



## Synthesis, characterization and self cleaning properties of titania nanoparticles grafted on polyester fabrics



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### ABSTRACT

Thanks to the excellent photocatalytic properties of titania (TiO<sub>2</sub>) nanoparticles (NPs) as self cleaning and anti bacterial agents, a great interest for engineering TiO<sub>2</sub> doped textile fabrics has been arising. This study was aimed to the preparation of self cleaning textile fabrics based on polyester (PES) fibres and TiO<sub>2</sub> NPs. In order to covalently bind TiO<sub>2</sub> to PES surface, commercial TiO<sub>2</sub> NPs were first modified by aminopropyl trimethoxysilane (APTMS) and then grafted to PES fibres. The coated PES fibres were characterized by FT-IR and FESEM and their characteristics compared with the bare fibres. The photocatalytic activity of TiO<sub>2</sub> was ascertained by the photodegradation of methylene blue in solution. Moreover, the capability of TiO<sub>2</sub> to photodegrade methylene blue stains adsorbed on the PES fabric surface was also tested.

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### 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) nanoparticles (NPs) have demonstrated to be non toxic, high efficient, stable, cheap and ecologically friendly photocatalysts in the degradation of organic pollutants [1,2]. The ability to destroy organic pollutants comes from the redox environment generated from photo-activation of TiO<sub>2</sub> [3]. Once excited with light of wavelength equal to or greater than the band gap energy (3.2 eV for anatase), the generation of electron pairs and holes in the semiconductor valence and conduction band respectively occurs [4,5]. The energized holes and electrons can either recombine and determine redox reactions with electron donors and acceptor species present nearby the TiO<sub>2</sub> NPs. Generally, the formation of reactive oxygen species (ROS) capable to photooxidize aliphatic and aromatic molecules into CO<sub>2</sub> occurs [6,7]. Hence, species coming from upon irradiation can reduce or oxidize environmental pollutants present on TiO<sub>2</sub> surfaces, including volatile components, leading to the breakdown of the pollutants into low molecular weight fragments.

The positive experience with the photocatalytic performance with TiO<sub>2</sub> NPs and the prospect of technical success and economical benefits were recognized by the textile industries and thus

the addition of TiO<sub>2</sub> NPs on fabrics is becoming the focus of many researchers.

There are many studies oriented towards the development of smart surfaces showing different chemistries containing TiO<sub>2</sub> NPs with photocatalytic properties which work as self cleaning surfaces against different types of organic pollutants [8–10]. In order to design self cleaning materials, TiO<sub>2</sub> micro/nanoparticles have been deposited onto different suitable supports using different techniques such as anodization [11,12], chemical vapour deposition [13,14], thermal oxidation of Ti metal, sol-gel [15–17]. Some methods that require high temperatures such as chemical vapour deposition would bring to the breaking or peeling of the film and preclude the coating on low thermal materials such as polymers [18]. Concerning textiles materials added with NPs, in spite of the numerous potential applications and benefits, there are still some concerns about their production for commercialization. The problematic issues deal with the maintenance of the properties of the textile fibres once coated with NPs [19]. Most of methods to deposit TiO<sub>2</sub> onto polymer substrates including polyesters, polystyrene, cotton fabrics deal with the sol-gel method due to the easy processing and acceptable blind treatment conditions [20,21]. Recently, in order to improve the binding efficiency of TiO<sub>2</sub> NPs on the polymer surface, different chemical functionalities have been inserted on the polymer surface. By taking into consideration that hydroxyl and carboxylic acid groups are good potential site for binding TiO<sub>2</sub> NPs, most of the strategies proposed so far concerns the introduction of these groups or molecules bearing them by different strategies including plasma treatments or chemical reactions [22,23]. Plasma

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treatments to modify the surface of fabrics with the aim to introduce new carboxylic and hydroxylic groups were applied especially to polyester or polyacrylic fibres [24] but altering the surface chemistry and topography of the fibres. Qi et al. report the preparation of TiO<sub>2</sub> NPs through a sol gel process method by the addition of small amount of acid which improved the adhesion of such NPs to the polymer fibres [25]. However, these acid treatments alter the fibres surfaces leading to a loss of the mechanical properties of the entire fabric. Hashemizad et al. reported the use of alkaline hydrolysis of polyethylene terephthalate fibres to bind TiO<sub>2</sub> NPs [26], but also in this case some modification of surface chemistry and morphology of fibres occur.

In this work we report a simple and effective method to coat polyester fibres with TiO<sub>2</sub> NPs without altering the fibres properties in order to get a self cleaning PES fabrics. Among different textile materials to be coated by TiO<sub>2</sub> NPs, polyester is one of the most challenging due to its low cost, flexibility, resistance and wide range of applications spanning from filter for air cleaning in rooms or cars to textile fabric for cloths [27–29]. Our approach consists of functionalizing TiO<sub>2</sub> NPs with an aminosilane molecule first and then to bind the silanized NPs to the polyester fibres. The adsorption and interaction of organosilanes onto TiO<sub>2</sub> NPs occurs via the formation of Si–O–Ti bond [30]. Thanks to the insertion of primary amine groups, silanized TiO<sub>2</sub> NPs can be covalently bound to polyesters via the breaking of ester bonds followed by the formation of an amide bond. The coated fibres were chemically analyzed by Attenuated Total Reflection-Fourier Transformed Infrared (ATR-FTIR) Spectroscopy. Field Emission Scanning Electron Microscopy (FESEM) and Energy Dissipative X-rays spectroscopy (EDX) analysis were used to characterize the morphology of the coated fibres and the distribution of the NPs on the fibres. The photocatalytic performance of coated fibres was evaluated by photodegradation of methylene blue as a model compound.

## 2. Materials

Titanium dioxide (TiO<sub>2</sub>) nanoparticles (NPs) with the anatase structure and a nominal diameter less than 100 nm were purchased from Sigma–Aldrich (Switzerland). Polyesters (PES) fabrics were kindly provided by Next Technology Tecnotessile (Italy). It consists of hydrophilic PES with a thickness of about 1 mm. (3-Aminopropyl)-trimethoxysilane (APTMS) as well as all the solvents were purchased from Sigma–Aldrich (Switzerland) and used without further purification.

## 3. Methods

### 3.1. APTMS TiO<sub>2</sub> NPs functionalization

Commercial titania NPs were surface functionalized by using (3-aminopropyl)-trimethoxysilane (APTMS) as already reported [31]. Briefly, 5 mL of (3-aminopropyl)-trimethoxysilane (APTMS) were added to a NP suspension containing 0.5 g of TiO<sub>2</sub> nanopowder in a 95/5% v/v ethanol/water mixture at pH 5. The functionalized NPs were precipitated by ultracentrifugation at 6000 rpm for 15 min and washed twice with ethanol, before being dried in a vacuum oven at 70 °C overnight. APTMS functionalized NPs are referred to as TiO<sub>2</sub>-NH<sub>2</sub> NPs.

### 3.2. TiO<sub>2</sub>-NH<sub>2</sub> NPs grafting process

PES fabrics were first immersed in a suspension containing TiO<sub>2</sub>-NH<sub>2</sub> NPs at a concentration of 1 mg/ml for 30 min and then heated at 70 °C in a preheated oven for 30 min. The TiO<sub>2</sub> grafted fabrics

were extensively washed with deionized water to remove the not bound NPs from the surface and let to dry in air.

### 3.3. Characterization of TiO<sub>2</sub>-NH<sub>2</sub> NPs fabrics

Infrared spectra were recorded using an FTIR spectrometer (Bio-rad FTS 6000) working in attenuated total reflection mode equipped with a 45° Ge ATR crystal and a mercury cadmium telluride detector. The spectra were an average of 512 scans at a resolution of 2 cm<sup>-1</sup>. Spectra were corrected for the baseline and smoothed.

Grafted and bare PES fibres were analyzed by a Field Emission Scanning Electron Microscope (SIGMA VP Zeiss, Germany) equipped by a Energy Dispersive X-ray Spectroscopy (EDX) system with an Oxford INCA detector. Samples were observed under partial pressure by using a VPSE detector once mounted on proper stubs. All samples were analyzed by using approximately the same parameters and settings of the microscope: accelerating voltage between 15 and 20 kV, working distance around 7 mm and a beam current of 2.4 A. The surfaces were imaged also in back-scattered electron mode in order to distinguish the inorganic NPs from the organic fabrics. Analysis of the elements was carried out by Energy Dissipative X-rays spectroscopy (EDX) by using an OXFORD INCA system. Smart dot-by-dot maps were also acquired by imaging Ti and Si signals over the surface to determine the TiO<sub>2</sub> NPs distribution over the surface.

### 3.4. Photocatalytic degradation of methylene blue under UV light irradiation

The photocatalytic properties of the TiO<sub>2</sub> grafted PES fabric were evaluated by measuring the photodecomposition of methylene blue (MB) in aqueous solution with an initial concentration of 10<sup>-5</sup> M. TiO<sub>2</sub> NPs grafted PES fabrics (round pieces about 3 cm in diameter) were dipped in 10 ml of a 10<sup>-5</sup> M solution of MB and stirred under dark conditions for two hours to achieve adsorption equilibrium. Then, the samples were irradiated by a 400 W UV-visible mercury lamp (Helios Ital Quartz) in a range between 200 nm and 800 nm at a distance of 30 cm. MB solution was taken out at regular intervals of 10 min and the MB residual concentration was measured by a UV spectrophotometer (Lambda 650 Perkin Elmer) at λ<sub>max</sub> = 664 nm until the absorbance was close to zero. Not irradiated TiO<sub>2</sub> NPs grafted PES fabrics and irradiated fabrics not containing TiO<sub>2</sub> NPs were taken as reference samples.

The photocatalytic decomposition was determined by the following equation:

$$C/C_0$$

where C<sub>0</sub> represent the initial MB concentration of the dye and C the concentration at each different experimental time.

Moreover, in order to evaluate the capability of TiO<sub>2</sub> NPs to photodegrade MB dye directly stained on PES, TiO<sub>2</sub> grafted fabrics were stained with 1 ml of a 10<sup>-5</sup> M solution of MB, dried at room temperature and then irradiated by UV lamp under the same conditions. The residual MB dye on the fabrics was determined by UV spectrophotometric measurements. The samples were fixed on the hole of the integrating sphere and the absorbance of MB stained on the surfaces was measured at λ<sub>max</sub> = 664 nm every 10 min until it was close to zero.

## 4. Results

### 4.1. Grafting of TiO<sub>2</sub>-NH<sub>2</sub> nanoparticles on PES fibres

The grafting of TiO<sub>2</sub> NPs on PES fibres was carried out in two steps as shown in Fig. 1:

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