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UV-protective compound-containing smart textiles: A brief overview

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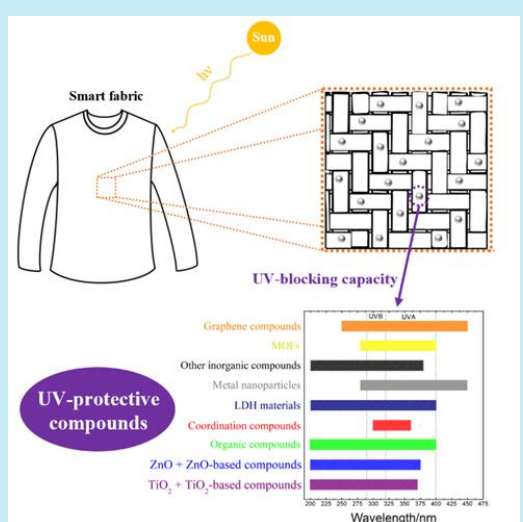
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ABSTRACT: Excessive exposure to solar ultraviolet (UV) radiation causes human health damages, such as sunburns and skin cancer. Thus, the use of sun-protective clothing is a simple, easy, and practical method for UV protection of the human organism. In this perspective, incorporation, coating, and anchorage of UV-protective compounds in textile fibers have been employed to enhance the UV-blocking ability and/or promote functional finishings to smart fabrics. This review describes recent research efforts on the development of UV-protective compound-containing smart fabrics highlighting the UV-blocking properties and multifunctional activities. Different compound class examples and discussions are presented in order to contribute to new insights into sun-protective clothing and future applications of multifunctional textiles.



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1. Introduction

The sun is essential for the Earth's life and its environment (Powers and Murphy, 2019); consequently, solar radiation effects provide human health benefits, such as physical and mental well-being (Flor *et al.*, 2007) and the stimulation of melanin (Serre *et al.*, 2018) and vitamin D biosynthesis (Baker *et al.*, 2017). However, the excessive solar radiation exposure cause sunburns (Sambandan and Ratner, 2011), irregular skin pigmentation, immune system depression, premature aging (Kockler *et al.*, 2012) and skin cancer (Bagde *et al.*, 2018). Among electromagnetic radiations emitted by the sun that reach the Earth's surface, the ultraviolet (UV) radiation is the main responsible for photochemical reactions in the human organism (Baker *et al.*, 2017). UV radiation may be subdivided into following regions: UVC (200–290 nm), UVB (290–320 nm) and UVA (320–400 nm) (Velasco *et al.*, 2008). Stratospheric ozone layer blocks a high percentage of the incident UVC radiation (Baker *et al.*, 2017); therefore, a combination of UVB and UVA radiation reaches the terrestrial surface (Fourtanier *et al.*, 2012). UV radiation penetrates in the upper and deeper layers on the skin causing cellular damages and immune system function modifications (Kockler *et al.*, 2012). Thus, sunscreens and UV-blocking fabrics can be used to minimize the human health risks induced by excessive UVB and UVA radiation exposure. According to the literature, UV blocking (Faure *et al.*, 2013) and UV shielding (Parwaiz *et al.*, 2019) are scientific terms commonly used to express the solar UV protection performance of photoprotective materials. However, UV blocking term is more used than UV shielding to designate the photoprotective capacity of textiles (Mondal, 2022).

The main constituents of photoprotective products are organic and inorganic filters, which are chemical compounds that absorb and/or scatter UV radiation without changes in their physicochemical properties (Saito *et al.*, 2021). Organic filters are organic molecules composed by chromophore groups that commonly exhibit high degree of the π -conjugated system (Saito *et al.*, 2021). The UV absorption capacity of organic filters depends on both the energy differences from electronic transitions between frontier orbitals and molar absorption coefficient (ϵ). In general, $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ transitions give rise the UV absorption mechanism of organic filters (Baker *et al.*, 2017; Flor *et al.*, 2007). Some examples of organic filters are beta-diketones and organic compounds derived from: benzophenone, anthranilate, salicylic acid, cinnamic acid, p-aminobenzoic acid and camphor (Antoniou *et al.*,

2008). Organic filters are widely used in sunscreen applications due to their UVB and/or UVA absorption capacity (Kockler *et al.*, 2012). Furthermore, these organic compounds show solubility in different dispersion mediums, which facilitates the use of them in the manufacturing process of photoprotective products (Forestier, 2008; Morabito *et al.*, 2011).

Organic filter decomposition under high temperature and/or oxidizing environment exposure results in changes and/or loss of the UV shielding ability and induces the free radical's production that could cause DNA, elastin and/or collagen damages (S. Jain and N. Jain, 2010).

Inorganic filters are inorganic compounds that exhibit UV-visible (UV-VIS) absorption capacity and, depending on the refractive index and/or particle size of them, can scatter UV radiation (Abuçafy *et al.*, 2016; Seixas and Serra, 2014). In general, UV-VIS absorption process in metal oxides (e.g., ZnO and TiO₂) involves electronic transitions between valence band and conduction band (VB $\rightarrow$ CB). The main advantages of inorganic filters are thermal stability, broad spectrum absorption (Seixas and Serra, 2014) and low toxicity to the human body (S. Wang *et al.*, 2010). For these reasons, inorganic filters are widely incorporated in cosmetic formulations and/or UV-blocking products intended for children and people with skin diseases or sensitive skin (Serpone *et al.*, 2007). However, these inorganic compounds can promote photocatalytic reactions (L. Wang *et al.*, 2018) that decompose cosmetic ingredients affecting on the UV shielding ability of photoprotective products.

The growing concern about deleterious effects of the UV radiation exposure combined with the negative aspects related to the use of commercial inorganic and organic filters has significantly promoted the development of photostable compounds with high UV protection and low toxicity to the human organism and the environment, i.e., UV-protective compounds (Saito *et al.*, 2018). In this perspective, UV-protective compounds have been obtained by the coordination of organic filters with transition metals (Ahmedova *et al.*, 2002; Pettinari *et al.*, 2016), association between inorganic and organic filters (Parisi *et al.*, 2016), encapsulation of organic (Morabito *et al.*, 2011) or inorganic filters (Frizzo *et al.*, 2019), and intercalation of organic filters into inorganic layered matrices (Franco *et al.*, 2020; Saito *et al.*, 2021).

One of the most important manufacturing steps of photoprotective products is the dispersion or incorporation of organic and/or inorganic filters in sunscreens, polymer matrices or textile fibers. Sunscreens are emulsions and/or particle dispersions,

whose main purpose is to protect the human skin from UV damages (Saito *et al.*, 2019). However, these cosmetic formulations can cause skin allergies depending on the ingredients present in their composition (Giokas *et al.*, 2007). Thus, the sun-protective clothing is a viable alternative for UV protection due to the lower occurrence of allergic reactions by skin contact and its simple, easy, and practical use. It is important to emphasize that the global smart fabrics market, which includes the promoting and selling of self-cleaning, flame retardant, antibacterial and UV-blocking fabrics, was estimated at US\$ 289.5 million in 2012. Before the COVID-19 pandemic, smart fabrics market projections for 2020 was quoted at US\$ 361.9 million, keeping similar growth rates and correcting inflation (SEBRAE, 2014).

2. Textile properties and UV protection relationships of the sun-protective clothing

The UV shielding ability of the sun-protective clothing is directly related to the physical and chemical properties of the fabric used in its manufacture. Therefore, the chemical composition, weave pattern and optical properties are the main factors that should be considered when making sun UV-blocking fabrics (Alebeid and Zhao, 2017).

In the last decades, several kinds of textile fibers or fiber blends have been used to fabric manufacturing (Jabbar and Shaker, 2016). Polyethylene terephthalate (PET), commonly named polyester, and cotton fibers are the most employed to produce sun-protective fabrics. Generally, PET (Fig. 1) is obtained by the condensation polymerization process of terephthalic acid and ethylene glycol under specific synthetic conditions (Jaffe *et al.*, 2020). In the first step of the PET polymerization, the bis(hydroxyethyl)terephthalate (BHET) monomer is produced by esterification of terephthalic acid. It is important to highlight that the esterification reaction produces a mixture of PET oligomers and BHET; consequently, water and impurity removal is essential to the ultimate achievement of the PET polymer. The next step of the PET polymerization consists in the ester interchange reaction between two BHET molecules to split off a glycol molecule, building polymer molecular weight. This condensation reaction must be catalyzed, being the antimony trioxide (Sb_2O_3) the catalyzer most used. Moreover, the melt-polymerization temperatures at or above 285°C are used to promote the uniform stirring of the reactional medium. In the last step, PET polymer is pelletized for melt spinning or putted on a spinning

machine and transformed to fiber (Jaffe *et al.*, 2020). The main reasons for the using of PET fibers in sun-protective clothing are the low cost, ease of blending with natural fibers and UVB absorption capacity (Curtzwiler *et al.*, 2017). Its UVB absorption ability is directly related to the presence of aromatic rings and carboxyl groups, i.e., chromophores groups in the polymeric structure.

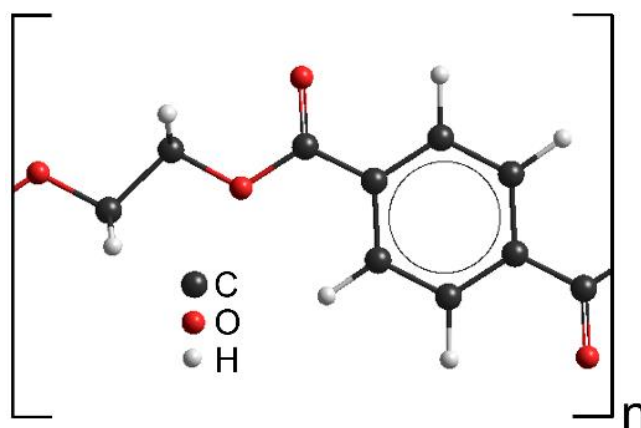


Figure 1. Polyethylene terephthalate (PET) monomer structure.

Cotton is a natural fiber formed by dried cell walls of formerly living cells of *Gossypium* genus plants (Ioelovich and Leykin, 2008; Liu, 2018). The cotton fiber formation starts in an ovary of the cotton flower and proceeds in a mature seed-containing cotton bowl (or fruit). Thus, fiber development includes initiation, primary cell wall formation for fiber elongation, secondary cell wall biosynthesis for cellulose deposition and cell wall thickening, and maturation. Cotton fibers are composed by cellulose (88.0–96.5%), proteins (1.0–1.9%), waxes (0.4–1.2%), pectins (0.4–1.2%), inorganic compounds (0.7–1.6%), and other substances (0.5–8.0%). It is important to emphasize that the chemical composition of cotton fibers depends on the cotton cultivar, growing environment and degree of fiber maturity (Liu, 2018). Cellulose, major chemical component of cotton fibers, consists in linear β -1,4-linked chains of D-glucopyranose (Fig. 2) produced by photosynthesis process (Yue *et al.*, 2012). In the cloth manufacturing, cotton fibers are widely used due to their low cost, softness, high air permeability, moisture-absorptive features, high thermal resistance, and hypoallergenic properties (H. Wang and Memon, 2020).

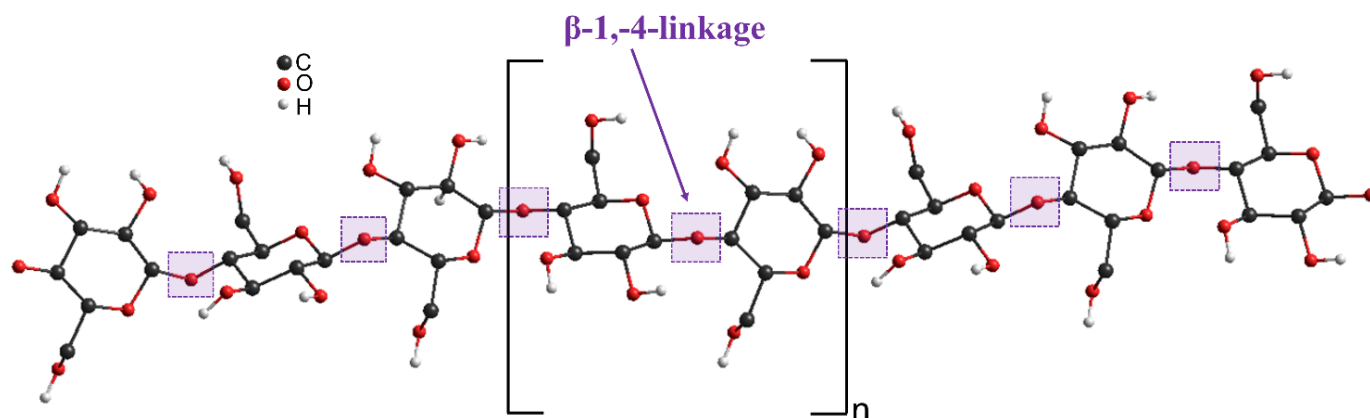


Figure 2. Schematic representation of the simplified cellulose structure.

Different weft types can be used in weaving stage of the sun-protective fabrics. The weft is the arrangement of intertwined threads that gives rise to fabric. This thread arrangement is classified into plain weave fabric and mesh (Pezzolo, 2007). In the plain weave fabric, the thread interweaving turns it more difficult to deform in shear. (Mohammed *et al.*, 2000; Pezzolo, 2007). While the mesh allows the stretching of the fabric because there are no fixed thread loops in its weft (Pezzolo, 2007).

Plain fabric's frames are commonly classified in taffeta, twill or satin. The taffeta has a weft design that

looks like a chessboard (Fig. 3a), which provides a higher mechanical resistant due to its homogeneous shape. Twill has a diagonal pattern (Fig. 3b), offering less dirt adhesion and easier cleaning, because its weft pattern provides more empty spaces among the plain weave fabric. Satin weft presents larger heels between the threads than other plain weave designs (Fig. 3c), consequently, this weft design influence on the fabric brightness (Pezzolo, 2007).

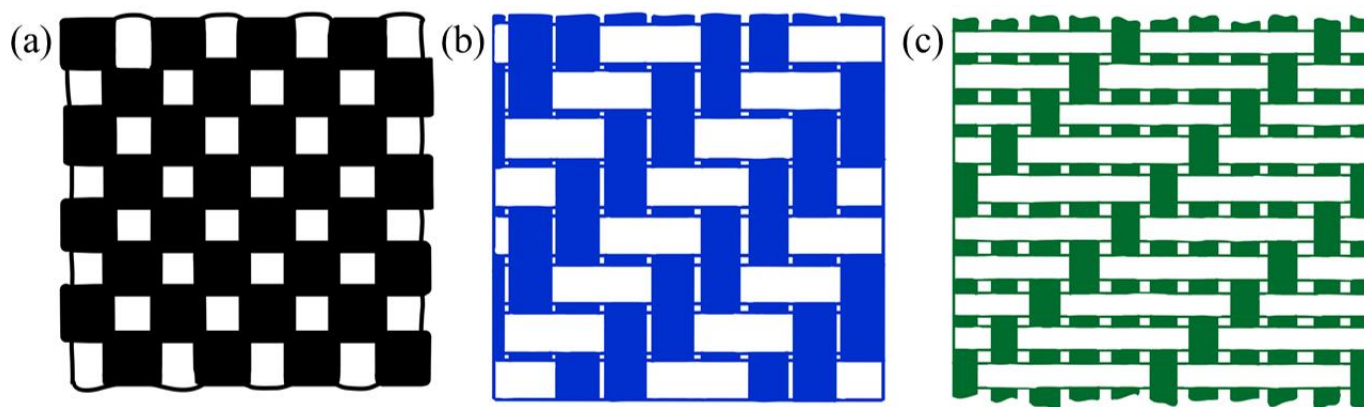


Figure 3. Schematic representations of plain fabric's frames: (a) taffeta, (b) twill and (c) satin.

After the weaving process, fabrics are submitted to the finishing stages (1st, 2nd, and 3rd stage) of the textile processing. The 1st finishing stage is mainly composed by the brushing, shaving, singeing and scouring processes. In the 2nd finishing stage, also known as dyeing and printing, pigments and/or dyes are adsorbed and/or anchored in the surface of textile fibers. Finally, the 3rd finishing stage consists in chemical processes used to generate specific physical-chemical properties in fabrics, e.g., waterproofing ability (Pezzolo, 2007). Among these chemical processes, the incorporation of

nanoparticles in textile fibers has been widely used (Chau *et al.*, 2007; Costa, 2012; Ferreira *et al.*, 2014; Sánchez, 2006) in order to create smart fabrics, i.e., fabric with self-cleaning, antibacterial or even flame-retardant properties. It is important to point that the 2nd stage can provide textile benefits similar to 3rd stage depending on the physical and chemical properties of pigments and/or dyes used. Thus, 2nd and 3rd stage can be understood as the same finishing stage of the textile processing.

UV protection on fabrics depends on the fiber type, weft design, fabric thickness, yarn linear density, and the optical properties of pigments or dyes. For example, the solar transmittance decreases, and the diffuse reflectance increases when yarn linear density, i.e., the number of weft yarns per unit length increases (Yildirim *et al.*, 2018). Besides textile properties, UV shielding capacity can be enhanced by incorporation, coating, or anchorage of UV-protective compounds in the textile fiber surface (Table 1a–d). Thus, the purpose of this review is to report

scientific results about UV-protective compound-containing smart fabrics in the period from 2010 to 2021.

It is known that the incorporation, coating and/or anchorage of UV-protective compounds in smart fabrics protects human skin against excessive UV radiation exposure and reduces the photodecomposition percentage of textile fibers. Nevertheless, this brief review focused in showing the main scientific results and potential applications of UV-blocking fabrics used to minimize the human health hazards.

Table 1a. Examples of UV-protective compound-containing textile fibers described in scientific literature between 2010 and 2012.

Textile fiber composition	UV-protective compound	Assessment method of the UV shielding performance	Additional fabric properties	Reference
PET and PET/wool (70:30) blend, PET/cotton (70:30) blend and PET/viscose (70:30) blend	Monochlorotriazinyl β -cyclodextrin, chitosan, ethylenediamine or Dyes (<i>Disperse Red FB 60</i> , <i>Disperse Blue 2BL 56</i> or <i>Disperse Orange 25</i>)	UPF	-	Ibrahim <i>et al.</i> (2010a)
Cotton	Europium(III) complex	UPF	-	Z. Chen and Yin (2010)
Linen	Metal salts ($M(CH_3COO)_2$, where $M = Cu^{2+}$, Zn^{2+} and Ca^{2+}), $ZrOCl$, Ag, ZrO , TiO_2 or Dyes (<i>C.I Basic Red 24</i> or <i>C.I Reactive Violet 5</i>)	UPF	Antibacterial	Ibrahim <i>et al.</i> (2010b)
Polyethersulfone	TiO_2	UPF	Antibacterial and self-cleaning	Mihailović <i>et al.</i> (2010)
PET	Ag/ TiO_2 nanocomposite	Diffuse reflectance spectra	Antibacterial, self-cleaning, and anti-staining	Dastjerdia <i>et al.</i> (2010)
Wool	TiO_2	Diffuse reflectance spectra	-	Montazer and Pakdel (2010)
PET/wool (45:55) blend	TiO_2	Diffuse reflectance spectra	Antibacterial and self-cleaning	Montazer and Seifollahzadeh (2011)
Cotton	ZnO	Diffuse reflectance spectra	-	Y. Li <i>et al.</i> (2011)
Cotton or viscose	Monochlorotriazine- β -cyclodextrin, Neem seed oil and Dyes (<i>Reactive Red 120</i> , <i>Reactive Red 141</i> , <i>Reactive Blue 160</i> , <i>Reactive Red 195</i> or <i>Reactive Red 198</i>)	UPF	Antibacterial	Ibrahim <i>et al.</i> (2011)
Nylon	TiO_2	Diffuse reflectance spectra	Antibacterial	Pant <i>et al.</i> (2011)
Polyethersulfone	TiO_2	UPF	Antibacterial and self-cleaning	Mihailović <i>et al.</i> (2011)
PET	SiO_2 -coated ZnO	Transmittance spectra	Waterproofing	Xue <i>et al.</i> (2011)
Cotton	Al	UPF	Waterproofing	Pan <i>et al.</i> (2012)
Cotton	ZnO	Transmittance spectra	Waterproofing and self-cleaning	Ates and Unalan (2012)
Cotton	SiO_2 -coated TiO_2 and Dye (<i>Bezaktiv Red S-3B 150</i>)	UPF	-	Fakin <i>et al.</i> (2012)
Cotton	ZnO	UPF	Antibacterial and self-cleaning	Çakir <i>et al.</i> (2012)
Cotton	Ag	UPF	Antibacterial and waterproofing	Shateri-Khalilabad and Yazdanshenas (2013a)
Cotton	ZnO	Transmittance spectra	-	Y. Li <i>et al.</i> (2012)

PET: Polyethylene terephthalate.

Table 1b. Examples of UV-protective compound-containing textile fibers described in scientific literature between 2013-2016.

Textile fiber composition	UV-protective compound	Assessment method of the UV shielding performance	Additional fabric properties	Reference
Cotton	Mg ₂ Al-LDH intercalated with 2-hydroxy-4-methoxybenzophenone-5-sulfonate anions	UPF	Waterproofing	Zhao <i>et al.</i> (2013)
PET	SiO ₂ -coated ZnO	Transmittance spectra	Waterproofing	Xue <i>et al.</i> (2013)
Cotton	ZnO	UPF	Bacterial inhibition	Shateri-Khalilabad and Yazdanshenas (2013b)
Cotton	ZnO	UPF	Antibacterial	Zhang <i>et al.</i> (2013)
PET	TiO ₂	Transmittance spectra	-	Nazari <i>et al.</i> (2013)
Cotton	TiO ₂	Diffuse reflectance spectra	Self-cleaning	Sadr and Montazer (2014)
Cotton	TiO ₂ , ZnO or CuO	UPF	-	Emam and Bechtold (2015)
Cotton	Graphene/polyurethane composite	UPF	Electrical conductivity and far-infrared emission	Hu <i>et al.</i> (2015)
Cotton	Ag	UPF	Antibacterial and waterproofing	Nateghi and Shateri-Khalilabad (2015)
PET	TiO ₂ /carbon nanotubes or TiO ₂ /nanocarbon black nanocomposites	Diffuse reflectance spectra	Electrical conductivity	Chimeh and Montazer (2016)
Cotton	Graphene oxide/Fe ₃ O ₄ nanocomposite	UPF	Antibacterial, electrical conductivity and magnetic properties	Mirjalili (2016)
Cotton	Graphene oxide/Chitosan composite	UPF	-	Tian <i>et al.</i> (2016)
Cotton	Ag/AgBr-TiO ₂ nanocomposite	UPF	Antibacterial	Rana <i>et al.</i> (2016)
PET	Graphene oxide/SnO ₂ nanocomposite	UPF	Electrical conductivity	Babaahmadi and Montazer (2016)
Cotton	ZnO/Chitosan nanocomposite	UVA and UVB blocking percentages	Antibacterial	Raza <i>et al.</i> (2016)

PET: Polyethylene terephthalate.

Table 1c. Examples of UV-protective compound-containing textile fibers described in scientific literature between 2017 and 2018.

Textile fiber composition	UV-protective compound	Assessment method of the UV shielding performance	Additional fabric properties	Reference
Cotton	ZnO	UPF	Self-cleaning	Thi and Lee (2017)
Cotton or Silk	MIL-MOFs* (MIL-68(In)-NH ₂ or MIL-125(Ti)-NH ₂)	UPF	-	Emam and Abdelhameed (2017)
Polyamine 6	TiO ₂	UPF	Antibacterial, self-cleaning, and waterproofing	Zhou <i>et al.</i> (2017)
Cotton	TiO ₂ and Ag	UPF	Antibacterial	S. Li <i>et al.</i> (2017)
Cotton	<i>Aloe vera</i> #/Chitosan nanocomposite	UPF	Antibacterial and waterproofing	Subramani <i>et al.</i> (2017)
Cotton	Au	UPF	Antibacterial	Tang <i>et al.</i> (2017)
PET	CuO	UV protection enhancement	Antibacterial and self-cleaning	Rezaie <i>et al.</i> (2017a)
Wool	CuO	UV protection enhancement	Antibacterial	Rezaie <i>et al.</i> (2017b)
PET	CuO	UV protection enhancement	Antibacterial and ammonia sensing	Rezaie <i>et al.</i> (2017c)
Cotton/nylon (50:50) blend	Graphene oxide	Diffuse reflectance spectra	Antibacterial, antifungal, and electrical conductivity	Hasani and Montazer (2017a)
Cotton/nylon (50:50) blend	Graphene oxide	Diffuse reflectance spectra	Antibacterial and electrical conductivity	Hasani and Montazer (2017b)
Cotton	TiO ₂ /SiO ₂ nanocomposite	UPF	Waterproofing	Xu <i>et al.</i> (2018)
Cotton	ZnO	UPF	Gas sensor	Subbiah <i>et al.</i> (2018)
Cotton	ZnO	UPF	Antibacterial	El-Naggar <i>et al.</i> (2018)
Cotton	Polyvinylsilsesquioxane/ZnO composite	UPF	Antibacterial and waterproofing	Mai <i>et al.</i> (2018)
PET	SiO ₂ , ZnO, TiO ₂ or ZrO	UPF	Antibacterial and self-cleaning	Ibrahim <i>et al.</i> (2018)
Cotton	Polyoxotitanate (Ti ₁₈ Mn ₄ O ₃₀ (OEt) ₂₀ Phen ₃)	Diffuse reflectance spectra	Antibacterial and waterproofing	N. Li <i>et al.</i> (2018)
Cotton	TiO ₂	UPF	Waterproofing	D. Chen <i>et al.</i> (2018)
Wool	<i>Cinnamomum camphora</i> extracts	UPF	Antibacterial	Khan <i>et al.</i> (2018)
Cotton	TiO ₂	UPF	-	Morshed <i>et al.</i> (2018)
PET	3,4-ethylene dioxythiophene polymer (PEDOT)/Fe ₃ O ₄ composite	Transmittance spectra	Antibacterial, electrical conductivity, microwave attenuation, and magnetic properties	Sedighi <i>et al.</i> (2018)
Wool	Marigold (<i>Tagetes erecta</i>) flower extract	UPF	Antioxidant	Shabbir <i>et al.</i> (2018)

PET: Polyethylene terephthalate. * MIL: Materials Institute Lavoisier. MOF: metal-organic framework. # Natural herbal nanoparticles prepared from shade-dried *Aloe vera* plant.

Table 1d. Examples of UV-protective compound-containing textile fibers described in scientific literature between 2019 and 2021.

Textile fiber composition	UV-protective compound	Assessment method of the UV shielding performance	Additional fabric properties	Reference
Cotton	BiPO ₄	UPF	Self-cleaning	Jin <i>et al.</i> (2019)
Silk	ZnO	UPF	Waterproofing	Huang <i>et al.</i> (2019)
Cotton	ZnO	UPF	-	X. Wang <i>et al.</i> (2019)
Cotton, Aramid or PET	MOF (<i>InOF-1</i>)	UPF	-	G.-P. Li <i>et al.</i> (2020)
Cotton	MOFs (<i>Cu-BTC</i> , <i>ZIF-8</i> or <i>ZIF-67</i>)	UPF	Noise reduction	Zhang <i>et al.</i> (2020)
PET	MO _x /polyvinylidene fluoride/Chitosan composite (MO _x = ZnO, TiO ₂ or SiO ₂)	UPF	-	Bouazizi <i>et al.</i> (2020)
Cotton	MOFs (<i>ZIF(Ni)</i> , <i>ZIF-8(Zn)</i> or <i>ZIF-67(Co)</i>)	UPF	Antibacterial	Emam <i>et al.</i> (2020)
Cotton	ZnO	UPF	Waterproofing	Khan <i>et al.</i> (2020)
Silk	Graphene oxide	UPF	Antibacterial	S.-D. Wang <i>et al.</i> (2020)
Cotton	ZnO	UPF	Antibacterial	Noorian <i>et al.</i> (2020)
Cotton	TiO ₂ and hollow glass microspheres	UPF	Thermal insulation, flame retardancy and noise reduction	Pakdel <i>et al.</i> (2020)
Cotton	TiO ₂	Transmittance spectra	Waterproofing and self-cleaning	Suryaprabha and Sethuraman, (2021)
Wool	TiO ₂ /Ce or ZnO/Ce nanocomposite	Transmittance spectra	Antibacterial and self-cleaning	Zohoori <i>et al.</i> (2021)
Cotton	TiO ₂	UPF	-	Riaz <i>et al.</i> (2021)
Wool	Se	UV protection enhancement	Antibacterial and antifungal	Razmkhah <i>et al.</i> (2021)
Cotton	Ag	UPF	Antibacterial	Čuk <i>et al.</i> (2021)

PET: Polyethylene terephthalate. MOF: metal-organic framework.

3. UV-protective compound-containing smart fabrics

The growing request for UV-protective textiles, especially for clothes manufacturing, has driven scientific studies about textile fibers with UV shielding properties. Therefore, incorporation, coating and/or anchorage of metal oxides, dyes, organic filters, graphene compounds, metal-organic frameworks (MOFs), coordination compounds, metal nanoparticles or composites in the fiber surface are widely related in the recent literature (Table 1a–d). Several different synthetic methods have been used to produce these textile fibers, including pad-dry-cure (Z. Chen and Yin, 2010), electrospinning (Pant *et al.* 2011), hydrothermal (Y. Li *et al.*, 2011), microwave (Y. Li *et al.*, 2012; Thi and Lee, 2017), microwave assisted hydrothermal (Ates and Unalan, 2012), simple spray coating (Rana *et al.*, 2016), electrostatic layer-by-layer self-assembly approach (Zhao *et al.*, 2013), solid-phase hot-pressing procedure (G.-P. Li *et al.*, 2020) and dip-pad-cure (Ibrahim *et al.*, 2010b). Among them, the pad-dry-cure method is the most used due to the easier synthetic procedures and high-efficiency fiber coating. In the pad-dry-cure process, fabrics are soaked in UV-protective compound solution or suspension under specific conditions, e.g., liquor to fabric ratio. Then, fabric specimens are padded through two dips and two nips using a padding machine. After padding step, fabrics are dried and cured at specific temperatures and times, which are based on fabric properties. Regardless of experimental method and/or fiber type used, UV-protective compounds incorporated, coated and/or anchored improve UV-blocking properties of textile fabrics (Fig. 4) as proven by UV-VIS spectroscopic measurements, e.g., *in vitro* UV protection factor (UPF) assessment. Moreover, these UV-protective compounds can promote other beneficial functions to textile fibers such as antibacterial and self-cleaning properties (Table 1a–d). In so many cases, a superhydrophobic coating in the textile fibers is also made to provides waterproofing (Table 1a–d). It is important to highlight that multifunctional textile fibers give rise smart fabrics, which offer new insights to clothing manufacturing.

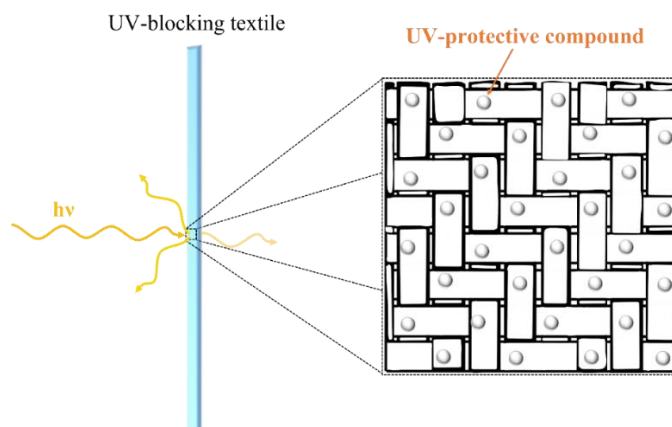


Figure 4. Schematic representation of a UV-protective compound-containing smart fabric.

3.1 TiO_2

Titanium oxide is a commercial inorganic filter commonly used in skin care products due to its UV absorption capacity (Abuçafy *et al.*, 2016; Seixas and Serra, 2014) and low skin toxicity (Abuçafy *et al.*, 2016). Besides UV shielding ability, TiO_2 exhibits photocatalytic activity that enable its use in self-cleaning systems (Banerjee *et al.*, 2015). According to the literature (Yadav *et al.*, 2016), this metal oxide also has antibacterial properties. For these reasons, TiO_2 -containing textile fibers have attracted considerable interest in the field of smart fabrics.

Mihailović *et al.* (2010; 2011), in two different scientific research publications, investigated the multifunctional properties of polyethersulfone (PES) fabrics loaded with TiO_2 prepared by oxygen, argon or air RF plasma or corona discharge pretreatment and subsequent dip-pad-cure process with titanium oxide. On both studies, oxygen, argon or air RF plasma and corona discharge pretreatments of PES fibers induced the enhanced deposition of TiO_2 nanoparticles ensuring excellent self-cleaning properties, UV protection and antibacterial activity. Considering UV blocking efficiency of PES fabrics obtained, high UPF values ($\text{UPF} > 66$) were reached and retained after five laundering cycles. The washing procedure used in the laundering durability test can be summarized as follows: the PES fabrics were washed in the bath containing 0.5% Felosan RG-N (Bezema) at liquor-to-fabric ratio of 40:1. After 30 min of washing at 40 °C, fabrics were rinsed once with warm water (40 °C) for 3 min and three times (3 min) with cold water. Subsequently, fabrics were dried at 70 °C.

Montazer and Pakdel (2010) reported the UV-blocking ability of TiO_2 -containing wool textiles obtained by ultrasonic bath method. The TiO_2 -protective

layer on fabric surface provided higher UV absorption in the 300-350 nm region. Moreover, the increase of the amount of TiO₂ on wool surface enhanced the UVB blocking capacity and decreased the UV photodegradation of wool fibers, i.e., photoyellowing of wool textile. In other scientific publication, [Montazer and Seifollahzadeh \(2011\)](#) prepared multifunctional textiles through enzymatic pretreatment of polyester/wool blend followed by the fiber coating with TiO₂ nanoparticles. These textile materials also exhibited higher UVB blocking ability and showed self-cleaning and antibacterial properties.

[Pant et al. \(2011\)](#) successfully prepared an electrospun nylon-6 spider-net like nanofiber mats containing TiO₂ nanoparticles. The addition of a small amount of TiO₂ NPs improved the hydrophilicity and mechanical strength of nylon-6 nanofiber mats and gave rise to antibacterial and UV blocking properties.

[Nazari et al. \(2013\)](#) developed UV-blocking polyester fabrics using TiO₂ as inorganic filter and polysiloxane as cross-linkable agent. The polysiloxane agent promoted the enhance of TiO₂ nanoparticles absorption and stabilized them on the polyester fiber surface. Consequently, the nano-TiO₂/polysiloxane coating improved the UV-blocking features of polyester fabrics as seen in UV-VIS transmission spectra.

[Zhou et al. \(2017\)](#) reported a facile and eco-friendly way to prepare a novel hybrid polyamine/nano TiO₂ fabric by a combination of UV irradiation and ultrasonic bath method. The research results indicated that TiO₂ were fixed on the fiber surface providing photocatalytic, antibacterial, UV blocking and superhydrophobic properties to polyamine fabrics. UPF values equal to 56 and 1123 were obtained.

[Sadr and Montazer \(2014\)](#), [Emam and Bechtold \(2015\)](#), [D. Chen et al. \(2018\)](#), [Morshed et al. \(2018\)](#), [Suryaprabha and Sethuraman \(2021\)](#) and [Riaz et al. \(2021\)](#) investigated the UV blocking properties of TiO₂-containing cotton fabrics. [Sadr and Montazer \(2014\)](#) reported the multifunctional features of TiO₂ nanoparticles coated cotton fabrics obtained by *in situ* sonosynthesis method. The sonochemical method had no negative influence on cotton fabric fibers and provided the formation of the nano-TiO₂ coating on the textile surface that led to UV-blocking and self-cleaning properties. Moreover, UV-protection rating of these cotton fabrics maintained even after 25 home launderings indicating an excellent washing durability. [Emam and Bechtold \(2015\)](#) immobilized TiO₂, ZnO or CuO particles into cotton and oxidized cotton fabrics by using pad-dry-cure method. The surface interactions between carboxylate groups of cotton fibers and metal oxides, mainly TiO₂, provided the enhancement of the

UV shielding capacity of cotton fabrics as seen in UV-VIS transmittance spectra and *in vitro* UPF values. [D. Chen et al. \(2018\)](#) developed UV-blocking, superhydrophobic and robust cotton fabrics by combination of polyvinylsilsesquioxane (PVS) and nano-TiO₂. Based on structural, thermal, mechanical, and spectroscopic results, the improvement on the UV protection, water repellency and rigidity of the fabrics were attributed to the synergism between the PVS polymer and nano-TiO₂. [Morshed et al. \(2018\)](#) reported to sonochemical synthesis of TiO₂ nanoparticles in cotton fibers via low temperature sol-gel technique. Ultrasonication time, ultrasonic power, and concentration of tetrabutyl titanate affected on UPF values of cotton fabrics. [Suryaprabha and Sethuraman \(2021\)](#) prepared multifunctional cotton fabrics based on the deposition of TiO₂ sol followed by surface modification using stearic acid (STA). STA-TiO₂ cotton fabrics exhibited UV-blocking ability and self-cleaning properties. Moreover, these superhydrophobic fabrics showed chemical durability and mechanical stability. Finally, [Riaz et al. \(2021\)](#) reported to the fabrication of cotton fabrics with TiO₂ nanoparticles modified with two different silane coupling agents using pad-dry-cure method. The presence of modified nanoparticles in the fiber surface improved the UV-blocking performance causing minimum effect on inherent properties of cotton textiles, e.g., sensorial comfort.

[Fakin et al. \(2012\)](#) investigated the SiO₂ coated TiO₂ particles performance in reactive dyeing of cotton fabrics. The incorporation of synthesized particles into the dyeing with reactive dyes brought about an outstanding UV blocking ability of the dyed fabrics even after 15 laundering cycles without considerable negative impact on color and comfortable properties. Washing process was performed according to the [BS EN ISO 105-C06:2010 \(2010\)](#) standard. UV protection, comfort, and dyeing properties of cotton fabrics were directly associated to dyeing temperature and amount of dye and SiO₂ coated TiO₂ particles.

[S. Li et al. \(2017\)](#) reported to the development of multifunctional cotton fabrics obtained by hydrothermal deposition of TiO₂ particles onto fiber surface followed by *in situ* deposition of Ag nanoparticles via reduction method. These fabrics exhibited high antibacterial activity with an inhibition rate higher than 99% against *Staphylococcus aureus* and *Escherichia coli* bacteria. Moreover, UPF values between 35 and 57 confirmed the UV-blocking capacity of them. Using a different two-step coating approach, [Pakdel et al. \(2020\)](#) prepared cotton fabrics coated with TiO₂ and hollow glass microspheres (HGMs). The presence of TiO₂ layer on cotton fibers gave rise to an excellent UV-blocking

activity as proved by UPF values higher than 190. In addition, HGMs coating reduced the inflammability of cotton fabrics and improved their thermal resistance and sound absorption capacity. Therefore, these TiO_2 + HGMs coated cotton fabrics exhibited multifunctional properties, i.e., UV-blocking ability, thermal insulation, flame retardancy and acoustic performance. It is important to highlighting that noise is considered a health hazard (Münzel *et al.*, 2020) and it is required to be eliminated for a better performance of humans in different areas (Pakdel *et al.*, 2020).

In different scientific publications, Dastjerdia *et al.* (2010), Rana *et al.* (2016), Chimeh and Montazer (2016), Xu *et al.* (2018), Bouazizi *et al.* (2020) and Zohoori *et al.* (2021) reported the development of UV-protective fabrics with different nanocomposites based on TiO_2 . Dastjerdia *et al.* (2010) investigated the multifunctional properties of Ag/TiO_2 nanocomposite coated polyester fabrics prepared by pad-dry-cure method. The results revealed that the nanocomposite coating gives a considerable antibacterial, self-cleaning, anti-staining and UV-blocking capacity to polyester textiles. In this scientific paper, authors focused on showing the main results of characterization techniques without in-depth discussions about physic-chemical phenomena involved. In similar scientific research, Rana *et al.* (2016) reported the preparation of multifunctional cotton fabrics with Ag/AgBr-TiO_2 nanocomposite coating by simple spray coating process. The results showed that the nanocomposite coating onto cotton fabrics improved textile mechanical properties and gave rise to antibacterial and UV-blocking abilities.

Chimeh and Montazer (2016) prepared polyester fabrics with nano- TiO_2 /carbon nanotubes or nano- TiO_2 /nanocarbon black composites through exhaustion method and post-curing. The composite coating increased the UV blocking capacity of PET textiles as seen in UV-VIS reflectance spectra. Furthermore, nano- TiO_2 /carbon composites imparted photocatalytic activity and electrical conductivity to fabrics. Also, Xu *et al.* (2018) successfully prepared superhydrophobic and UV-protective cotton fabrics by the incorporation of $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles followed by hydrophilization with hexadecyltrimethoxysilane. $\text{TiO}_2/\text{SiO}_2$ composite nanostructures onto fibers made the textiles rougher, which contributed to the formation of superhydrophobic surfaces, and decreased the UV transmittance of cotton fabrics promoting UPF values higher than 80.

Bouazizi *et al.* (2020) reported the design and functionalization of new composite-based PET fibers with UV protection. The fixation of MO_x /polyvinylidene fluoride/Chitosan composite ($\text{MO}_x = \text{TiO}_2$, ZnO or SiO_2)

into PET fibers improved both the thermal stability and UV protection of textiles. High UPF values (80.5 – 113.4) of textiles indicated their excellent UV-blocking capacity.

Zohoori *et al.* (2021) prepared wool fabrics coated with TiO_2/Ce or ZnO/Ce nanocomposite coated wool fabrics by ultrasonic method. XRD, EDX and SEM results showed the formation of nanocomposites and indicated a good distribution of them on the wool surface. The wool fabrics coated with TiO_2/Ce or ZnO/Ce nanocomposites showed lower UV transmission percentage than raw wool fabric indicating an improvement on the UV protection. Also, these fabrics exhibited antibacterial and self-cleaning activity.

3.2 ZnO

Zinc oxide is also a commercial inorganic filter widely used in cosmetic formulations and/or self-cleaning systems. Like TiO_2 , zinc oxide has UVB absorption capacity (Flor *et al.*, 2007; Seixas and Serra, 2014), low skin toxicity (Abuçafy *et al.*, 2016), photocatalytic and antibacterial ability (Qi *et al.*, 2017). Consequently, fabric fibers with zinc oxide or nanocomposite based on ZnO have been investigated to provide new insights in UV-protective textile manufacturing.

Y. Li *et al.* (2011) reported the preparation of cotton fabric with ZnO , in which ZnO particles were *in situ* synthesized inside of textile fibers, via two-step hydrothermal method. The results showed that zinc oxide particles were successfully assembled into the lumen and the mesoporous cotton fibers. Therefore, UV-blocking ability of the cotton fabric was significantly improved by assembling ZnO inside the fibers.

Ates and Unalan (2012) investigated to self-cleaning, superhydrophobic and UV-blocking properties of zinc oxide nanowire-containing cotton fabric prepared by microwave assisted hydrothermal method and subsequently functionalized with stearic acid. The results showed the superhydrophobic nature of textile fibers, the decrease of the transmission intensity in UV spectral region and considerable degradation of methylene blue under UV light irradiation, one of the main photodegradation methods to investigate self-cleaning properties.

Çakir *et al.* (2012) successfully prepared ZnO coated cotton fabrics that exhibit UV-blocking, self-cleaning and antibacterial properties. It is important to emphasize that ZnO nanoparticles were synthesized in reverse micelle cores of $\text{PS}(10912)\text{-b-PAA}(3638)$ copolymer obtained by atom transfer radical polymerization. The ZnO nanoparticles coating onto textile fibers provided

photocatalytic activity on degradation of methylene blue and antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* bacteria. Moreover, ZnO coated cotton fabrics exhibited UPF values greater than 60.

Y. Li *et al.* (2012) investigated UV blocking property and water-wash durability of nano-ZnO assembled cotton fibers obtained by microwave assisted precipitation and crystallization process synchronously *in situ* for the first time. UV-VIS transmission spectra showed an excellent UV-blocking activity in the 225–380 nm region. The water-washing process of nano-ZnO assembled cotton fibers did not change their UV absorption capacity as seen in UV transmission measurements. The water-washing durability test was carried out in a domestic washer (XQB45-846B National, Panasonic), where nano-ZnO assembled cotton textiles were washed with water ($v = 33$ L) for 20, 40 and, 60 min.

Shateri-Khalilabad and Yazdanshenas (2013b) and Zhang *et al.* (2013) successfully prepared smart fabrics via *in situ* synthesis of ZnO on the cotton fiber surface. In both publications, ZnO coated cotton fabric exhibited high UV-blocking ability as proven in UPF values (105.61 [Shateri-Khalilabad and Yazdanshenas, 2013b] and 136 [Zhang *et al.*, 2013]). Moreover, it showed bacterial inhibition (Shateri-Khalilabad and Yazdanshenas, 2013b) or antibacterial (Zhang *et al.*, 2013) activity.

The pad-dry-cure method was used by Raza *et al.* (2016) and El-Naggar *et al.* (2018) in the preparation of cotton fabrics coated with chitosan/ZnO nanocomposites and ZnO nanoparticles, respectively. Nanocomposite (Raza *et al.* 2016) and ZnO (El-Naggar *et al.*, 2018) coated cotton fabrics exhibited antibacterial activity and UV-blocking capacity.

Thi and Lee (2017) reported the development of self-cleaning and UV-blocking cotton fabric with modification of photoactive ZnO coating via microwave method. ZnO coated cotton fabrics synthesized at pH range equal 6–7, 8–9 and 10–11 showed UPF values of 222.52, 162.68 and 202.57, respectively. In addition, these cotton fabrics exhibited excellent self-cleaning ability proved by high removal degree of the coffee stains under UV irradiation at different air humidity levels.

Subbiah *et al.* (2018) successfully prepared nanostructured ZnO modified cotton fabrics via sol-gel and sputter seed layer-coated sol-gel techniques. All modified cotton fabrics exhibited greater UPF values than raw fabric, but the seed layer-initiated sol-gel modified cotton fabric showed the highest UPF value (378). Moreover, these modified cotton fabrics showed

room temperature gas sensing response towards volatile organic compounds enabling their use as gas sensor.

Mai *et al.* (2018) reported the development of multifunctional polyvinylsilsesquioxane/ZnO coated cotton fabrics. Composite coatings improved UV-blocking, superhydrophobic and antimicrobial properties of cotton fabrics compared to the reference textiles. In addition, polyvinylsilsesquioxane/ZnO coatings enhanced the mechanical properties of cotton fabrics and did not compromise their thermal stability.

X. Wang *et al.* (2019) successfully prepared UV-protective fabrics via grafted polymer brushes for *in situ* growth of ZnO on modified cotton fiber using the electroless deposition method. According to the results, the functionalized fabrics exhibited UV blocking properties and wash durability due to the presence of the ZnO on the inner wall of cotton fibers and the polymer-tethered structure.

Khan *et al.* (2020) reported a novel microwave hydrothermal method to grow aligned ZnO nanorods on cotton fibers. The ZnO coated cotton fabrics obtained showed greater UPF values than pristine cotton fabric, which indicated that ZnO nanorods improved the UV protection of cotton textile. Moreover, the functionalization of ZnO coated cotton fabrics with non-fluorinated silane provided superhydrophobic properties and oil–water separation performance.

Noorian *et al.* (2020) prepared antibacterial and UV-blocking fabrics by pretreatment of cotton fibers with 4-aminobenzoic acid (PABA) followed by *in situ* sonochemical synthesis of ZnO nanoparticles. The PABA treatment provided significant sites for the growth of the ZnO nanoparticles and maintained cross-linking property between oxidized cellulosic fibers and the ZnO nanoparticles. Synergistic effects from ZnO and PABA association imparted UPF values higher than 65 and antibacterial activity against *E. coli* and *S. aureus* to the cotton fabrics.

Xue *et al.* (2011; 2013), in two different scientific research publications, investigated the superhydrophobic and UV-blocking properties of PET fabrics coated with ZnO/SiO₂ core/shell particles and hexadecyltrimethoxysilane. The coated PET textiles exhibited superhydrophobic surface and UV-blocking ability as seen in water contact angle and UV-VIS spectroscopy results. In addition, the SiO₂ shell inhibited the photocatalytic activity of ZnO ensuring the superhydrophobicity of PET surfaces when exposure to UV radiation. Huang *et al.* (2019) also investigated the superhydrophobic and UV-blocking properties of silk fabrics prepared by combining a one-step *in situ* synthesis of ZnO nanorods on fiber surface and hydrophobic treatment with n-octadecanethiol. The

presence of ZnO nanorods in the silk fibers increased surface roughness and induced a rise in UPF values of fabrics indicating the improvement of UV-blocking ability. Also, obtained superhydrophobic surface showed mechanical and chemical stability.

3.3 Graphene compounds

Singular properties of graphene compounds described in the recent literature (Tiwari *et al.*, 2018) explain their several multifunctional applications in different systems and/or devices. In the smart fabric field, UV-blocking, electrical conductivity and/or antibacterial activity are mainly graphene compound properties investigated in the last scientific publications (Babaahmadi and Montazer, 2016; Hasani and Montazer, 2017a; b; Hu *et al.*, 2015; Mirjalili, 2016; Tian *et al.*, 2016; S.-D. Wang *et al.*, 2020). Electrically conducting textiles produce clothes with static dissipation, anti-spark and electromagnetic interference shielding (Varesano and Tonin, 2008) that can be used in the smart clothing design, e.g., innovative sportswear.

Hu *et al.* (2015) prepared multifunctional cotton fabrics coated with graphene and waterborne anionic aliphatic polyurethane composites by pad-dry-cure method. Graphene/polyurethane coatings significantly enhanced the UPF values indicating high UV-blocking capacity of cotton fabrics. In addition, graphene/polyurethane coated cotton fabrics exhibited far-infrared emissivity up to 0.911 in the wavelength range of 4–18 μm and lower electrical resistivity than pristine cotton fabric. Far-infrared emitting fabrics are commonly used in health care and therapeutic clothing manufacturing because the far-infrared radiation (6–15 μm) promotes the enhancement of blood microcirculation and metabolism (Vatansever and Hamblin, 2012).

Mirjalili (2016) investigated the UV-blocking, electrical conductivity, magnetic and antibacterial properties of the reduced graphene oxide/ Fe_3O_4 nanocomposite coated cotton fabric. UV-blocking ability of the nanocomposite coated cotton fabric was proved by the increase of the UPF value compared to raw cotton textile. This fabric also displayed a low electrical resistivity, antibacterial activity, and magnetic properties.

Tian *et al.* (2016) successfully prepared cotton fabrics coated with graphene oxide and chitosan by the electrostatic layer-by-layer self-assembly approach. These fabrics showed higher UPF values than control cotton fabric and washing durability even after 10 times water laundering. It is important to emphasize that the water laundering durability test of cotton fabrics was

performed by following the American Association of Textile Chemists and Colorists AATCC 61 (2006).

Babaahmadi and Montazer (2016) investigated electrical conductivity and UV-blocking properties of reduced graphene oxide/ SnO_2 nanocomposite coated PET textile obtained by modified exhaustion method. Electrical resistivity decreased and UPF value increased with reduced graphene oxide/ SnO_2 nanocomposite coating of PET fibers, which indicated the formation of an electroconductive and UV blocking textile. Moreover, electrical resistivity and UV-blocking results demonstrated the good durability of nanocomposites on surface of PET fabrics after 10 washes with deionized water.

In different scientific papers, Hasani and Montazer (2017a; b) reported the multifunctional properties of reduced graphene oxide-coated cotton/nylon fabrics. According to the UV-VIS reflectance results, textile materials showed high UV absorption in the 200–400 nm region indicating their potential as UV-protective fabrics. These fabrics also exhibited lower electrical resistance, antibacterial activity against *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Enterococcus faecalis* bacteria and antifungal activity against eukaryotic fungus *C. albicans*.

S.-D. Wang *et al.* (2020) successfully prepared a multifunctional silk fabric by grafting graphene oxide (GO) nanosheet dispersion onto the fabric surface. The silk fabrics modified with GO showed higher UPF values than control silk, which indicated the enhancement of UV-blocking properties. Furthermore, modified silk fabrics exhibited excellent antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* bacteria.

3.4 MOFs

Zhang *et al.* (2020) developed a series of multifunctional textiles prepared via *in situ* modified MOFs nanocrystals on the cotton surface. Based on structural and spectroscopic characterizations, it was confirmed the existence of chemical bonds between MOFs and hydroxyl and/or carboxyl groups belonging to cotton fibers. In addition, a uniform distribution of MOFs nanocrystals in textile surface was observed. The MOFs/cotton textiles exhibited greater UV blocking activity and acoustic absorption performance than blank cotton that demonstrated their potential use as fabrics for UV protection and noise reduction. According to the literature (Münzel *et al.*, 2020), excessive exposure to the noise environment induces adverse cardiovascular effects and mental annoyance.

Emam *et al.* (2020) investigated the multifunctional properties of cotton fabrics with zeolitic imidazole

frameworks (ZIFs). ZIF(Ni), ZIF-8(Zn) and ZIF-67(Co) were *in situ* synthesized into cotton fabrics before or after silicate modification on the fiber surface. When silicate functionalization was performed before the ZIFs formation, the silicate acted as cross-linker between ZIFs and cotton fibers providing the increment of MOFs amount in the fabric surface. Modified cotton fabrics showed higher UPF values than pristine cotton textile and washing durability (AATCC M6, 2010). Also, they exhibited antibacterial activity against *Staphylococcus aureus*, *Bacillus cereus*, *Escherichia coli*, and *Candida albicans* bacteria.

Emam and Abdelhameed (2017) reported the incorporation of MIL-68(In)-NH₂ or MIL-125(Ti)-NH₂ (MIL = Matériaux de l'Institut Lavoisier) into cotton or silk textiles using quite simple and one-pot process to produce UV-blocking textiles. All MIL-MOFs incorporated textiles exhibited UV-blocking activity; however, MIL-MOFs and metal contents in natural fibers influenced on the UPF values obtained. After five washing cycles (AATCC M6, 2010), these textiles showed a slight decrease of UPF values, which proved their laundering durability.

G.-P. Li *et al.* (2020) investigated the UV-blocking properties of InOF-1 coated cotton, polyester or aramid textiles prepared by hot-pressing method. Regardless of textile fiber type used, InOF-1 coating provided a significantly increasing in the UV-blocking performance. Moreover, the interactions between InOF-1 and textile fibers, as proven in FTIR results, enhanced the tensile strength and elongation at break of MOF coated textiles.

3.5 Organic compounds

Ibrahim *et al.* (2010a) investigated the transfer printability and UV blocking properties of polyester-based textiles obtained by pretreatment of polyester fibers and polyester/wool, polyester/cotton, and polyester/viscose blend fibers with monochlorotriazinyl β -cyclodextrin (MCT- β -CD), chitosan or ethylenediamine followed by transfer printing with sublimable disperse dyes. Hydrophobic cavities generated via grafting of MCT- β -CD, amine functional groups incorporated via aminolysis of the polyester and/or chitosan fixed onto textile matrix afforded an improvement of UV-blocking capacity, transfer printing and fastness properties of modified post-printed fabric samples. In other scientific publication, Ibrahim *et al.* (2011) reported the development of multifunctional cotton and viscose fabrics printed with reactive dyes through combined reactive printing and MCT- β -CD loading in one-step followed by subsequent treatment

with Neem oil. The post-treatment with Neem oil provided the improvement of the antibacterial activity of the treated reactive prints without adversely affecting the UV-blocking properties of the final products.

Subramani *et al.* (2017) investigated multifunctional properties of the Aloe vera-chitosan nanocomposite coated cotton fabric prepared by pad-dry-cure method. Cotton fabric coated with herbal nanocomposite exhibited excellent UV-blocking ability (UPF > 52), superhydrophobicity, and antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* bacteria.

In different scientific publications, Khan *et al.* (2018) and Shabbir *et al.* (2018) reported the development of UV-blocking fabrics from natural plant extracts. Khan *et al.* (2018) successfully prepared UV-blocking and antibacterial fabric by wool treatment with aqueous and alkali extracts of *Cinnamomum camphora* leaves. Camphor leaves extract imparted dyeing, UV-blocking and antibacterial properties to wool fabric. Shabbir *et al.* (2018) reported UV-protective and antioxidant finishing of wool fabric dyed with marigold (*Tagetes erecta*) flower extract. Carotenoid compounds of marigold extract are main responsible for UV-blocking and antioxidant properties of this organic dye. Marigold dyed wool fabrics showed UPF values higher than 30 and capacity to capture peroxide reactive species; therefore, dyed fabrics can be used as potential UV-blocking and antioxidant textiles.

3.6 Inorganic compounds, metal nanoparticles, LDH material and coordination compounds

Z. Chen and Yin (2010) investigated the UV-blocking capacity of Eu(III) complex-containing cotton fabrics prepared by pad-dry-cure method. Based on spectroscopic results, Eu(III) complex-cotton fabrics showed higher UPF values than blank cotton fabric and red-light emission. These results are similar to the Eu(III) doped LDH intercalated with cinnamate anions reported by Saito *et al.* (2018). The Eu(III) doped LDH material exhibited UV-shielding ability and low-intensity red emission that could be inducing collagen production (Saito *et al.*, 2018). Thus, Eu(III) complex-containing cotton fabrics can be able to induce the collagen biosynthesis depending on its intensity emission.

Ibrahim *et al.* (2010b) prepared functional finishes of linen-containing fabrics by fiber surface modifications using oxygen or nitrogen plasma followed by subsequent dip-pad-cure process with metal salts, nano-scale metal or metal oxides, ionic dyes, quaternary ammonium salt or antibiotics. The linen-based textile results indicated the loading of metal salts, nano-scale metal or metal

oxides or ionic dyes onto the plasma treated substrates provided antibacterial activity and a remarkable improvement in UV blocking capacity. Moreover, these functional properties were retained even after 10 laundering cycles (AATCC 124, 1996). In other scientific publication, Ibrahim *et al.* (2018) reported the multifunctional properties of PET fibers obtained via premodification with sodium hydroxide followed by coating with SiO₂, TiO₂, ZnO or ZrO₂ nanoparticles using gelatin as a green binding agent. The results showed an improvement on antibacterial, UV blocking, self-cleaning and softness properties of PET fabrics, which are maintained after 15 laundering cycles (AATCC 135, 2000).

In a series of scientific papers (Rezaie *et al.*, 2017a; b; c) Rezaie and coworkers reported the multifunctional properties of CuO-containing wool and/or polyester fabrics. Based on the results of the UV protection enhancement (%) method described by Noorian *et al.* (2015) CuO-containing fabrics exhibited higher UV-blocking ability and self-cleaning activity. In addition, these fabrics showed antibacterial activities toward two pathogen bacteria including *Staphylococcus aureus* as Gram-positive and *Escherichia coli* as Gram-negative bacteria with no adverse effects on human dermal fibroblasts based on MMT cytotoxicity test (Montazer *et al.*, 2015). The CuO-containing PET fabrics also exhibited a rapid and effective colorimetric response for ammonia detection indicating their potential as ammonia sensing.

Zhao *et al.* (2013) successfully prepared cotton fabrics coated with amino-functionalized Mg₂Al-HMBS-LDH (HMBS = 2-hydroxy-4-methoxybenzophenone-5-sulfonate anions) by electrostatic layer-by-layer assembly technique. Based on thermal analyses, intercalated HMBS showed higher thermal stability than HMBS pristine due to host-guest interactions in the interlayer region. All cotton fabrics assembled with amino-functionalized Mg₂Al-HMBS-LDH showed water contact angles greater than 150° suggesting superhydrophobic ability. In addition, these superhydrophobic fabrics exhibited the enhancement of UPF values compared to untreated cotton textile demonstrating UV-blocking capacity.

Sedighi *et al.* (2018) investigated the multifunctional properties of 3,4-ethylene dioxythiophene polymer (PEDOT)/magnetite nanoparticles coated PET fabrics. PEDOT/magnetite nanoparticles coating improved the UV-blocking capacity of PET fabric especially in UVB and UVC regions. This nanoparticle coating also provided significant antibacterial activity against *S. aureus* bacteria, electromagnetic interference (EMI) shielding behavior and superparamagnetic properties. In

this paper, EMI shielding corresponds to microwave attenuation ability of these multifunctional PET fabrics.

N. Li *et al.* (2018) reported a novel coating technique involving *in situ* self-assembly of the polyoxotitanate (POT) cage [Ti₁₈Mn₄O₃₀(OEt)₂₀Phen₃] to fabricate multifunctional cotton fabrics in a single step. The POT cage coating imparted excellent UV-blocking performance (89% blocked at 350 nm), hydrophobicity (water contact angle > 148°) and antibacterial activity (*Escherichia coli*, *Staphylococcus epidermidis*, and *Staphylococcus aureus* bacteria) to cotton fabrics.

Jin *et al.* (2019) successfully prepared bismuth phosphate (BiPO₄) nanorods coated cotton fabrics by two-dip-two-nip technique. Chitosan and acetic acid acted as cross-linking agents between BiPO₄ and cotton fibers as seen in UV-VIS absorption and FTIR results. The coated fabrics exhibited UV-blocking ability confirmed by UPF values greater than blank cotton fabric and self-cleaning activity.

A series of scientific publications (Čuk *et al.*, 2021; Nateghi and Shateri-Khalilabad, 2015; Pan *et al.*, 2012; Razmkhah *et al.*, 2021; Shateri-Khalilabad and Yazdanshenas, 2013a; Tang *et al.*, 2017) reported multifunctional features of metal nanoparticles coated smart fabrics. In this perspective, silver nanoparticles had widely used due to their antibacterial ability. Shateri-Khalilabad and Yazdanshenas (2013a) investigated superhydrophobic, antibacterial, and UV-blocking properties of the silver nanoparticles (AgNPs) coated cotton fabric. AgNPs coating was formed on the cotton surface through an alkali preactivation followed by *in situ* reduction of silver nitrate. Then, AgNPs coated cotton fibers were subjected to superhydrophobic treatment with octyltriethoxysilane (OTES). AgNPs coated cotton fabric showed UPF value equal to 266, water contact angle greater than 150° and shedding angle equal to 8°. Also, coated fabric exhibited antibacterial activity against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* bacteria.

Nateghi and Shateri-Khalilabad (2015) also investigated multifunctional properties of the silver nanowires (AgNWs) coated cotton fabric prepared by dip-dry method followed by superhydrophobic treatment with Danasylan F 8815. SEM/EDX results indicated a thin and uniform AgNWs coating on the cotton fibers. AgNWs coated cotton fabric also exhibited UV-blocking (UPF > 113), superhydrophobic (water contact angle > 150° and shedding angle < 10°) and antibacterial properties. In other scientific paper about Ag nanoparticles coated textiles, Čuk *et al.* (2021) reported the development of multifunctional fabrics using plant food waste (green tea leaves, avocado seed and pomegranate peel) and alien invasive plant extracts

(Japanese knotweed rhizome, goldenrod flowers and staghorn sumac fruit) as reducing agents for the *in-situ* synthesis of silver nanoparticles in cotton fibers. Regardless of the reducing agent used, all silver nanoparticles containing cotton fabrics showed UPF values above 50 and antibacterial activity against *E. coli* and *S. aureus* bacteria.

Pan *et al.* (2012) successfully prepared a superhydrophobic and UV blocking cotton fabric via sol-gel method and self-assembly using inexpensive and ordinary reagents, aluminum nitrate and sodium stearate. The interactions between aluminum coating and sodium stearate in cotton fabrics was confirmed by XPS results. Cotton fabric treated with 1.5% Al sol and 20 mmol L⁻¹ sodium stearate exhibited excellent hydrophobic properties (water contact angle > 146°) and UV blocking ability (UPF = 164).

In other scientific publication about nanoparticle-containing cotton fabrics, Tang *et al.* (2017) reported the development of gold nanoparticles (AuNPs) coated cotton fabrics prepared by *in situ* synthesis of AuNPs onto fiber surface using a heating method. The localized surface plasmon resonance of the AuNPs imparted the cotton fabric with colors, showing good colorfastness to washing and rubbing. It is important to highlight that the colorfastness to washing and rubbing were evaluated in accordance with Australian Standard AS 2001.4.15–2006 and Australian Standard AS 2001.4.3–1995, respectively. The AuNPs coating improved the UV-blocking ability of cotton textiles and resulted in UV-protective fabrics with remarkable antibacterial activity. In addition, AuNPs coated cotton fabrics exhibited catalytic activity, which did not influence on their dyeing with reactive dyes.

Razmkhah *et al.* (2021) reported the UV-blocking and antibacterial properties of selenium nanoparticles coated wool fabrics. Based on the results of the UV protection enhancement (%) method (Noorian *et al.*, 2015), the coated fabrics exhibited UV-blocking ability. In addition, these fabrics showed reasonable bactericidal and fungicidal performances toward *Escherichia coli*, *Staphylococcus aureus* and *Candida albicans*.

For comparative purposes, Fig. 5 and 6 were made to analyze and discuss the main scientific information of UV-protective compound-containing smart fabrics described above. Thus, Fig. 5 shows the number of scientific publications for each UV-protective compound class presented in the chemical composition of smart fabrics and Fig. 6 illustrates the UV-blocking range of UV-protective compound-containing fabrics. It is important to highlight that UV-blocking range corresponds to the UV-shielding performance of

compound class including specific UV spectral region of each compound.

Analyzing the number of scientific publications about UV-protective compound-containing smart fabrics in the period from 2010 to 2021 (Fig. 5), it is observed that TiO₂, ZnO and nanocomposites based on TiO₂ or ZnO were the most used in the development of UV-blocking fabrics. Probably, low human skin toxicity (Abuçafy *et al.*, 2016) and UV-shielding (Abuçafy *et al.*, 2016; Flor *et al.*, 2007; Seixas and Serra, 2014), self-cleaning (Banerjee *et al.*, 2015; Qi *et al.*, 2017) and antibacterial (Qi *et al.*, 2017; Yadav *et al.*, 2016) properties of these oxides and/or nanocomposites combined with several synthetic methods used to obtain them (Montazer and Pakdel, 2011; Montazer and Amiri, 2014) encouraged this great number of scientific studies. In general, synthetic approaches use low-cost and easy-to-obtain reagents and, depending on the synthetic route, allow to control the morphology, surface, and particle size of TiO₂, ZnO and/or nanocomposites based on TiO₂ or ZnO. Despite the smaller number of scientific papers, other UV-protective compounds, mainly LDH, MOFs and Graphene compounds, demonstrate growing potential to be used in the development of novel smart fabrics due to their new multifunctional features, increasingly reported in the recent literature. Thus, a promise increasing of scientific publications about this type of smart fabrics could be expected.

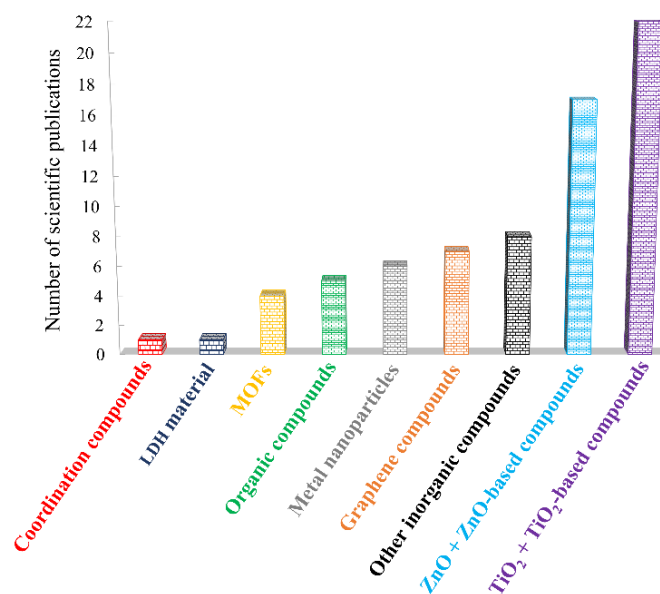


Figure 5. Number of scientific publications of the UV-protective compound-containing smart fabrics per UV-protective compound class in the period from 2010 to 2021.

Another relevant aspect to be considered is that the smart fabrics with LDH, MOFs or graphene compounds exhibited UV-blocking range situated in the UVB and UVA regions (Fig. 6) indicating broad-spectrum action, i.e., capacity to protect the human skin from both UVB and UVA radiation. Organic compounds or metal nanoparticles containing smart fabrics also had same broad-spectrum behavior, while other fabrics showed UVB-blocking capacity (Fig. 6). Therefore, UV-protective compound presented in the textile composition determines the UV radiation region that smart fabrics have higher protection efficiency.

Although organic compounds can undergo decomposition under certain conditions, e.g., high temperature and/or oxidizing environment, the synergistic effects from interactions between these compounds and textile fibers improve their thermal, chemical and/or photochemical stability. Moreover, synergistic properties reduce the fiber photodegradation of smart fabrics. In this perspective, molecular interactions between textile fibers and UV-protective compounds provide specific physicochemical properties to textile materials and ensure lower occurrence of skin allergies by fabric contact.

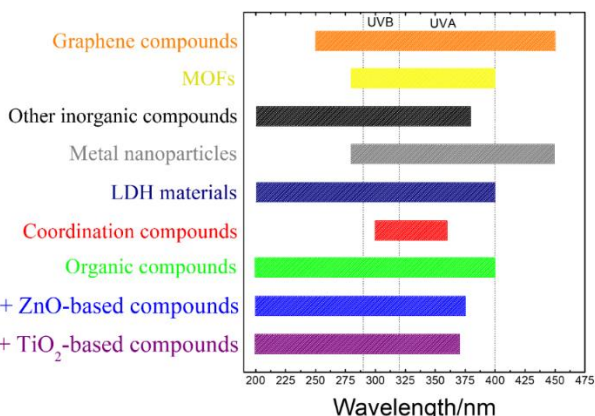


Figure 6. UV-blocking range of the UV-protective compound-containing smart fabrics per compound class.

Besides the UV-blocking range, UPF values are commonly used to indicate the UV protection of smart fabrics. Analogous to sun protection factor (SPF) of sunscreens, UPF is a parameter defined as the ratio of the average effective UV irradiance calculated for unprotected skin to the average effective UV irradiance calculated for skin protected by the smart fabric (Hoffmann *et al.*, 2001). Many scientific publications have shown that UV-VIS spectroscopic measurements are accurate and reproducible *in vitro* test method to determining UPF (Montazer and Amiri, 2014), which is obtained by Eq. 1:

$$UPF = \frac{\int_{290}^{400} E_{\lambda} S_{\lambda} d\lambda}{\int_{290}^{400} E_{\lambda} S_{\lambda} T_{\lambda} d\lambda} \quad (1)$$

where E_{λ} is the relative erythral spectral effectiveness and S_{λ} is the solar spectral irradiance of the source. The T_{λ} corresponds to spectral transmission of the test fabric as a function of wavelength (λ) and the wavelength integration limits refers to the combined UVB and UVA wavelength range.

According to Hoffmann *et al.* (2001), UPF values between 15 to 24 (ratings 15 and 20, respectively) indicate a good UV-protection, UPFs of 25 to 39 (ratings 20, 30 and 35, respectively) demonstrate a very good UV-protection, and UPFs ≥ 40 correspond to an excellent UV-protection (ratings 40, 45, 50 and 50+). Analyzing the UPF values of scientific publications cited in this review, it is observed that more than 90% of them exhibited UPF values higher than 40. Therefore, smart fabrics had an excellent UV-protection regardless on the UV-protective compound presented in the textile fibers. However, some precautions must be considered in the analysis and interpretation of these UPF results. One of the most important aspects is the UV-VIS transmission measurements, which undergo spectral changes and/or deviations depending on the experimental conditions used and/or optical properties of smart fabrics. In this perspective, opaque and translucent smart fabrics, which exhibit nonlinear behavior of Lambert–Beer law, must be carefully analyzed to avoid mistakes in the interpretation of UPF results.

4. Conclusions

In this review, recent literature on UV-blocking textiles have been reported to give an overview of their importance and prospects in sun-protective methods. UV-protective compounds incorporated, anchored, or coated textile fibers compose a useful class of UV-blocking materials for the development of smart fabrics as proved by the large number of scientific publications in the last years. Different UV-protective compounds, mainly TiO₂ and ZnO, are used to improve UV-blocking ability of fabrics and, often, they also impart to additional fabric properties, e.g., antibacterial, and self-cleaning activities. Analyzing from spectroscopic point of view, the elucidation of UV-blocking mechanisms gives an important information about electronic structure and optical properties of UV-protective textiles; therefore, it can be more investigated and discussed in the literature. A remarkable point is the reduced number of scientific papers that reported the use of organic filters in smart fabrics although these UV-protective compounds have

high UV absorption capacity and, depending on their molecular structure, can interact to fiber surface without the presence of cross-linker compounds. UPF is a good parameter to indicate the UV-blocking ability of UV-protective compound-containing smart fabrics, however, some aspects must be considered in the analyses and interpretation of UPF results. Among them, (i) the amount of the UV-protective compound per textile area, (ii) textile thickness, and (iii) textile properties changed by the incorporation, coating and/or anchorage with UV-protective compounds, e.g., textile roughness. In this perspective, new scientific studies need to be undertaken to know the effective contribution of UV-protective compounds in the UPF values. Considering the growing requirement for simple, cheap, and practical sun-protective products, UV-blocking textiles are one of the best alternatives. Thus, scientific research in the field of smart fabric and/or UV-blocking textile, especially UV-protective compounds incorporated, anchored, or coated textile fibers, must be encouraged in order to promote new insights in sun-protective clothing and future applications of multifunctional textiles.

Authors' contribution

Conceptualization: Lupino, J. H. B.; Saito, G. P.; Cebim, M. A.; Davolos, M. R.

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Supervision: Davolos, M. R.

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Data sharing is not applicable. In this review, all scientific publications reported were found in the Web of Science™ database (<https://www-webofscience.ez87.periodicos.capes.gov.br>).

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