PHOTOSWITCHABLE NANOMATERIALS FOR THE DESIGN OF LIGHT-RESPONSIVE SMART TEXTILES: FROM COATING TO ADVANCED FIBER-SPINNING TECHNOLOGY

Pinto T. V.[1], Costa P.[1], Sousa C. M.[2], Fernandes D. M.[1], Guedes A.[4], Silva C.[3], Pereira M. F. R.[5], Coelho P. J.[2], Pereira C.[1] and Freire C.[1]

[1] *REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal*

[2] *Departamento de Química e CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal*

[3] *CeNTI, Centro de Nanotecnologia e Materiais Técnicos, Funcionais e Inteligentes, 4760-034 Vila Nova de Famalicão, Portugal*

[4] *Centro de Geologia e Departamento de Geociências, Ambiente e Ordenamento do Território, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal*

[5] *Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE-LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, 4200-465 Porto, Portugal*

tpinto@fc.up.pt

ABSTRACT

This work reviews our recent achievements on a novel generation of UV/sunlight responsive silica nanoparticles (SiO_2 NPs) and smart textiles. Photoresponsive organic – 2*H*-naphtho[1,2-*b*]-pyran (2*H*-NPT) and 3*H*-naphtho[2,1-*b*]pyran (3*H*-NPT) derivatives – and inorganic – phosphomolybdic acid (PMo_{12}) – compounds were selected to tune the photochromic response and color palette range of the SiO_2 NPs and corresponding smart textiles. The SiO_2 NPs were functionalized by covalent *post*-grafting of 2*H*-NPTs and 3*H*-NPTs, and by non-covalent electrostatic immobilization of PMo_{12}. The resulting hybrids were incorporated onto fabric substrates by screen-printing and within fibers through advanced fiber-spinning processes − wet spinning and melt spinning − at pre-industrial scale.

Keywords: Photochromism, Light-responsive Silica Nanoparticles, Naphthopyrans, Polyoxometalates, Smart Textiles

1. INTRODUCTION

Smart textiles have the ability to sense, respond or adapt themselves, in a predetermined way, to the environmental conditions or stimuli (*e.g.*, chemical, electrical, magnetic, mechanical, thermal).[1,2] In 2015, the global market value for smart textiles was USD 544.7 million, being expected to reach USD 9.3 billion in 2024, with a compound annual growth rate (CAGR) above 35% from 2016 to 2024. In the same year, Europe owned more than 30% of the market share and the military and defense sectors were the largest segments, holding 25.5% of the global market.[3]

Photoresponsive textiles (*i.e.*, textiles which undergo a reversible light-induced color change) have attracted considerable attention due to their aesthetics, UV-blocking and UV/solar sensing properties. Furthermore, potential use on brand protection (anti-counterfeiting), military, sports hunting (camouflage), fashion and decoration suggest endless frontier applications. Photochromic organic and inorganic compounds are potential scaffolds to produce photoresponsive textiles due to their switchable color generation under UV and/or sunlight irradiation. Among organic compounds, naphthopyrans (NPTs, also known as chromenes) have attracted much interest since the 1990's because they are easy to prepare, show an efficient colorability, rapid color reversibility, good fatigue resistance, and are very versatile molecules.[4,5] Nevertheless, the prolonged exposure to UV irradiation in outdoor applications often leads to the loss or decrease of their photochromic performance.[4] Inorganic compounds such as polyoxometalates (POMs) have attracted increased scientific interest owing to their distinct architectures, excellent physicochemical properties, including strong Brønsted acidity, fast reversible multielectron redox transformations, proton mobility, and high thermal stability.[6,7] Also, POMs based on early transition metals such as Mo or W can undergo a reversible electron transfer to become mixed-valence colored species, making them promising candidates to photo- and electrochromic applications. However, the slow bleaching kinetics associated to these materials is a serious limitation for optical applications that require fast and reversible photoresponse.[8]

Photoresponsive textiles have been mainly produced through the incorporation of spirooxazine and naphthopyran derivatives, in dispersed form, by exhaust dyeing [9–11], by screen-printing processes [12,13], or by attaching microcapsules containing photochromic dyes to the fabrics surface.[14,15] Recently, advanced fiber-spinning techniques such as melt [13,16] and electrospinning [17,18] have been used to produce photoresponsive fibers. Nevertheless, the production of light-responsive textiles continues to be a complex and challenging process since the dyestuffs are often sensitive to heat, which limits the maximum temperature used in curing and fiber-spinning processes.[19]

To overcome these limitations, silica nanoparticles (SiO_2 NPs) have been successfully used as supporting matrices for direct organic [20,21] or chromic (*e.g.* fluorescent [22], photochromic [23,24] and thermochromic [25]) dyes on textiles, enhancing the photostability of the dyes and the washing fastness.[19,26]

The present report reviews our recent developments on the design, fabrication and characterization of a new generation of high-performance photochromic SiO_2 NPs and smart textiles with enhanced washing and light fastness. Distinct UV/sunlight responsive organic and inorganic compounds were selected in order to tune the color-switching response and the color palette range of the resulting hybrid nanomaterials and corresponding textiles. Photoresponsive SiO_2 NPs were firstly prepared by covalent *post*-grafting of photochromic organic molecules – naphthopyran (NPT) derivatives [27]–, as well as by non-covalent electrostatic immobilization of a photochromic polyoxometalate – Keggin-type phosphomolybdic acid.[28] The resulting hybrid nanomaterials were incorporated on fabric substrates by coating technology − screen-printing [23] − and within fibers through advanced fiber-spinning processes – wet spinning [29] and melt spinning [28] − at pre-industrial scale. The morphological, chemical and photochromic properties of the hybrid nanomaterials and respective textiles/fibers were evaluated by several techniques, such as scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, UV-vis spectroscopy and colorimetry.

2. EXPERIMENTAL SECTION

2.1. Preparation of photoresponsive SiO_2 NPs

Photoresponsive SiO_2 NPs were prepared by two distinct routes: *i)* a two-step procedure consisting on the microwave-assisted NPTs (2*H*-naphtho[1,2-*b*]-pyran (2*H*-NPT) and 3*H*-naphtho[2,1-*b*]pyran (3*H*-NPT) derivatives) silylation, followed by the covalent *post*-grafting onto SiO_2 NPs (denoted as SiO_2@NPTs) [27]; and *ii)* non-covalent electrostatic immobilization of Keggin-type phosphomolybdic acid (PMo_{12}) onto positively-charged amine-functionalized SiO_2 NPs (denoted as SiO_2@PMo_{12}).[28] The respective procedures and detailed characterization are reported elsewhere.[27,28] A schematic representation illustrating the distinct approaches is displayed in Figure 1.

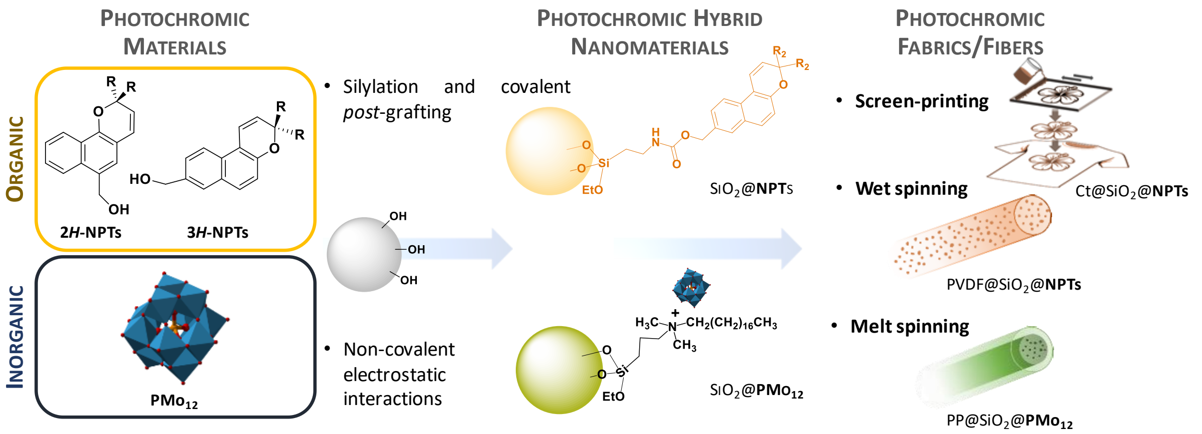

Figure 1. Schematic representation (not drawn to scale) of the immobilization of NPT derivatives (2*H*-NPTs and 3*H*-NPTs) and PMo_{12} onto SiO_2 NPs and subsequent incorporation onto cotton fabrics by screen-printing or within PVDF and PP fibers by advanced fiber spinning technologies (wet spinning and melt spinning, respectively). Adapted with permission from refs. [23,27].

2.2. Preparation of light-responsive textiles

The photoresponsive SiO_2 NPs were incorporated on fabrics by screen-printing and within fibers through advanced fiber-spinning processes – wet spinning and melt spinning − at pre-industrial scale.

Screen-printing: Photoresponsive cotton fabrics (Ct@SiO_2@NPTs) were produced by screen printing. Firstly, 10 wt% of SiO_2@NPTs (where NPTs = 2*H*-NPT and 3*H*-NPT derivatives) were dispersed on aqueous-based inks and then applied to cotton by the conventional screen-printing technique.[23]

Wet spinning: Photoresponsive polyvinylidene fluoride (PVDF) fibers (PVDF@SiO_2@NPTs) were prepared through dry–jet wet spinning.[29] Firstly, 4 wt% SiO_2@NPTs (where NPTs = 2*H*-NPT derivatives) were dispersed in a mixture of PVDF and *N*,*N*-dimethylacetamide and then extruded by a 30-hole spinneret with diameter of 0.15 mm. After passing through a coagulation bath, in which the PVDF was solidified, and through a set of godets and washing baths, the filaments were collected on a bobbin.

Melt spinning: Photoresponsive polypropylene (PP) fibers (PP@SiO_2@PMo_{12}) were fabricated by melt spinning technique through the incorporation of SiO_2@PMo_{12}.[28] SiO_2@PMo_{12} (5 wt%) were mixed with PP by melt compounding; this mixture was then extruded simultaneously with PP (50:50) by a 36-hole spinneret with diameter of 0.35 mm. The filaments were solidified in a chamber, pulled through a set of rolls and rolled on a bobbin. Afterwards, the fibers were knitted into a mesh.

The detailed procedures and characterization are reported elsewhere.[23,28,29]

3. RESULTS AND DISCUSSION

Photoresponsive SiO_2@NPTs

SiO_2@NPTs based on the covalent grafting of silylated NPTs onto spherical nano-sized silica (15 ± 3 nm) were successfully prepared.[27] These nanomaterials were characterized by several techniques such as TEM, elemental analyses, TGA and FTIR, which allowed confirming the preservation of the NPTs structure after silylation and subsequent grafting onto SiO_2, as well as the spherical morphology and particle size of the nanosupport (15 ± 3 nm). All SiO_2@NPTs revealed direct and reversible photochromic properties, changing from an off-white coloration to intense colorations under UV ($\lambda = 365$ nm) and sunlight exposure (Figure 2A). In particular, the SiO_2 NPs functionalized with 3*H*-NPTs exhibited excellent optical color contrast (ΔE^*_{ab} = 54.7) and fast coloration and decoloration kinetics, coloring in 1 min and fading in less than 2 min. Also, the SiO_2 NPs functionalized with 2*H*-NPTs showed fast coloration and high optical contrast (ΔE^*_{ab} = 53.7), but presented slower fading rates, taking more than 2 h to return to their original uncolored state. In addition to the color palette range (from red to purple), the SiO_2@NPTs revealed good photostability under prolonged UV exposure, preserving their photochromic performance for at least twelve successive UV irradiation (during 1 min) and dark (during 28 min) cycles.

Photoresponsive Ct@SiO_2@NPT fabric

The SiO_2@NPTs were successfully incorporated onto cotton fabrics by screen-printing.[23] The presence of SiO_2@NPTs was confirmed by SEM-EDS, FTIR and TGA. All nano-coated cotton fabrics showed direct photochromism under UV (λ = 365 nm) and sunlight irradiation, exhibiting high color contrast (ΔE^*_{ab} = 27.9–53.1), good coloration and bleaching kinetics (*e.g.*, coloring in 1 min and losing 50% of their coloration in less than 2 min), low residual color, high photostability, and resistance to photodegradation. In general, the photochromic performance of the nano-coated fabrics was identical to that observed for the SiO_2@NPTs (Figure 2A).

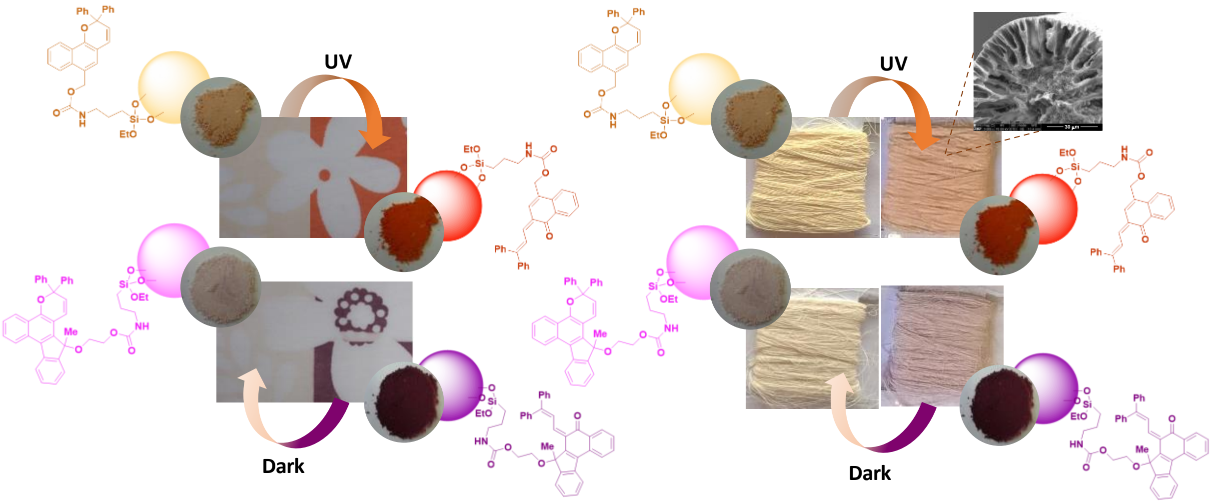

Figure 2. Photographs of SiO_2@2*H*-NPT nanomaterials and corresponding A) nano-coated cotton fabrics (produced by screen-printing) and B) doped PVDF fibers (produced by wet spinning) before and after UV irradiation (λ = 365 nm) for 1 min at room remperature. Adapted with permission from refs. [23,27,29]. Copyright (2019) American Chemical Society and Elsiver.

Photoresponsive PVDF@SiO_2@NPT fibers

SiO_2@NPTs based on 2*H*-NPT derivatives were incorporated within fibers through dry–jet wet spinning.[29] The SEM micrographs of the resulting fibers revealed 98–133 μm filaments with an internal asymmetric morphology composed of large finger-like macrovoids and porous sponge-like structures with narrow cavities in the middle (Figure 2B). Following a similar trend to that observed for the parent SiO_2@NPTs and respective Ct@SiO_2@NPTs, PVDF@SiO_2@NPT based fibers showed light-responsive properties (Figure 2B), coloring in 1 min under UV (λ = 365 nm) or sunlight irradiation with good color contrast (ΔE^*_{ab} = 7.2 – 15.1). The color contrasts were lower than those observed for the corresponding nano-coated fabrics (10 wt%) owing to the reduced amount of SiO_2@NPTs used to dope the PVDF fibers (4 wt%). Furthermore, the presence of polar groups ($-CF_2-$) in the PVDF polymeric matrix stabilized the open colored form of the NPTs, contributing to the slower bleaching of the PVDF@SiO_2@NPTs fibers (requiring 1−2 h to return to their initial uncolored state). Nevertheless, some technical adjustments should be considered to improve the features of the final product (*e.g.*, increase the mechanical properties of the fibers) and, therefore, increase its applicability.

Photoresponsive SiO_2@NPTs

Keggin-type PMo_{12} was successfully immobilized onto positively-charged SiO_2 NPs through electrostatic interactions.[28] SiO_2@PMo_{12} was characterized by several techniques (*e.g.*, chemical analysis, FTIR and Raman spectroscopies and SEM-EDS) that proved the presence and preservation of the PMo_{12} structure onto the silica surface and the spherical morphology and particle size (96 ± 18 nm) of the parent SiO_2 NPs. SiO_2@PMo_{12} exhibited photochromic properties under UV exposure (λ = 254 nm), changing from yellow to an intense green-blue coloration (ΔE^*_{ab} = 36.7 after 7 h). The coloration/decoloration kinetics were very slow when compared to those of SiO_2@NPTs due to the intrinsic photochromic mechanism involved in POMs. The bleaching process of the SiO_2@PMo_{12}, at room temperature, took several days to occur. However, it could be accelerated by heating (~110 °C).

Photoresponsive PP@SiO_2@PMo_{12} fibers

Bi-component core-sheath PP fibers were subsequently produced by melt spinning. The SEM micrographs of the resulting PP@SiO_2@PMo_{12} fibers showed a longitudinal smooth surface with diameter of 37 ± 3 μm.[28] The presence of SiO_2@PMo_{12} on the fibers was confirmed by EDS. The good mechanical features of the PP@SiO_2@PMo_{12} fibers allowed the knitting of a mesh. The resulting mesh showed similar photochromic response to that of the parent SiO_2@PMo_{12}, despite the lower color contrast (ΔE^*_{ab} = 16.2 after 7 h) owing to the loading of SiO_2@PMo_{12} used to produce the doped fibers (5 wt% in the PP masterbatch and 50 wt% of masterbatch in the final core-sheath doped fibers).

4. CONCLUSIONS

In this work our recent developments on the design of distinct high-performance photoresponsive SiO_2 NPs based on photo-switchable organic (NPTs) and inorganic (Keggin-type PMo_{12}) compounds were reviewed. The SiO_2@NPTs revealed tunable UV/sunlight responsive properties, with fast coloration/decoloration kinetics, good color contrast and photostability. The resulting SiO_2@NPTs nanomaterials were successfully incorporated on cotton fabrics by screen-printing and within PVDF fibers by wet spinning. On the other hand, SiO_2@PMo_{12} exhibited good color contrast even though the coloration/decoloration kinetics were slower than SiO_2@NPTs nanomaterials.

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