dioxide (TiO_2) has been investigated intensively in the last decades grace to the chemical properties and high commercial availability of this material. Considering its high band gap energy, only the high energy blue and UV light photons, which represent ~3% of the solar spectrum, can excite electrons to the conduction band. Thus, the research was focused on finding approaches to tailor the electronic features of TiO_2, the doping being one of the most convenient methods. In this way, TiO_2 doped or co-doped with metals [1,2] and non-metals [3] was extensively investigated in order to create photocatalytic textiles able to decompose the usual pollutants, including microorganisms, under the visible light exposure. Recent efforts to enhance the photocatalytic activity of TiO_2 and develop self-cleaning [4], antibacterial [5] and antifungal cotton fabrics [6] are currently focused on the preparation of TiO_2 composites with multi-wall carbon nanotubes (MWCNT) [7,8], graphene [9–11], reduced graphene [12,13] or graphene oxide [14,15].

It has been described the attachment of TiO_2 nanoparticles (NPs) on the two-dimensional graphene nanosheets by several approaches, such

* Corresponding author at: Department of Biochemistry and Molecular Biology, Faculty of Biology, University of Bucharest, 91–95 Splaiul Independentei, 050095 Bucharest, Romania.
E-mail address: miruna.stan@bio.unibuc.ro (M.S. Stan).

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as through the bonding [16] of the free electrons existing on the TiO_2 surface with unpaired π electrons of the carbon atoms to form a Ti−O−C structure. Also it was described an electrostatic interaction [17] between the negatively-charged oxide functional groups of graphene oxide (GO) and the positively-charged Ti^{4+}, and an attachment through hydrogen bonds formed by TiO_2 with the existing functional groups of graphene oxide [18]. These composites increase the wavelength absorption across the entire visible light spectrum due to the graphene highly conjugated structure forming Ti−O−C chemical bonds, and to the reduction of TiO_2 band gap due to carbon doping [19].

Having a large surface area, graphene and graphene oxide act as adsorbent, electron acceptor and photosensitizer, and efficiently enhance the contaminants photodecomposition [20,21]. Different studies indicated a high photocatalytic activity of graphene composites [22–25] towards degradation of azo dyes, such as methyl orange, rhodamine B and methylene blue (MB), and also reported the photoinactivation of various bacteria, such as *Escherichia coli* [26,27].

The photoreactivity of TiO_2/graphene nanocomposites involves the destruction of any type of organic compound, their potential toxic risk on environment and human health being demonstrated previously [28]. Therefore, it is very important to undertake a human risk assessment study of these nanocomposites using valid and standardized methodology, such biocompatibility and cytotoxicity protocols on human cell cultures, instead of in vivo experiments, in order to respect the principles of the 3Rs (Replacement, Reduction and Refinement) and to safeguard animal welfare.

Taking into consideration all the aspects discussed above, our study reports the fabrication and characterization (surface morphology, hydrophobicity/hydrophilicity, photocatalytic efficiency) of cotton fibers treated by various methods with graphene oxide decorated with Fe, N-doped TiO_2 nanoparticles (TiO_2-Fe(1%)-N + 2% GO nanoparticles abbreviated GOT NPs). The doping of iron and nitrogen onto TiO_2 NPs, further decorated on GO, was necessary to enhance the photocatalytic activity of TiO_2 in visible light and to achieve a higher efficiency in the degradation of chemical agents (such as dyes) and pathogens. Designed as prospective industrial self-cleaning, antimicrobial and biocompatible textiles, microbiological and cytotoxicity tests were performed on these GOT-treated fibers to validate their qualities.

2. Materials and methods

2.1. Synthesis and characterization of photocatalysts

Firstly, the TiO_2 NPs doped with 1% Fe and nitrogen were obtained by simultaneous co-precipitation in hydrothermal conditions at 200 °C/2 h using urea, in Teflon lined autoclave, followed by a calcination at 400 °C for 120 min in air, achieving a uniform volume distribution of Ti and Fe ions as described in our previous work [29]. We started with appropriate quantities of $TiCl_3$ (15 wt% $TiCl_3$ in 10 wt% HCl, Merck solution) and $FeCl_3{\cdot}6H_2O$ (p.a. Merck, Darmstadt, Germany) which were dissolved and mixed in water, and then pH ~9 was reached by adding NH_4OH (25 wt%, Merck, Darmstadt, Germany). In order to obtain Ti and Fe oxyhydroxides, Ti^{3+} was oxidized to Ti^{4+} under air bubbling. After washing and drying, the co-precipitate was placed in a Teflon lined autoclave (~400 cm^3) with stirring. The hydrothermal treatment, in the presence of urea, was then carried out in two steps: 105 °C/30 min succeeded by a treatment at 200 °C/120 min. After washing and drying, the resulted crystalline powder was calcined at 400 °C/120 min in air [29]. Secondly, these nanoparticles were dispersed in distilled water in the presence of poly diallyl dimethyl ammonium chloride (PDDA) (20 wt%, Sigma Aldrich, St. Louis, MO, USA) as dispersing/reducing/stabilizer agent, and then, were mixed with GO (2 wt% GO with respect to TiO_2; Sigma-Aldrich) in order to obtain TiO_2-Fe(1%)-N decorated GO following the details reported in the previous paper [29]. All the steps required for this synthesis of TiO_2-Fe(1%)-N + 2% GO NPs were schematically represented in Fig. 1. The further structural characterization of obtained GOT NPs by X-ray diffraction (XRD), Mössbauer and Raman spectroscopy showed the unique presence of anatase and of a single Fe^{3+} quadrupole doublet in the samples. In addition, the decoration of reduced GO (RGO) sheets with TiO_2-Fe(1%)-N NPs was evidenced by Raman spectra recorded as described previously [29]. Moreover, the morphology of GOT NPs was observed by transmission electron microscopy (TEM) on Tecnai G2 F-20 TWIN microscope (FEI, Netherlands) using particle dispersions in deionized water or methyl alcohol and deposited on carbon holey copper grids (type S160). Using the scanning transmission/energy dispersive X-ray (STEM/EDX) system, the elemental analysis of GOT NPs was performed. The EDX analysis was performed using SDD Apollo 10 detector type with a resolution of 152.22, tilt: 10.00, take-off: 44.94, AmpT: 0.8, and an energy of 10.01 kV. The spectrum was collected in raster scan mode over an area of 0.3030 × 0.2367 mm with a magnification of 1000×. The GENESIS software was used for spectrum collection, peak identification and element quantification using the ZAF algorithm.

2.2. Treatment of cotton fabrics with photocatalysts

Two types of fabrics were used within this study: (i) scoured and chemically bleached knitted cotton fabric – noted Control K (188 g/m^2 weight, 0.927 mm thickness, 36.9% air permeability and 763 L/m^2/s water permeability) and (ii) scoured and chemically bleached woven cotton fabric – noted Control W (249 g/m^2 weight, 0.581 mm thickness, 414/212 yarns/10 cm; 70.14 L/m^2/s air permeability).

GOT NPs were applied to cotton fabrics according to the following methods:

- for the first sample noted K-S1, the cotton knit was treated with 0.32 g/L GOT NPs prepared by dispersing the GOT powder in 0.04 g/L sodium dodecyl sulphate (SDS) for 180 min at 30 °C on ultrasound bath. The fabric treatment was performed by immersing the knit, successively three times in above prepared dispersion and maintaining the fabric at 40 °C in an ultrasonic bath for 30 min;
- for the second sample noted K-S2, to eliminate the influence of SDS on the antimicrobial activity and to ensure in the same time a good dispersability of particles, a less concentrated dispersion (0.1 g/L GOT NPs) was prepared by sonicating the GOT powder in distillated water for 30 min at 30 °C. The knit fabric treated with 1 g/L PVP was immersed twice in the prepared dispersion and sonicated for 30 min at 60 °C and then dried in an oven at 100 °C;
- for the third sample noted K-S3, in order to protect the fabric against degradative effects of photocatalyst, the cotton knit was pretreated with 1 g/L polyvinylpyrrolidone (PVP) on ultrasound bath for 30 min at 60 °C. The wet treated fabric was immersed in the dispersion remained after the 3rd treatment of the knit sample S1, was sonicated for 30 min at 60 °C and then dried in an oven at 100 °C. Treatment temperature was raised to facilitate the absorption of higher quantities of NPs due the cotton swelling;
- for the last type of sample noted W-S4, 0.64 g/L particle dispersion was prepared by sonicating the GOT powder in 0.04 g/L SDS for 60 min at 60 °C. The woven fabric was immersed in the prepared dispersion and sonicated for 60 min at 40 °C and then dried in an oven at 100 °C.

2.3. Characterization of photocatalysts-treated fabrics

The surface of the treated fabrics was characterized by scanning electron microscope (SEM, Quanta 200, FEI, The Netherlands) equipped with an energy dispersive analysis of X-rays (EDX).

Contact angles were measured with a 5 μL distillated water droplet on a VCA Optima (AST Products, USA) instrument which captures the droplet image and calculates the contact angle measurement by Sessile Drop method.

To evaluate the photocatalytic efficiency, the fabrics (5 cm × 5 cm) were immersed in 50 mL of 0.0064 g/L methylene blue (MB) for 30 min to be uniform stained and to achieve adsorption equilibrium. The dried