INVITED REVIEW: SOL-GEL, HYBRIDS AND SOLUTION CHEMISTRIES

Hybrid sol-gel materials for realization of radiation protective coatings—a review with emphasis on UV protective materials

Boris Mahltig [1] · Tilmann Leisegang[2,3] · Melanie Jakubik[1] · Helfried Haufe[4]

Abstract
This review reports on hybrid sol-gel coatings used for radiation protective purposes. The different types of electromagnetic radiation are usually distinguished by their wavelength, frequency or photon energy. There is a broad range of types of radiation that humans, materials or electric devices are exposed to, starting from radio waves, microwaves, infrared radiation, visible light, UV light, X-ray and gamma-ray radiation. Gamma-ray radiation is thus at the end of the electromagnetic spectrum with smallest wavelengths, highest frequencies and highest photon energies. Protection against radiation make sense, as it can pose health risks or interfere with technical and electronic equipment for example. Radiation protection can be realized by materials that are able to absorb or reflect the radiation, which leads to a considerable reduction in radiation transmission. These radiation protection materials are specific to different types of radiation or spectral widths, e.g., a material with excellent protective properties against UV light is not automatically suitable for protection against infrared light. The main aim of this review article is to report, what types of hybrid sol-gel materials can be used to provide ideal protection against a specific category of radiation. Additional to the broad view on all types of radiations, focusing in particular on materials exhibiting UV protective properties.

Graphical Abstract
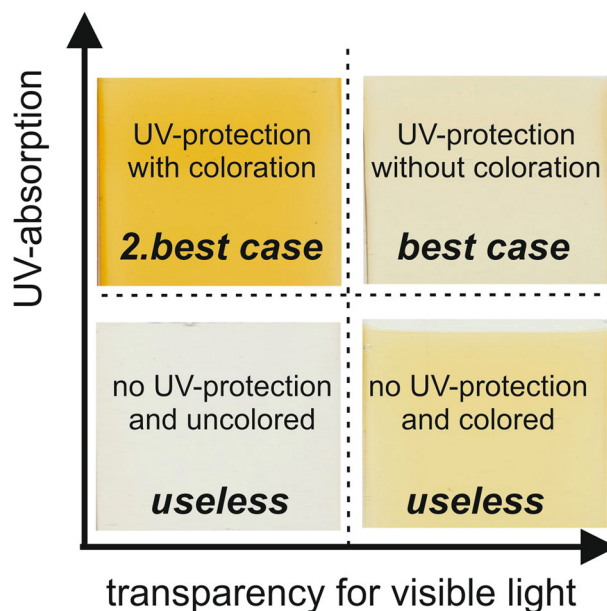
✉ Boris Mahltig
  boris.mahltig@hs-niederrhein.de

1 Faculty of Textile and Clothing Technology, University of Applied Sciences Niederrhein, Mönchengladbach, Germany

2 Saxray GmbH, Dresden, Germany

3 Institut für Experimentelle Physik, Technische Universität Bergakademie Freiberg, Freiberg, Germany

4 Department of Functional Coatings, Gesellschaft zur Förderung von Medizin-, Bio- und Umwelttechnologien e. V., Radeberg, Germany

Highlights
- Full overview on hybrid sol–gel materials for radiation protection.
- View a fundamental issue of radiation protection.
- Categorization of special sol–gel materials for protection against specific type of radiation.
- Discussion of relation of UV-protective properties and coloration of materials.

1 Introduction to radiation protection

Under the term electromagnetic radiation, a broad range of different types of radiation are summarized. Each type of electromagnetic radiation is characterized by a particular range of wavelengths, frequencies and photon energies. Probably the most commonly perceived radiation is visible light, which has wavelengths in the range of 400–750 nm. Radiation with smaller wavelength <400 nm is named ultra violet (UV) light, while radiation with >750 nm is called infrared light (IR) or thermal radiation. Table 1 summarizes the different types of radiation from radio waves to X-ray radiation [1]. In addition to the range of wavelengths and frequencies, Table 1 also lists some prominent reasons for protection from these radiations. For radiation with shorter wavelengths (UV-light or X-rays) the main focus is on health risks, as these can cause serious damages to health.

For radiation with longer wavelength, radiation protection is mostly aimed at technical concerns, such as heat management, prevention of bleaching or protection of electronic devices from interfering radiation effects. A material is capable of providing radiation protection if the radiation intensity is reduced when passing through that material. This transmitted intensity is named transmission T (usually given in percent). Figure 1 schematically visualizes the transmission of radiation. This schematic drawing is valid for all different types of radiation. The transmission can be reduced by two processes—the reflection R and the absorption A of radiation. Reflection refers to scattering and specular or non-specular reflection. Absorption refers to different physical processes in which, for example the energy of the electromagnetic wave is converted into vibrational modes of atoms or molecules or used to ionize atoms of the protective material. If the intensity of the initial radiation I_0 is set to 100%, the following equation applies, which gives the relationship between transmission T, reflection R and absorption A (all parameters are given in percent):

$$I_0 = 100\% = R + A + T \tag{1}$$

For the measurement of transmission, it is important to distinguish between the directly transmitted radiation T_{direct} and the radiation that is scattered through the material. The scattered radiation changes direction when passing through the absorbing material (scattered transmission, $T_{scattered}$) (Fig. 2). The intensity of the total transmitted light (direct plus scattered) is named diffusive transmission $T_{diffusive}$:

$$T_{diffusive} = T_{direct} + T_{scattered} \tag{2}$$

Depending on the type of protective material and the final application, it is important to determine the total diffusive transmission rather than just the direct transmission. For coated glass slides or polymer foils, measuring direct transmission is often sufficient to assess their radiation protective properties. For turbid materials, such as textiles with particular scattering characteristics, on the other hand, the determination of the diffusive transmission is critically important in order to evaluate the radiation protective properties.

The ability of a particular material to support radiation protection is primarily related to its capacity to absorb radiation. This absorption is determined by the material composition (chemical constituents: elements and molecules) and the type of radiation to be protected. In other words, a material does not protect equally against all types of radiation. Commonly specific components are used as absorbers for a particular spectral range of electromagnetic radiation [2]. A good example here is titanium dioxide TiO_2, which can be used as UV-absorber to provide UV protection properties [3]. Typical radiation absorbers are known for each type of electromagnetic radiation. A summary of some typical absorbers can be found in Table 2.

In Table 2 the range for visible light is given for wavelengths from 400 to 780 nm. However, it should be kept in mind that the human eye is also sensitive to light with wavelengths between 380 nm and 400 nm [4, 5]. Often the range for visible light is given for a range of 400–700 nm, since the sensitivity of the human eye to light in the two spectral ranges 380–400 nm and 700–780 nm is low [6].

In addition to absorptive materials, special reflectors can also be used to provide protection against initiate radiation. This strategy is often used to protect against IR radiation because most IR radiation absorbing materials are inadequate or expensive. Well-known examples of IR reflective

Table 1 Overview on different types of radiation and main reasons for protection

Radiation type	Wavelength range [nm]	Frequency range [Hz]	Photon energy range [eV]; [J]	Reasons for protection
Microwaves & radiowaves	$>10^6$	$<300 \times 10^9$	$<0.1 \times 10^{-3}$; 1.6×10^{-23}	Protection of electronic devices & personal identity; shielding from electrosmog
Infrared (IR) light	$780–10^6$	300×10^9 to 385×10^{12}	~ 0.1; 1.6×10^{-20}	Camouflage; thermal management
Visible light	400–780	385×10^{12} to 750×10^{12}	~ 1; 1.6×10^{-19}	Camouflage; optical protection; protection of light sensitive materials
Ultra violet (UV) light	10–400	750×10^{12} to 30×10^{15}	~ 10; 1.6×10^{-18}	Prevention of sun burns, eye damages & skin cancer; protection of UV sensitive materials
X-rays	<10	$>30 \times 10^{15}$	$>1 \times 10^3$; 1.6×10^{-16}	Prevention of cancer/tumors & radiation damages
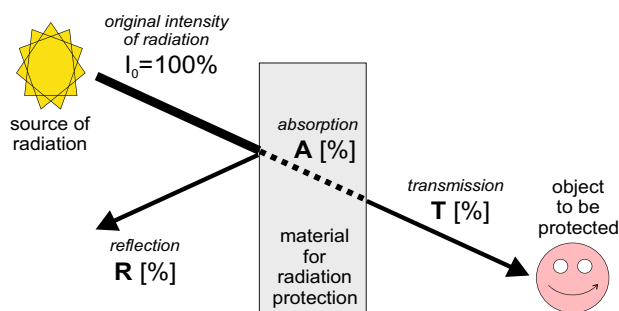
Fig. 1 Schematic drawing showing the interaction of radiation with radiation protection material. The radiation can be of different types (radio waves, microwaves, infrared light, visible light, UV-light and X-rays)
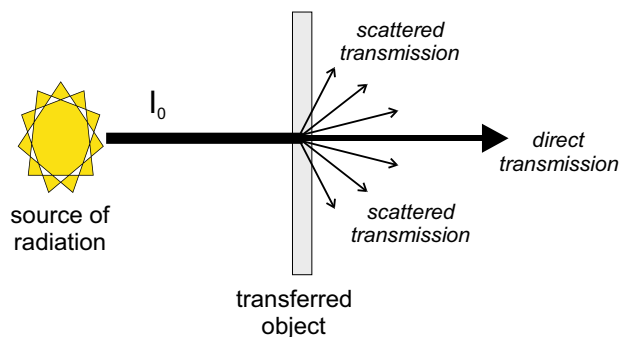
Fig. 2 Schematic drawing illustrating different types of transmitted radiation when an object is irradiated. The radiation can be of different types (radio waves, microwaves, infrared light, visible light, UV-light and X-rays)

coatings include those containing aluminum metal effect pigments, where the metal pigments act as a mirror for IR light [7].

Usually, simple sol-gel coatings from silica or alumina do not exhibit strong interactions with electromagnetic radiation, so they cannot be used in isolation for the preparation of radiation protective materials. To produce a radiation protective sol-gel coating, the coating has to be modified with agents that exhibit strong absorbing or reflecting properties toward the particular radiation hazard

being addressed. For this purpose, special hybrid sol-gel materials have to be designed that contain organic or inorganic compounds in addition to the sol-gel matrix that can support radiation protection. In addition to different compositions and hybrid approaches, the morphology of incorporated particles (size, shape, crystallinity) can also be used to develop special protective materials. However, it should be indicated that there is no single universal sol-gel hybrid material or coating that can provide protection for every type of radiation.

2 Radiation protective sol-gel coatings

This section describes sol-gel coatings that can provide protection against radiation, with each sub-section focusing on a specific category electromagnetic radiation.

2.1 Microwaves and radio waves

There are often well-defined technical reasons for protecting electronic devices from microwaves or radio waves, including personal identity or data protection [8]. For example, a pocket made from such a protective material can be a safe place to store devices such as mobile phones or credit cards [7].

Another field of application is the shielding of so-called electrosmog—also known as EMI-shielding (EMI, for ElectroMagnetic Interference) [9, 10]. There are several reports of possible negative health effects due to exposure to radio waves. However, the effect and influence of such radiation on health are part of a controversial debate that has not been decided. Nevertheless, products developed for EMI-shielding are highly sought after by consumer and can often command a premium purchase price [10].

Electroconductive materials are often used for shielding against microwaves and radio waves. Suitable materials can be, for example, coatings with copper or silver pigments as additives [11]. However, sol-gel materials applied as coatings or as bulk materials can also be used for these purposes. A rather simple approach involves the use of

Table 2 Summary of different radiation absorbers categorized according to type of radiation

Type of radiation	Typical absorbers or reflecting agent	Literature related to the use in sol-gel materials
Microwave & radiowaves	Electric conductive materials, $C/SiO_2/SiC$-based aerogels	[12–15]
Infrared (IR) light	Organic IR absorbers, infrared reflecting pigments, effect pigments, doped indium oxides, zirconium carbide	[23–25, 58–61]
Visible light	Organic dye stuffs or inorganic color pigments	[62, 63]
Ultra violet (UV) light	Inorganic absorbers, such as TiO_2, ZnO or CeO_2; Organic absorbers, such as cinnamate or benzotriazole derivatives	[48, 49, 64–67]
X-rays	Materials built up from chemical elements with high atomic numbers, such as lead, HfO_2 or $BaSO_4$	[54, 55]

hybrid sol-gel materials containing a conductive additive, such as the organic and conductive polyaniline embedded in a silica sol matrix [12]. Carbon nanotubes can also be used here as a conductive material to realize sol-gel based shielding materials on cotton fabrics [13]. A special approach is the use of aerogels based on a combination of carbon, silica and silicon carbide [14]. In addition to hybrid materials, special mixed metal oxides for effective electromagnetic shielding have also been reported, including a nanostructured strontium doped lanthanum manganese oxide $La_{0.7}Sr_{0.3}MnO_3$ [15].

The main factors determining whether these materials will reach practical applications, apart from the shielding efficiency, are price and suitable processes for their application, e.g., as coatings. For cost and resource reasons, compounds containing lanthanum or other lanthanoids such as cerium are less favored for use in commercially available shielding materials.

2.2 Infrared radiation

Infrared radiation (IR light) is also known as thermal radiation. Often, protection from IR radiation is associated with heat management. Of interest, for example, are window coverings that exclude thermal radiation from buildings in the summer. However, in winter, conversely, thermal radiation should be allowed to illuminate the indoor side of the window to save on heating costs and trap thermal radiation within the building [16]. Sun glasses incorporating IR protection can also protect the human eye from excessive exposure [17]. Another interesting area for manipulating IR light interaction is camouflage of clothing used in military applications. To support perfect camouflage even against night vision devices, it is necessary to consider IR reflective and absorptive properties of textiles [18].

Typically, a reduction of transmission T of infrared radiation is achieved by using IR reflective materials such as coatings of metallic aluminum or aluminum-based effect pigments [7, 19]. Textiles equipped with such reflective coatings are used as workwear for people working in hot environment where reflection of thermal radiation is required as part of personal protection. However, other IR reflective pigments can also be used as part of coating recipes [20, 21].

Unlike IR-reflective materials, IR-absorbing materials are less widely used, mainly for two reasons [22]. First, IR absorbers are less effective in their ability to reduce IR light transmission. Second, the IR absorber can heat up considerably due to exposure to IR light, which can lead to discomfort for the wearer. Sol-gel based IR absorbers can be realized by modified types of indium oxide, which are used as coatings for windows, for example [23]. Another prominent IR-absorber is zirconium carbide (ZrC), which can also be realized in a hybrid sol-gel material containing ZrC and SiC [24]. For practical applications, nanocrystalline ZrC prepared in aqueous solvent can be advantageous [25]. In contrast to recipes based on organic solvents, such water-based recipes have several advantages in terms of work safety, ecology and cost. A commercially available IR absorber is supplied under the brand name Calorsil (CHT, Tübingen, Germany). This absorber is based on modified tin oxide and can be incorporated in conventional sol-gel coatings.

A combination of the Calorsil product with a commercial silica sol can be applied as coating agent on textile materials. Microscopic images of such coatings on cotton and polyester fabrics are shown in Fig. 3. The commercial silica sol used is iSys HPX (CHT, Tübingen, Germany), which was originally developed for application on textiles. This silica sol product is non-flammable and can be diluted by adding water. The application of this silica sol alone on textile fabrics leads to smooth and regular coatings. No cracks or peeling of the coating can be observed (Fig. 3). If this coating recipe is applied together with the Calorsil product, the complete textile surface is regularly covered by the hybrid sol-gel coating. Due to the irregular fiber structure of cotton and its thicker fabric, a higher up-take of the sol-gel solution by the cotton fabric is observed compared to that of polyester fabric (Fig. 3). The optical transmission spectra of related uncoated and coated textile fabrics are shown in Fig. 4. These spectra

Fig. 3 Scanning electron micrographs of textile fabrics made from cotton and polyester fibers. Shown are untreated fabrics and fabrics with silica sol coating and hybrid coatings from silica and an inorganic IR absorber from doped tin oxide
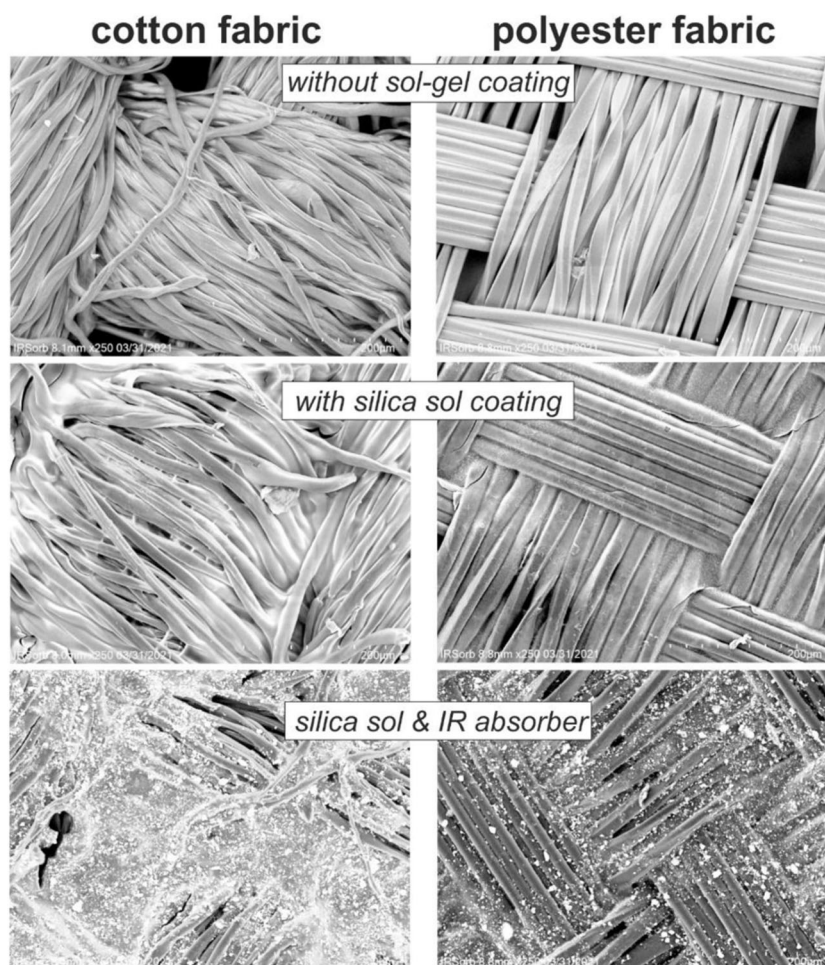
show the transmission in the range of 220–1400 nm and illustrate the transmission for near infrared light in the range of 700–1400 nm. In this spectral range of near infrared light, the applied pure silica sol coating does not change the transmission behavior of the textile fabrics. Only by applying the hybrid sol-gel coating that also contains the inorganic IR absorber can a significant decrease in transmission be achieved (Fig. 4). However, also the optical properties with visible light are changed, so the coated fabrics exhibit a light blue coloration. In comparison to applications with inorganic UV absorbers, it is also not possible to reduce the IR transmission down to values near 0% [22].

Transmission spectra for infrared light in the range from 2500 to 17500 nm are presented in Fig. 5. These spectra clearly show the peaks typical for the fiber materials in polyester and cotton fabrics. These peaks are caused by related vibrations of chemical bonds present in the polymers building up the fiber materials [26, 27]. Following application of the silica sol coating without additional additives, new peaks arising from vibrational modes of Si-O-Si species are observed in the transmission spectra, with the strongest of these observed near 12500 nm [28–30]. Even though IR transmission is significantly reduced in the spectral region near these peaks a simple silica coating alone is unlikely to protect against IR radiation, because transmission is still high in other regions of the IR spectrum. A significant improvement can only be achieved by application of the sol-gel hybrid coating containing silica and the inorganic IR absorber. With this hybrid sol-gel coating the IR transmission can be reduced significantly over the entire observed IR range (Fig. 5).

2.3 Visible light & coloration

Visible light is, of course the best known type of radiation. However, in many everyday situations it is not recognized as "radiation" per se and particularly not as radiation against which protection might be necessary. However, irradiation with visible light can also damage material objects. In particular, the color properties of materials can be bleached out by visible light. For this reason, radiation protection applications that target visible light are often used to protect materials especially in outdoor applications. Not surprisingly, applications that combine UV light and visible light absorption are common here.
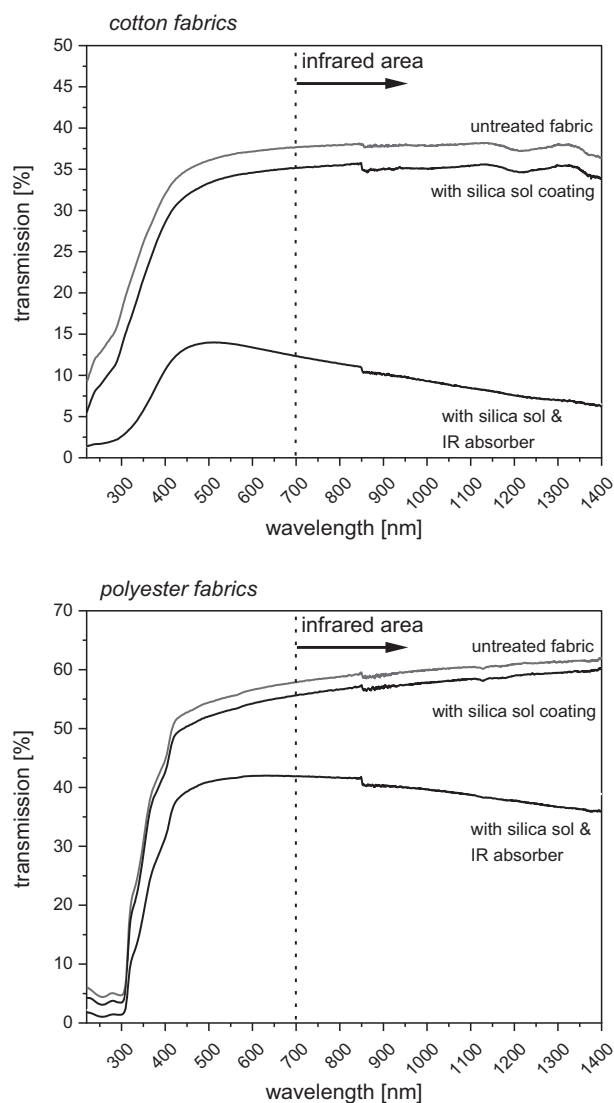
Fig. 4 Optical transmission spectra of textile fabrics made from cotton and polyester fibers with and without different sol-gel coatings. The infrared region is indicated

Fig. 5 Infrared spectra of textile fabrics made from cotton and polyester fibers with and without different sol-gel coatings

A prominent example is the use of modified sol-gel coatings to protect wood from sun light and weathering [31–33]. For this application, silica sols can be modified with color pigments of various iron oxides. Iron oxide pigments are often used for wood treatment (timber treatment) as they are known for their good light stability and for dark color shades [34]. These dark shades support the natural appearance of wooden materials. Iron oxide pigments can be obtained in different colors such as black, red or yellow. These different colors are related to the different chemical composition of iron oxides – Fe_2O_3 for iron oxide red; $Fe(OH)_3$ for iron oxide yellow and Fe_3O_4 for iron oxide black [34–36]. The pigment iron oxide brown is a combination of various iron oxides and manganese dioxide MnO_2 [36].
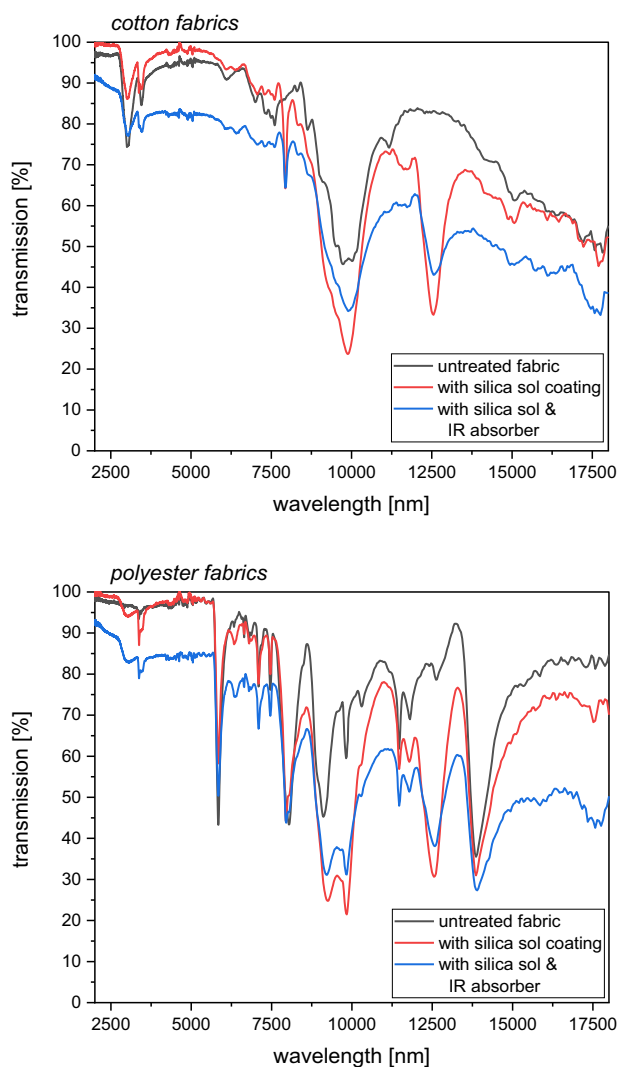
In addition to the chemical composition of iron oxide pigments, the size of the pigment particles also influences the color shade of the pigment. So-called transparent iron oxides, which contain particles with smaller particle diameters, are of particular interest for use with sol-gel systems. Due to their smaller size, these transparent pigments also have a greater penetration depth when applied to wooden materials.

Sol-gel coatings can also be modified by embedding organic dye stuffs. This modification enables a wide range of different colors to be generated, depending on the types of dyes used [37–39]. For incorporating dyes in silica-based sol-gel coatings, cationic dyes in particular are recommended to achieve a good stability against washing, leaching and wet rubbing. Due to a negative net charge of the silica matrix, the cationic dye is electrostatically attracted to the surrounding matrix [40, 41]. Hybrid sol-gel

materials based on silica/alumina compositions can also complex mordant dyes. This effect leads to improved leaching stability and an enhancement of coloration intensity [42]. In addition, sol-gel coatings containing titania can also complex embedded organic molecules. In systems where colorless UV light absorbing compounds are incorporated, a strong color shift into the visible range can occur and a yellow-colored sol-gel hybrid coating can be realized.

2.4 UV radiation

Mitigating exposure to UV radiation is probably the most widely studied area of radiation protection, due to the amount of UV radiation in sunlight and associated health risks arising from outdoor exposure to excessive sunlight [43, 44]. Besides sunlight, there are also artificial sources for UV light, such as conventional lighting systems, UV black light lamps or UV emitting LEDs [45, 46]. These light sources are used for illumination, industrial processes and identification procedures. However, indoor lighting in particular can lead to material damages. This is the case with historical artwork presented under illumination. Here, sol-gel based materials can be very effective at mitigating the effects of UV exposure, particularly in the form of coatings on glass display cases [47].

Sol-gel coatings can be a perfect tool to implement UV protection properties on different materials, such as glass, polymer foils or textiles [48]. For this purpose, conventional silica sol coatings are often modified with UV-light absorbing components. Alternatively, sol-gel coatings containing titania can be used for UV-protection. However, also the combination of titania with embedded organic UV-absorbers can be an advantageous combination to support a complete UV protection over the whole spectral range of UV-light [49].

Organic UV-absorbers that are well suited for combination in hybrid sol-gel systems include those of cinnamate or benzotriazole basic structure [37]. Examples of four cinnamate based UV absorbers are shown with their chemical structures in Fig. 6. These UV absorbers are supplied under the brand name semasorb by the company sema GmbH (Coswig, Germany).

Photographs of related UV-absorber containing silica-based sol-gel coatings on glass plates are shown in Fig. 7. These coatings are prepared by a dip-coating procedure. The optical transmission spectra of these coated glass substrates are shown in Fig. 8. These hybrid sol-gel coatings are based on silica and contain other silane additives, such as N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPM), 3-glycidyloxypropyltriethoxysilane (Glyeo) and aminopropyltriethoxysilane (APS). It can be clearly seen that some of the UV protective coatings have a strong coloration—yellow to orange. Even when using the same
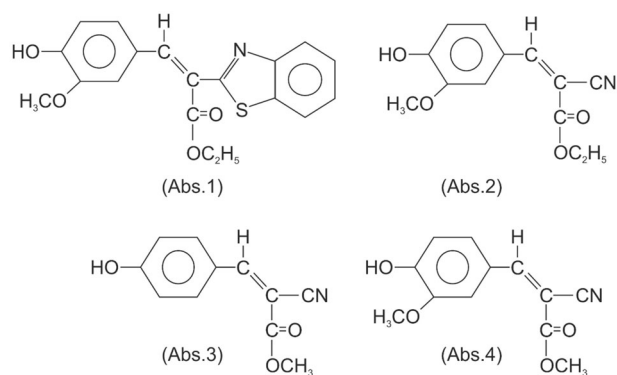
Fig. 6 Summary of chemical structures of different organic UV absorbers (Abs.1 to Abs.4) used for embedding in hybrid sol-gel coatings
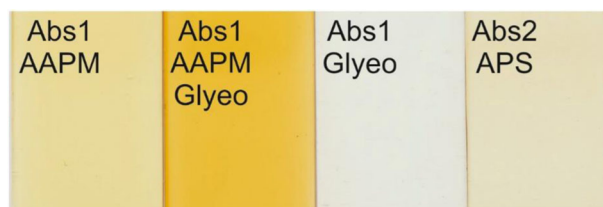
Fig. 7 Photographs of glass substrates coated with different hybrid sol-gel materials containing embedded UV-absorbers. The sol-gel is SiO_2 based, different absorbers and additives are indicated for each coating
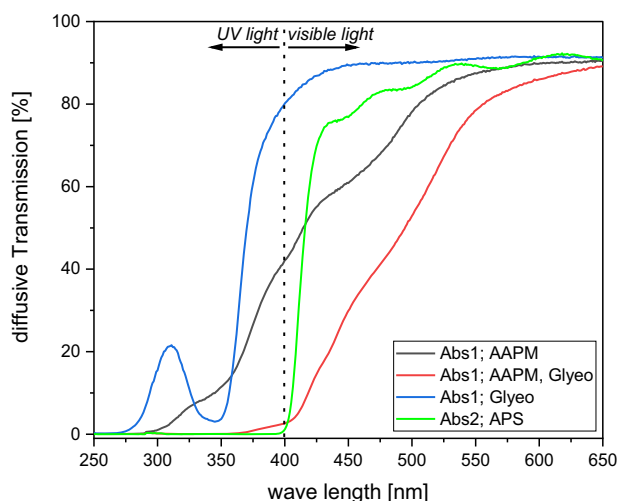
Fig. 8 Comparison of different hybrid sol-gel coatings with embedded UV-absorbers deposited on glass substrates

type of absorber, the coloration of the final coating can vary, depending on the type of additional silane additives. It is likely that the surrounding sol-gel matrix has an influence on the auxochromic groups of the UV-absorbers, resulting in a change in coloration. Whether coloration of a UV-protective coating is acceptable depends on the final

application of the coated substrate. In the case of a glass window for use in buildings or in the automotive sector, there is often a requirement for no coloration. Here, a high degree of transparency for visible light is required, as this visible light illuminates the interior and an unrestricted view to the outside area is also required. Any coloration of the coating would reduce this.

For other applications, the total transparency for visible light is not required. Also, a coloration is not a hindrance for several industrial issues. It should be kept in mind, however, that the coloration of a coating itself does not indicate its UV protective characteristics. Even though it is often mentioned in the literature that dark colored materials offer better UV-protection, this is not automatically the case. The coloration only indicates the interaction of the material with visible light and does not give any further information about the interaction with any other types of radiation. The only method for determining UV-protective properties is optical spectroscopy in the UV-range of the electromagnetic spectrum. If the transmission for UV-light in the wavelength range from 200 to 400 nm is almost zero, one can assume perfect UV protection for the corresponding material. For this purpose, the optical transmission spectra of the four coated glass slides are shown in Fig. 8.

Each coated sample exhibits a different transmission spectrum typical of a particular category (Fig. 9). The coating with absorber Abs1 in the presence of AAPM results in insufficient UV-protection and a yellowing of the coated substrate. The protection is insufficient due to the high transmission values, especially between 350 nm ($T = 11\%$) and 400 nm ($T = 42\%$). In addition, the yellow
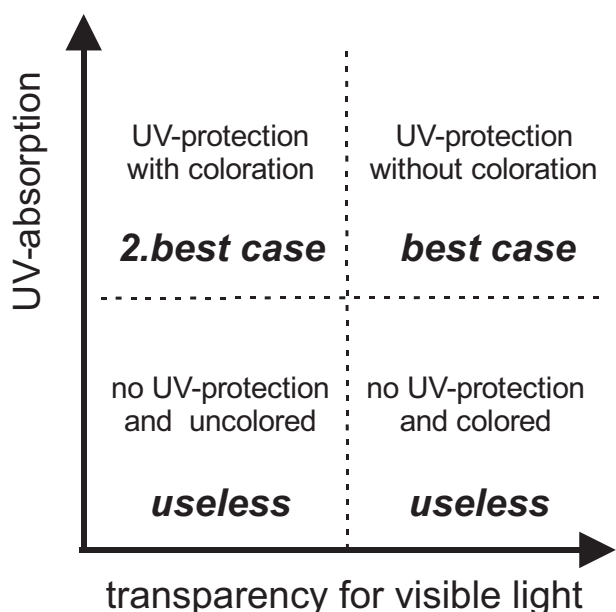

Fig. 9 Schematic drawing illustrating the four different categories of materials related to UV-protection and coloration

coloration is indicated in the spectrum by lower transmission values in the visible range of light from 400 to 500 nm. This type of coating is an example of a colored coating without sufficient UV-protection.

In contrast, the coating with absorber Abs1, AAPM and Glyeo results in excellent UV protective glass substrates with transmission values $T < 1.2\%$ for the entire range of UV-light. However, the significant decrease in transmission for visible light correlates with the strong yellow/orange coloration of the coated glass substrate. Although the UV protection is excellent, this coating is only acceptable for applications where such coloration does not interfere. The coating containing absorber Abs1 and Glyeo is almost transparent to visible light and thus colorless. However, its UV protection is insufficient, due to the high transmission in the UV range. Probably the best type of coating is demonstrated by the combination of the absorber Abs2 with APS in a silica sol coating. Here the UV protection is excellent with transmission values $T < 1.2\%$ over the entire UV range. Furthermore, the influence on the coloration is low. The schematic drawing in Fig. 9 illustrates the four situations as a function of UV-absorption and transparency to visible light. In fact, the best option is a sol-gel hybrid material that combines the properties of "strong UV light absorption" with "high visible light transparency".

Besides glass substrates, other materials can also be coated by sol-gel hybrid materials to provide UV-protective properties. One area of application is the functionalization of textiles to produce UV-protective clothing or home textiles. Related to this application, Fig. 10 shows transmission spectra of a polyester fabric before and after the application of two different UV-protective hybrid sol-gel coatings. By applying these sol-gel coatings, the transmission over the entire UV range is below <5%, thus indicating good UV protection of this textile fabric. Also, a lower transmission for visible light in the range of 400–450 nm is evident, which is associated with a yellow coloration of the coated textile. Such a coloration is acceptable for many textile applications, such as outdoor clothing or clothing for young children. Another interesting feature is the high transmission for visible light in the range of 475–800 nm after application of the sol-gel coating. As can be seen in the corresponding micrographs (Fig. 11), the sol-gel material mainly fills in cavities between the fibers that comprise the polyester yarn. Presumably, this improves the transmittance for visible light.

2.5 X-rays

To demonstrate the difference between, for example, irradiating a person with IR radiation and X-rays, we compare the energy emitted by a cup of hot coffee with the same amount of energy emitted by a conventional X-ray tube.

Fig. 10 Comparison of different hybrid sol-gel coatings with embedded UV-absorbers deposited on textile substrates (PET fabric)
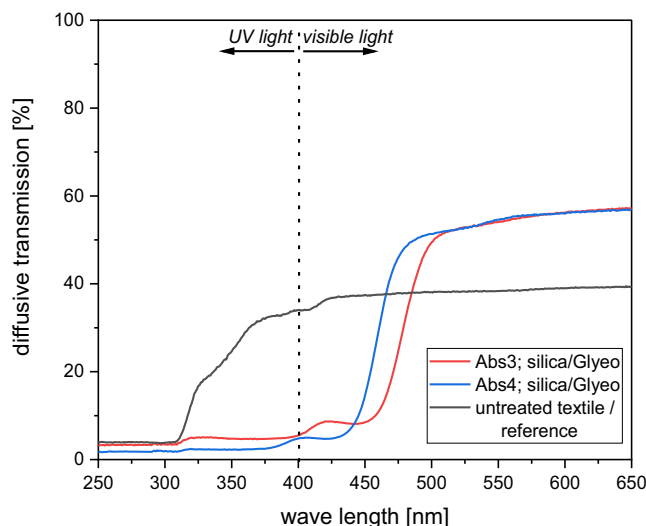
According to the Stefan Boltzmann law, a cup of hot coffee emits energy equivalent to about 400 J in 10 s. We assume that this energy is emitted as IR radiation. We further consider a person of 75 kg weight. If the person is in front of this cup, after 10 s a specific energy of 5 J/kg has been absorbed. A hard X-ray photon has an energy of 10^{-14} J. An energy of 400 J would therefore correspond to 10^{16} photons, the amount that a conventional X-ray tube can emit. If the person is in front of this X-ray source, he or she has also absorbed a dose of 5 Gy (Gray). While in the first case the person hardly feels anything, in the second case the person feels a health problem after 30 min, because a lethal dose with a mortality rate of 60% has been absorbed. However, much smaller doses can also shorten lifetime. This is attributed to the ability of X-rays to ionize matter, especially chemical and biological materials, which are damaged as a result [48, 50].

Nevertheless, X-ray-based methods are widespread (e.g., in medical imaging, medical treatment or materials science). X-rays are present in various occupational fields (e.g., nuclear reactors, mining or aviation industry) and occur in nature (radon gas in cellars or cosmic radiation during overseas flights). Therefore, protection against X-rays is of broad interest.

Compared to IR, X-rays have a much higher penetration depth for matter, i.e., a higher transmission T. Figure 12 schematically shows the transmission T of a fiber as a function of photon energy, frequency and wavelength. It can be seen that the transmission is not the same over the entire range, nor is it a linear function. Rather, it depends on the electronic structure of the constituents of the fiber. To obtain a low T at high energies (small wavelengths), the material thickness must be increased or the atomic composition must contain chemical elements with a high atomic number.
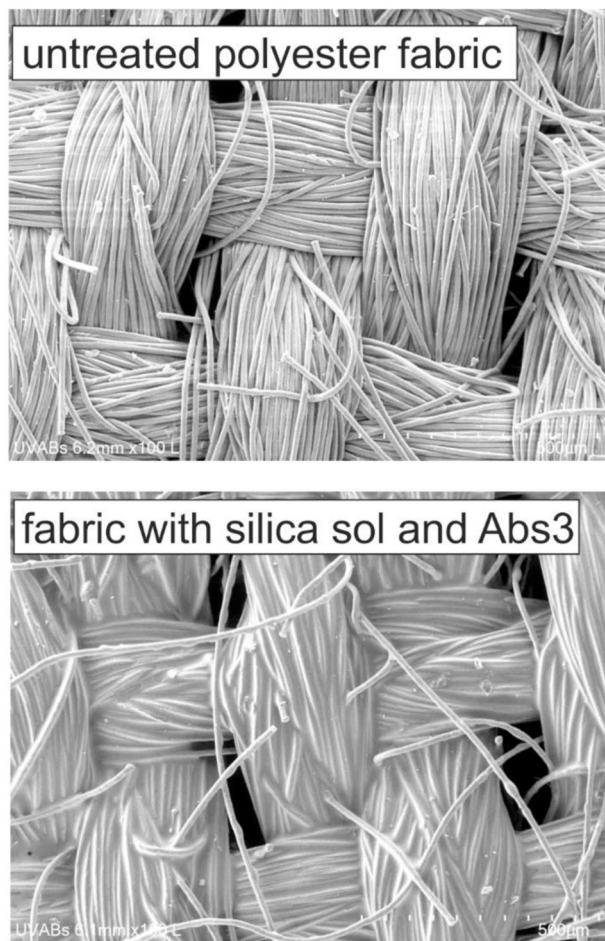

Fig. 11 Scanning electron micrographs of two polyester fabrics—untreated and after coating with a silica sol containing an UV absorber (Abs.3)

Figure 12 also shows that protection from X-rays is the most demanding challenge because X-rays, unlike other types of radiation, have a higher photon energy. The photon
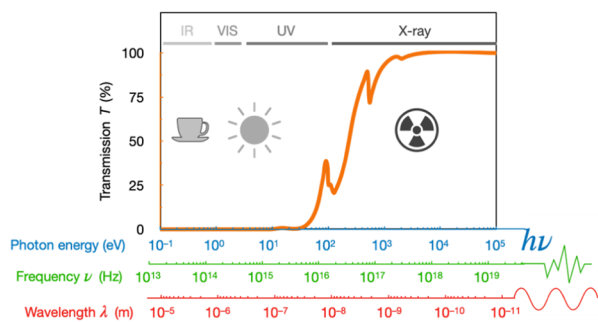
Fig. 12 The transmission T of radiation is shown schematically. A SiO_2 filament with a thickness of 0.1 μm and a density of 2.2 g/cm^3 was assumed, calculated according to [56, 57]. Note that the intervals given for the different types of radiation are only an approximation, since they usually overlap

Fig. 13 X-ray transmission spectra of textile fabrics coated with silica hybrid sols containing barium sulfate $BaSO_4$ as X-ray absorber

energy of X-rays can vary over a wide range from 250 eV to several MeV [51–53].

A significant decrease in the transmission of high energy X-ray photons in the MeV range is only possible, if a lead plate of several millimeter thickness is used. It is not to be expected that a sol-gel coating of several micrometer thickness can be used here. However, X-ray photons with smaller energies of 2–10 keV can be shielded to a certain extent by modified sol-gel coatings [54].

Materials with high X-ray absorbance are composed of densely arranged chemical elements of high atomic numbers such as lead, barium or bismuth. Common sol-gel materials based on silica, alumina or titania are almost completely transparent to X-rays. In contrast sol-gel materials containing heavy metals such as $PbWO_4$ can provide X-ray shielding [55]. However, it should be noted that the use of lead-based materials is limited due to the toxicity of lead [50]. An alternative is the use of barium sulfate ($BaSO_4$) as X-ray absorber, which is not toxic. $BaSO_4$ particles can be used as an additive for silica sols to produce hybrid sol coatings with X-ray absorptive properties [54]. The application of these sol-gel coatings on textiles is possible and leads to textile materials with lower X-ray transmission [54]. An example of the X-ray transmission spectra of such textiles is shown in Fig. 13.

3 Summary & conclusion

The term "protection against radiation" covers many different types of radiation and it is important to identify the type of radiation against which protection is required. In particular, the design of the required protective material is dependent on the type of radiation, e.g., radio waves or UV-light. A material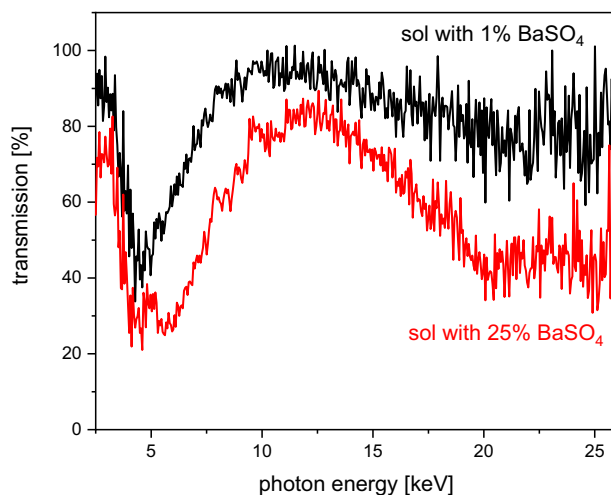 that offers excellent protection against one type of radiation can be useless for protection against another type of radiation. Hybrid sol-gel materials offer an appropriate tool to produce radiation protective coatings for each type of radiation. The sol-gel matrix is an ideal carrier for the absorbing or reflective components, which are necessary to achieve radiation protection. Nevertheless, the limits of such protective sol-gel coatings must also be recognized. It is absolutely clear that a sol-gel coating with micrometer thickness will not be able to protect against high energy X-rays with several MeV photon energy. Probable best results are obtained for hybrid sol-gel coatings in the field of UV-protection and the shielding of radio waves.

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

Ethical approval The data presented in the included figures were measured in our laboratories.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

References

1. Zamanian A, Hardiman CJHFE (2005) Electromagnetic radiation and human health: a review of sources and effects. High Freq Electron 4:16–26

2. Hoque MT, Mahltig B (2020) Realisation of polyester fabrics with low transmission for ultraviolet light. Coloration Technol 136:346–355

3. Liu Y, Liu Y, Lin J, Tan H, Zhang C (2014) UV-protective treatment for Vectran® fibers with hybrid coatings of TiO$_2$/organic UV absorbers. J Adhesion Sci Technol 28:1773–1782

4. Luo Y-R (1999) Why is the human visual system sensitive only to light of wavelengths from approximately 760 to 380 nm?: an answer from thermochemistry and chemical kinetics. Biophys Chem 83:179–184

5. Kojima D, Mori S, Torii M, Wada A, Morishita R, Fukada Y (2011) UV-sensitive photoreceptor protein OPN5 in humans and mice. PLoS ONE 6(10):e266388

6. Wardman RH (2018) An introduction to textile coloration. John Wiley & Sons Ltd, Hoboken

7. Mahltig B, Zhang J, Wu L, Darko D, Wendt M, Lempa E, Rabe M, Haase H (2017) Effect pigments for textile coating: a review of the broad range of advantageous functionalization. J Coat Technol Res 14:35–55

8. Yener SC, Cerezci O (2016) Material analysis and application for radio frequency electromagnetic wave shielding. Acta Phys Polonica A 129:635–638

9. Geetha S, Kumar KKS, Rao CRK, Yijayan M, Trivedi DC (2009) EMI shielding: methods and materials – a review. J Appl Polym Sci 112:2073–2086

10. Poser M (2017) Elektrosmog. Crotona Verlag GmbH, Amerang

11. Topp K, Haase H, Degen C, Illing G, Mahltig B (2014) Coatings with metallic effect pigments for antimicrobial and conductive coating of textiles with electromagnetic shielding properties. J Coat Technol Res 11:943–957

12. Gonzalez M, Soares BG, Magioli M, Marins JA, Rieumont J (2012) Facile method for synthesis of polyaniline/silica hybrid composites by simultaneous sol-gel process and "in situ" polymerization of aniline. J Sol-Gel Sci Technol 63:373–381

13. Nasirizadeh N, Dehghani M, Yazdanshenas ME (2015) Preparation of hydrophobic and conductive cotton fabrics using multi-wall carbon nanotubes by the sol-gel method. J Sol-Gel Sci Technol 73:14–21

14. An Z, Ye C, Zhang R, Qu Q (2019) Multifunctional C/SiO$_2$/SiC-based aerogels and composites for thermal insulators and electromagnetic interference shielding. J Sol-Gel Sci Technol 89:623–633

15. Reshi HA, Singh AP, Pillai S, Yadav RS, Dhawan SK, Shelke V (2015) Nanostructured La$_{0.7}$Sr$_{0.3}$MnO$_3$ compounds for effective electromagnetic interference shielding in X-band frequency range. J Mater Chem C 3:820–827

16. Stevanovic S (2013) Optimization of passive solar design strategies: a review. Renew Sustain Energy Rev 25:177–196

17. Sliney DH (2002) How light reaches the eye and its components. Int J Toxicol 21:501–509

18. Rubežienė V, Padleckienė I, Baltušnikaitė J, Varnaitė S (2008) Evaluation of camouflage effectiveness of printed fabrics in visible and near infrared radiation spectral ranges. Mater Sci Medziagotyra 14:361–365

19. Rashid MM, Mahltig B, Mamun K (2019) Surface modification of cotton fabric with effect pigment – a review of improved textile optical functionalization. Int J Text Sci 8:10–15

20. Malshe VC, Bendiganavale AK (2008) Infrared reflective inorganic pigments. Recent Pat Chem Eng 1:67–79

21. Meenakshi P, Selvaraj M (2018) Bismuth titanate as an infrared reflective pigment for cool roof coating. Sol Energy Mater Sol Cells 174:530–537

22. Mahltig B, Bendt E, Grethe T, Hess O, Weide T (2021) Biophysical concept for textile skin protection. Technical Textiles 64:154-156

23. Gosh S, Biswas PK, Neogi S (2014) Effect of solar radiation at various incident angles on transparent conducting antimony doped indium oxide (IAO) film developed by sol-gel method on glass substrate as heat absorbing window glass fenestration. Sol Energy 109:54–60

24. Li F, Bao W, Ni DW, Huang X, Zhang GJ (2019) A thermoset hybrid sol for the syntheses of zirconium carbide–silicon carbide foam via replica method. J Porous Mater 26:409–417

25. Wang JX, Ni DW, Dong SM, Yang G, Gao YF, Kan YM, Chen X-W, Cao Y-P, Zhang XY (2017) Synthesis of nanocrystallized zirconium carbide based on an aqueous solution-derived precursor. RSC Adv 7:22722–22727

26. Mahltig B (2021) High performance fibers – a review of properties and IR-spectra. Tekstilec 64:96–118

27. Flesner J, Mahltig B (2017) In: Thakur VK, Thakur MK, Kessler MR (eds) Handbook of composites from renewable materials, vol 4–Functionalization. Srivener Publishing LLC Wiley, New Jersey

28. Günzler H, Gremlich H-U (2002) IR Spectroscopy. Wiley-VCH, Weinheim

29. Moreno-Maldonado V, Acosta-Torres LS, Barcelo-Santana FH, Vanegas-Lancon RD, Plata-Rodriguez ME, Castano VM (2012) Fiber-reinforced nanopigmented poly(methyl methacrylate) as improved denture base. Appl Polym Sci 126:289–296

30. Ravichandran R, Gandhi S, Sundaramurthi D, Sethuraman S, Krishnan UM (2013) Hierarchical mesoporous silica nanofibers as multifunctional scaffolds for bone tissue regeneration. J Biomater Sci Polym Edition 24:1988–2005

31. Tshabalala MA, Libert R, Schaller CM (2011) Photostability and moisture uptake properties of wood veneers coated with a combination of thin sol-gel films and light stabilizers. Holzforschung 65:215–220

32. Zheng R, Tshabalala MA, Li Q, Wang H (2015) Weathering performance of wood coated with a combination of alkoxysilanes and rutile TiO$_2$ hierarchical nanostructures. BioResources 10:7053–7064

33. Lu Y, Xiao S, Gao R, Li J, Sun Q (2014) Improved weathering performance and wettability of wood protected by CeO2 coating deposited onto the surface. Holzforschung 68:345–351

34. Schauwecker CF, McDonald AG, Preston AF, Morrell JJ (2014) Use of iron oxides to influence the weathering characteristics of wood surfaces: a systematic survey of particle size, crystal shape and concentration. Eur J Wood Wood Products 72:669–680

35. Christie RM (2001) Colour Chemistry. Royal Society of Chemistry RSC, Cambridge

36. Seilnacht T (2018) Pigment und Bindemittel, 2nd edn. Seilnacht Verlag & Atelier, Bern

37. Mahltig B, Haufe H, Böttcher H (2005) Functionalization of textiles by inorganic sol–gel coatings. J Mater Chem 15:4385–4398

38. dos Santos C, Brum LFW, Vasconcelos RDF, Velho SK, dos Santos JHZ (2018) Color and fastness of natural dyes encapsulated by a sol–gel process for dyeing natural and synthetic fibers. J Sol–Gel Sci Technol 86:351–364

39. Trepte J, Böttcher H (2000) Improvement in the leaching behavior of dye-doped modified silica layers coated onto paper or textiles. J Sol–Gel Sci Technol 19:691–694

40. Mahltig B, Knittel D, Schollmeyer E, Böttcher H (2004) Incorporation of triarylmethane dyes into sol-gel matrices deposited on textiles. J Sol-Gel Sci Technol 31:293–297

41. Mahltig B, Textor T (2006) Combination of silica sol and dyes on textiles. J Sol-Gel Sci Technol 39:111–118

42. Mahltig B, Böttcher H, Knittel D, Schollmeyer E (2004) Light fading and wash fastness of dyed nanosol-coated textiles. Text Res J 74:521–527

43. Armstrong BK, Kricker A (2001) The epidemiology of UV induced skin cancer. J Photochem Photobio B 63:8–18

44. Narayanan DL, Saladi RN, Fox JL (2010) Ultraviolet radiation and skin cancer. Int J Dermatol 49:978–986

45. Böttcher H, Mahltig B, Sarsour J, Stegmaier T (2010) Qualitative investigations of the photocatalytic dye destruction by TiO_2-coated polyester fabrics. J Sol-Gel Sci Technol 55:177–185

46. Dalponte E, Mahltig B, Breckenfelder C (2018) In: Mahltig B (eds) Textiles advances in research and applications. Nova Science Publishers Inc, New York

47. Zayat M, Pardo R, Castellon E, Torres L, Almendro D, Parejo PC, Alvarez A, Belenguer T, Garcia-Revilla S, Balda R, Fernandez J, Levy D (2011) Optical and electro-optical materials prepared by the sol-gel method. Adv Mater 23:5318–5323

48. Mahltig B, Textor T (2008) Nanosols and Textiles. World Scientific, Singapore

49. Mahltig B, Böttcher H, Rauch K, Dieckmann U, Nitsche R, Fritz T (2005) Optimized UV protecting coatings by combination of organic and inorganic UV absorbers. Thin Solid Films 485:108–114

50. Mahltig B, Günther K, Askani A, Bohnet F, Brinkert N, Kyosev Y, Weide T, Krieg M, Leisegang T (2017) X-ray-protective organic/inorganic fiber–along the textile chain from fiber production to clothing application. J Text Inst 108:1975–1984

51. Attwood D (2007) Soft X-rays and extreme ultraviolet radiation. Cambridge University Press, Cambridge

52. Chen LM, Forget P, Toth R, Kieffer JC, Krol A, Chamberlain CC, Hou BX, Nees J, Mourou G (2003) High resolution hard X-ray spectroscopy of femtosecond laser-produced plasmas with a CZT detector. Rev Sci Instrum 74:5035–5038

53. Kirz J, Jacobsen C, Howells M (1995) Soft X-ray microscopes and their biological applications. Q Rev Biophysics 28:33–130

54. Mahltig B, Haufe H, Leisegang T, Gutmann JS, Textor T (2011) Verminderte Röntgentransmission durch beschichtete Textilien. Melliand Textilber 92:36–39

55. Zhang Q-P, Liang D-M, Zhu W-F, Liu J-H, Wu Y, Xu D-G, Bai X-Y, Wie M, Zhou Y-L (2019) Fabrication of h-BN@$PbWO_4$ with a facile sol-gel method towards enhanced photocatalytic and radiation shielding properties. J Solid State Chem 269:594–59

56. Henke BL, Gullikson EM, Davis JC (1993) X-ray interactions: photoabsorption, scattering, transmission, and reflection at E=50-30000eV, Z=1-92. At Data Nucl Data Tables 54(2):181–342. https://henke.lbl.gov/optical_constants/filter2.html

57. Hubbell JH, Veigele WJ, Briggs EA, Brown RT, Cromer DT, Howerton RJ (1975) Atomic form factors, incoherent scattering functions, and photon scattering cross sections. J Phys Chem Ref Data 4:471–538. erratum in 6, 615-616 (1977)

58. van Aert H, van Damme M, Nuyken O, Schnöller U, Eichhorn K-J, Grundke K, Voit B (2001) Imagewise structuring of diazo-sulfonate polymer films by UV light and laser irradiation – a comparison. Macromol Mater Eng 286:488–496

59. Zhu C, Lin W, Chen L, Lv J, Zhang J, Feng J (2019) Deep color, heat-reflective, superhydrophobic and anti-soiling coatings with waterborne silicone emulsion. Sol Energy Mater Sol Cells 199:129–135

60. Feng X, Mao Q, Lv Q, Wang Z, Cui S (2016) Solar reflection characteristics of phthalocyanine green / TiO_2 composite green pigments prepared via different approaches. Mater Sci Forum 849:725–731

61. Rashid MM, Mahltig B (2018) Inorganic effect pigment-binder system following sol-gel process–application for optical textile functionalization. J Fash Technol Text Eng 6:2

62. Mahltig B, Swaboda C, Roessler A, Böttcher H (2008) Functionalising wood by nanosol application. J Mater Chem 18:3180–3192

63. Mahltig B, Arnold M, Löthman P (2010) Surface properties of sol-gel treated thermally modified wood. J Sol-Gel Sci Technol 55:221–227

64. Abidi N, Hequet E, Tarimala S, Dai LL (2007) Cotton fabric surface modification for improved UV radiation protection using sol-gel process. J Appl Polym Sci 104:111–117

65. Farouk A, Textor T, Schollmeyer E, Tarbuk A, Grancacic AM (2009) Sol-gel derived inorganic-organic hybrid polymers filled with ZnO nanoparticles as ultraviolet protection finish for textiles. AUTEX Res J 9:114–120

66. Aklalouch M, Calleja A, Granados X, Ricart S, Boffa V, Ricci F, Puig T, Obradors X (2014) Hybrid sol-gel layers containing CeO_2 nanoparticles as UV-protection of plastic lenses for concentrated photovoltaics. Sol Energy Mater Sol Cells 120A:175–182

67. Wang W, Zhang B, Jiang S, Bai H, Zhang S (2019) Use of CeO_2 nanoparticles to enhance UV-shielding of transparent regenerated cellulose films. Polymers 11:458