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Regular Article

Multifunctionalization of wool fabrics through nanoparticles: A chemical route towards smart textiles

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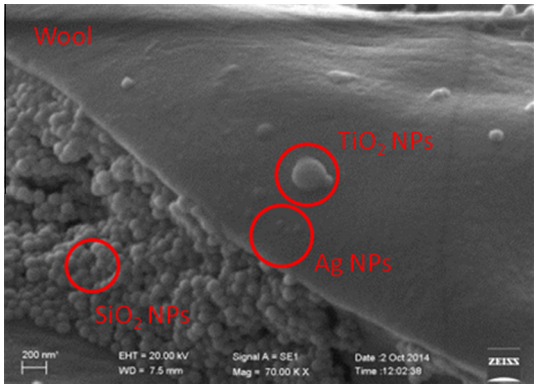
GRAPHICAL ABSTRACT



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ABSTRACT

A new approach towards the design of smart nanotextiles with innovative properties is presented. Silica (SiO_2), titania (TiO_2), and silver (Ag) nanoparticles (NPs), were synthesized without the use of any toxic organic compound and then were used, alone and in combination, to functionalize wool fabrics. Electrostatic forces, influenced by a low pH of the solutions, allowed the interactions between wool fabrics and NPs, enabling a robust functionalization. This was verified by X-ray microfluorescence and visualized by scanning electron microscopy measurements. The antibacterial Ag NPs were embedded in a polymer, alginic acid, to reduce the possible side effect due to their direct contact with the skin. SiO_2 NPs, instead, were used to change the hydrophilicity of wool while the functionalization with TiO_2 NPs was chosen to provide self-cleaning properties. The antibacterial activity of the fabrics was studied against the bacteria *Escherichia coli*, while the hydrophilicity of wool was studied by contact angle measurements and the self-cleaning properties were tested by estimating the visible discoloring of a dye stain under sunlight irradiation. Interestingly the combination of three different types of NPs provided the best results. SiO_2 and Ag made the wool superhydrophilic providing at the same time the best antibacterial properties, while fabrics with titania (alone or in combination) were hydrophobic and showed the best self-cleaning properties.

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1. Introduction

Wool is a widely used biomaterial mainly composed of fibrous proteins that are insoluble and tough, such as keratins [1]. These filaments of keratins are aligned in the fiber axis constituting macrofibrils with diameter around 300 nm that are covered by a lipid membrane and linked by a intermacrofibrillar matrix called cell membrane complex (CMC). The fiber formation is due to the peptide bonds that facilitate the alignment of cysteine, allowing the formation of disulfide cross-links that give thermal stability and rigidity to these materials. Although their excellent physical properties as biological materials, wool fibers suffer the disadvantage of being photosensitive to UV, having bad sweat venting properties, and scarce water absorption [2]. This feature, in particular limits their use by affecting the dyeing, the finishing and the wearing comfort of the fabrics; hydrophobicity, in fact, can create discomfort to people for its static charge on wool tissues. A second major disadvantage in the use of wool is the tendency to sheltering microorganisms providing good energy source of nutrients for their growth. This generally causes fiber damages and skin irritations [3], especially in the case of garments and carpets [4]. Loading antimicrobials is therefore of capital importance for the production of advanced hygienic and medical textiles based on wool. Up to now, despite different approaches have been explored to improve the hydrophilic properties of wool fabrics, the use of nanotechnology seems a promising route for mastering the surface properties of this biomaterial. Nanotechnology, in fact, enables a smart functionalization of the biofibers providing new features such as antibacterial activity, photo-degradation and self cleaning. Nanomaterials, and in particular nanoparticles (NPs), are able to use incident light to decompose dirt, stains and microorganisms through photocatalysis, and protect tissues against UV degradation, fulfilling the needs for innovation in the fields of garments, carpets and building materials.

In previous years, the wool functionalization was carried out through a single type of nanoparticle having a specific chemical composition, such as silver (Ag) and silica (SiO_2) or titania (TiO_2). Some research groups used Ag NPs to improve the colour strength of fabrics and their antibacterial properties. In these studies, however, the Ag NPs where directly used, without embedding the particles in specific polymers [5,6]. This approach has some drawbacks as NPs-modified garments, for instance, can lead to a human skin irritation or damage. Furthermore, some of these studies used a not-environmental friendly method that exploited toxic reducing agents for the synthesis of AgNPs, such as sodium borohydride $NaBH_4$ [3,5], butylamine ($ButNH_2$) [6], sodium hypophosphite (SHP) [7], sodium dithionite and sodium bisulfite [8].

Silica NPs were often added to wool fiber in order to obtain a superhydrophilic fabric by modifying the surface roughness, the surface energy and the water absorption of wool [9]. This type of approach is interesting because the degree of hydrophobicity of the wool seems to be controlled by the density and the size of the NPs.

Finally, the functionalization with TiO_2 NPs was used with the aim to improve the UV protection of the fibers and the photocatalytic properties [10,11]. The self cleaning properties of modified wool with TiO_2 were also described by Daoud et al. [2] and Behzadnia et al. [12], and its effect against the photoyellowing was demonstrated by Zhang et al. [13]. The functionalization with this type of NPs, however, causes a decrease in the tensile properties of the wool fibers. More recently, a high efficiency in stain removal, antibacterial and superhydrophilic properties of the wool fibers were obtained by using a combination of Ag with TiO_2 or SiO_2 NPs, and TiO_2/SiO_2 nanocomposite [7,14,15]. To the best of our knowledge, however, the combination of three different NPs and the possible effects on wool fabrics was not reported yet.

In the present work self-cleaning, UV-resistance, hydrophilicity, and antibacterial properties of the wool were explored by anchoring TiO_2, SiO_2 and Ag NPs to the fabrics. In addition, we tried to design new multifunctional textiles through the combination of the three different NPs, taking the advantages of their specific properties. This approach can be important because the functional properties of every single material could benefit of the combined functionalization.

2. Materials and methods

2.1. Reagents

Tetraethyl orthosilicate (TEOS) (98%, Aldrich), ethanol (99.99%, Aldrich), and ammonium hydroxide (30%, Aldrich) were used without any further purification. Milli-Q water (18.2 Ω) was used throughout the experiment. 100% of untreated wool fabric was purchased from La robbia (Sardinia) and used as substrate. Titanium isopropoxide (TIP, 97%) and absolute ethanol were purchased from Sigma–Aldrich (Germany). $AgNO_3$ solution (99.9%), Glacial acetic acid, Methylene Blue, Alginic acid sodium salt, LB agar were purchased by Aldrich, Germany. The chemicals were used as received. *Escherichia coli* (*E. coli* ATCC 11299) was chosen as typical microorganism.

2.2. Synthesis of nanoparticles

2.2.1. Synthesis of silica NPs

The SiO_2 particles were obtained by hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol. TEOS (3 mL) was added drop by drop to a solution of EtOH (50 mL), ammonium hydroxide (30% w/v, mL) and water (1 mL) and left under shaking for 5 h. After 48 h at room temperature (25 °C) the white suspension was centrifuged at 13,000 rpm for 10′ with different washing steps to eliminate the solvents. Then, the NPs were collected and dispersed in 100 mL of water to a 0.05 M final concentration.

2.2.2. Synthesis of titania NPs

TiO_2 NPs were prepared by an alcohothermal method without the use of any specific organic reagent. The Titanium isopropoxide (TIP) precursor was added dropwise into a stirred mixture containing water and ethanol (TIP/water/ethanol volume ratio 3:4:90 v/v). After sonication for 1 h, the crystallization of TiO_2 was achieved in a mitten at 180 °C for 24 h. The obtained TiO_2 NPs were collected by centrifugation and then resuspended in water to a 0.01 M final concentration.

2.2.3. Synthesis of alginate capped AgNPs (AlgnAg NPs) composite

Alginate capped Ag NPs were synthesized by adding 2 mL of freshly prepared 1×10^{-2} M $AgNO_3$ solution to 50 mL of 0.2% (w/v) alginate solution, with constant stirring at 90 °C. The obtained solution was diluted to 100 mL with a final 0.01 M concentration. A brown color of the solution indicated the formation of Ag NPs.

2.3. Characterization of nanoparticles

The formation of Ag NPs was monitored by UV–Vis spectroscopic measurements with a spectrophotometer (Cary 3E UV–visible, Varian).

Morphological examination of NPs was performed by environmental scanning electron microscopy (ESEM) (Zeiss LS10, Germany). A drop of NPs aqueous suspension was deposited on aluminum stub and dried until complete water evaporation. The samples were then analyzed at 20 kV acceleration voltage after