

Sol-gel coatings with the fluorescence dye Rhodamine B for optical modification of cotton

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ABSTRACT

The sol-gel method is a versatile tool for the modification and functionalization of textiles. This method can be also used to support the application of dyes on textile materials. This paper is related to the application of the fluorescence dye Rhodamine B together with an industrial sol-gel component. Beside fluorescence spectroscopy, also scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) are used for the investigation of the produced textile samples. The realized fluorescence effects are strongly related to the applied dye concentration and can be drastically enhanced by presence of the applied sol-gel system. By use of sol-gel method also the dry and the wet rubbing fastness can be improved. These results could be the starting point for future development of new fluorescent textile materials.

Keywords

fluorescence,
UV light,
sol-gel,
silica,
nano-sol,
optical functionalization,
Rhodamine B,
textile finishing,
cotton

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1 Introduction

The sol-gel technology is a versatile technique to realize functional coatings on many types of different substrates as, e.g., glass, polymer foils, wood or metal [1-8]. First applications on textile and fiber materials are reported in the 1990th on glass fiber materials [9-11]. This starting point is quite reasonable because from the chemical point of view, glass fibers and silica based sol-gel coatings are in a certain way similar. Also, later works refer to dye containing sol-gel coatings on glass fibers [12]. As starting point for sol-gel applications on textile materials in general, a patent from 1997 invented by Textor et al. should be considered [13]. In the following years many sol-gel based functional textiles were developed [14-16]. Recently these developments are discussed in recent review articles [17, 18]. One interesting part of sol-gel technology on textiles is related to hydrophobic and oleophobic textiles and the combination of these repellent properties with antistatic properties [19-21]. Important developments are

also done in the field of antimicrobial sol-gel recipes for textile functionalization [22-25]. Strong efforts are also made for the development of sol-gel based flame retardant functionalization of textiles [26-28].

One interesting experiment was the embedding of dye stuffs into sol-gel coatings deposited on textiles [30-39]. By this technique the fastness against water and light can be improved. Especially the use of a combined sol-gel material from silica and alumina is advantageous to reach good fastness properties. This effect is probable related to an interaction of the dye molecules to aluminum ions similar to a mordant effect during application of natural dyes [30]. Also, a UV protection is aimed for the combination of dyes and sol-gel coatings on textiles. The embedding of photoactive dyes could even lead to antibacterial textiles [40]. Luminescent sol-gel coatings are used to realize textile-based pH sensors [41].

Luminescent textiles and especially fluorescent textile products are broadly available in commercial textiles and clothing products [42-44]. Applications of fluorescent textiles are often related to highly visible clothes or optical brightening of white textile materials [42,43,45]. Other applications are related to protection against UV light or anti-counterfeiting [42,46-48]. For application on polyester fabrics, mostly fluorescent disperse dyes are used [49,50]. For cotton fabrics and fabrics from regenerated cellulose, the fluorescent properties are often realized by application of fluorescent direct or reactive dyes [51,52]. An innovative technology to apply fluorescent properties to textile materials is also the use of microwave supported dyeing processes and preparation techniques [53,54].

With the background on intensive investigations of sol-gel technology on textile substrates over the last years and the importance of fluorescent textile products, it is also of interest to evaluate a commercially available sol-gel agent in combination with a fluorescence dye and its application on textile fabrics. For this, the aim of the current paper is to investigate the application of the fluorescence dye Rhodamine B on cotton fabrics in combination with a sol-gel agent. Reference applications are performed with similar aqueous solutions of Rhodamine B. An earlier study investigated already the application of the dye Rhodamine B with silica sols on polyester and viscose fabrics. However, the main focus of this earlier study was the leaching behavior of the dye from prepared textile materials, but not the fluorescence effect [55]. In contrast, the main aim of the current investigation is the reached fluorescence effects. Finally, it is shown that the fluorescence intensity of the treated textiles is drastically influenced by the applied dye concentration and the presence of the sol-gel agent.

2 Experimental

2.1 Materials

All preparations are done on white plain-woven cotton fabric. The mass per unit area of this cotton fabric is around 8.4 g/m². As fluorescence dye, Rhodamine B is used (see chemical structure in Fig. 1). This dye is represented by the chemical sum formula C₂₈H₃₁ClN₂O₃ and has the molecular weight 479 g/mol. The actually used dye is supplied by Carl Roth GmbH (Karlsruhe, Germany). As sol-gel product, the silica-based product iSys HPX supplied by the company CHT (Tübingen, Germany) is used.

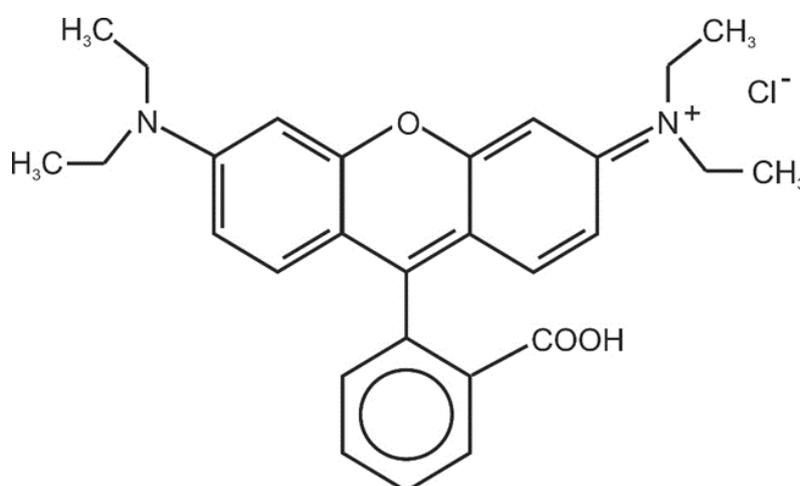


Fig. 1 Chemical structure of the fluorescence dye Rhodamine B.

2.2 Preparations

The dye Rhodamine B is applied on the cotton fabrics from three different solutions – from water, from a mixture of water and the agent iSys HPX (ratio 1:1), and from pure isys HPX. In these solutions the dye is dissolved in three different concentrations of 0.5 wt-%, 1 wt-% and 3 wt-%. All recipes are applied by padding which is done twice for each fabric. During padding, the fabric passes into the water-based recipes, under a submerged roller and out of the bath. Afterwards the fabric is squeezed to remove excess liquid. For padding application, a laboratory padding equipment is used (CH-8155 Niederhasli/Zürich Laboratory padding Equipment, Werner Mathis AG, Switzerland).

After padding, a thermal treatment is done at 120 °C for three minutes, by use of a Mathis Labdryer type LTE (supplied by the company Werner Mathis AG, Switzerland). This thermal treatment is done for drying of the samples and curing of the applied iSys HPX agent. After the thermal treatment of the samples, no further rinsing procedure is performed.

2.3 Analytical methods

Microscopic investigations are done with a scanning electron microscope (SEM) Tabletop TM3000 from Hitachi (Japan). This microscope is equipped with an EDS unit (Electron Dispersive Spectroscopy) Quantax 70 supplied by Bruker. This EDS unit enables the determination of chemical elements on sample surfaces. However, the chemical element hydrogen cannot be detected by this method.

Fluorescence measurements are performed with a fluorescence spectrometer RF-6000 (Shimadzu, Japan). For documentation of the optical appearance of prepared textile samples under different kind of illumination a commercially available illumination chamber CAC 60 (VeriVide Limited, Leicester, England) is used. This chamber allows the illumination with artificial day light-lamp D65 (20 Watt) and with UV black light (UV-lamp with a maximum intensity around 365 to 370 nm from Philips Lighting Holding B.V.).

The wet and dry rubbing fastness is measured using a crockmeter according to ISO 105-X12. For this rubbing test, specimens of the textile are rubbed with a dry rubbing cotton fabric and with a wet rubbing cotton fabric. The change of coloration is determined using a Gray Scale evaluating the staining of the rubbing cloth.

3 Results and discussion

3.1 Microscopic investigations

First microscopic investigations are performed on the prepared textile samples to support general sample information on topographic structure and surface composition. The surface composition of the samples is determined by EDS. The related EDS spectra and ratio of detected chemical elements are shown in Figure 2. The EDS spectrum of the untreated cotton substrate exhibits two signals related to the chemical elements carbon and oxygen. The chemical element hydrogen cannot be detected by EDS method [56]. The ratio of carbon and oxygen is the same as expected from the chemical structure of cellulose building up cotton [57]. This EDS spectrum from cotton is compared to three cotton samples with different applications of the dye Rhodamine B. If the dye is applied from aqueous solution, the surface content of carbon is higher compared to oxygen. This change in element content can be explained by the high carbon content in the dye.

The dye molecule contains also nitrogen but the sensitivity of the EDS method for the element nitrogen is low, so it is not detected on this sample surface [58]. In comparison the element chlorine can be detected with a small surface concentration of 0.3 wt-%. Chlorine is present in the used dye as chloride counter ion. The sensitivity of EDS for the detection of chlorine is quite good compared to the lower sensitivity for lower weight chemical elements, so here chlorine can be detected even in low concentration [58]. However, it is not possible to calculate from the determined content of chemical element chlorine directly the concentration of the up-taken dye stuff in the complete fiber, because by EDS only the surface concentration is determined. Both EDS spectra (C and D in Figure 2) exhibit also a

signal caused by silicon as a result of the applied silica sol-gel recipe. By application with the undiluted sol-gel agent iSys HPX (spectrum D), the determined silicon content is nearly doubled compared to the application with the diluted iSys HPX (spectrum C).

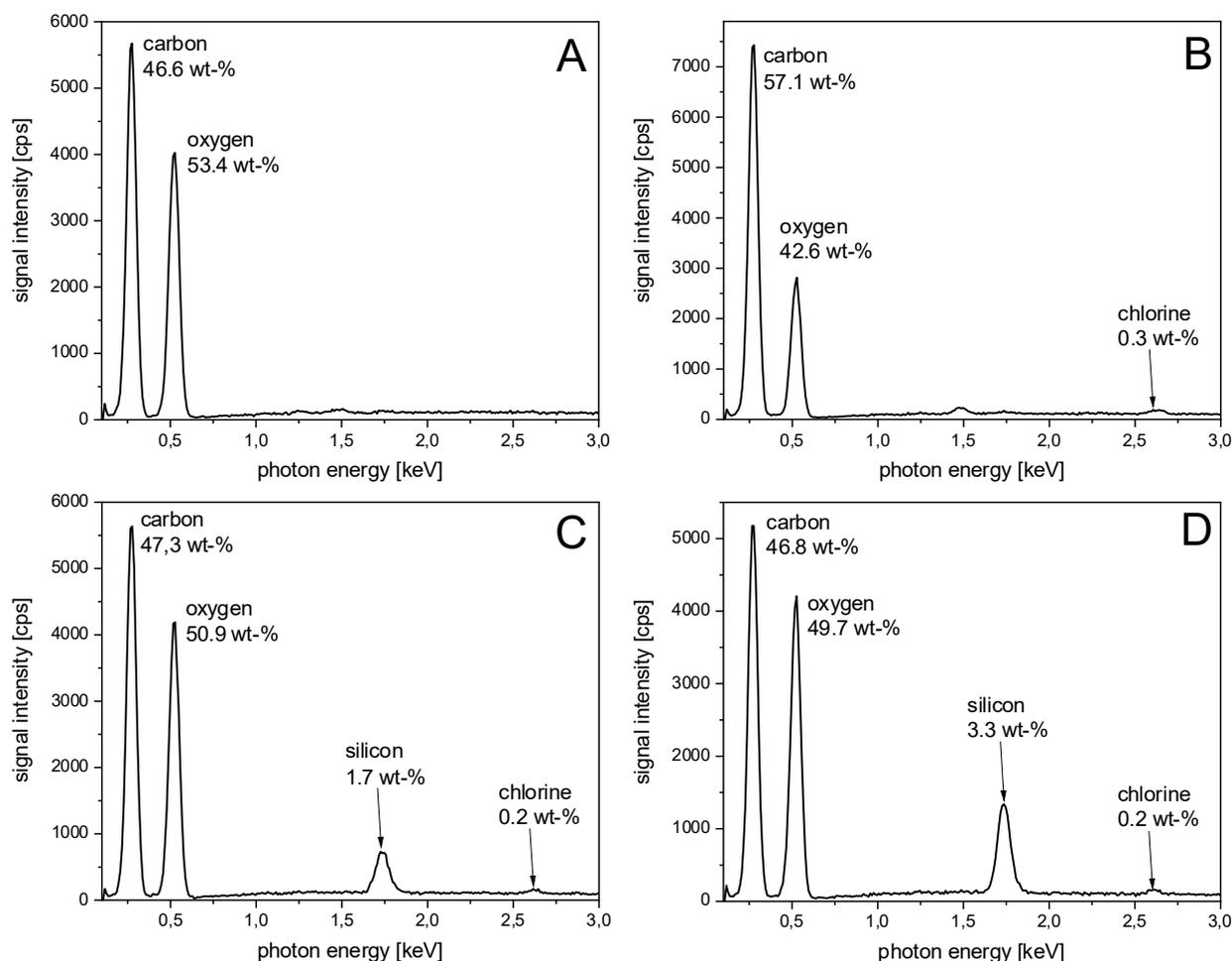


Fig. 2 EDS spectra of prepared cotton samples, the signal for the detected chemical element are indicated together with the determined surface concentration – the following samples are shown: (A) untreated cotton reference; (B) cotton sample after application of Rhodamine B 3 wt-% from aqueous solution; (C) cotton sample after application of Rhodamine B with 3 wt-% in mixture iSys HPX:water; (D) cotton sample after application of Rhodamine B with 3 wt-% dissolved in pure iSys HPX.

The microscopic images taken by SEM show mainly the cotton fiber structure of the cotton substrates (Figure 3). The applied dye molecules cannot be detected by this microscopic method, because of limits in the magnification. The application of the sol-gel recipe leads to a certain flattened fiber surface. However, mainly in some areas between single cotton fibers a bridging of the fibers by deposited sol-gel material is obvious. Probably in these areas between the cotton fibers the main content of sol-gel material is deposited.

The investigation by EDS mapping after treatment with a sol-gel based recipe shows a complete coverage of the sample surface by silicon (Figure 4). However, in areas between the cotton fibers the determined content of silicon is higher which support the proposed bridging of cotton fibers by silica. In contrast, the element carbon is only determined at areas on the topography, where the cotton fibers are placed.

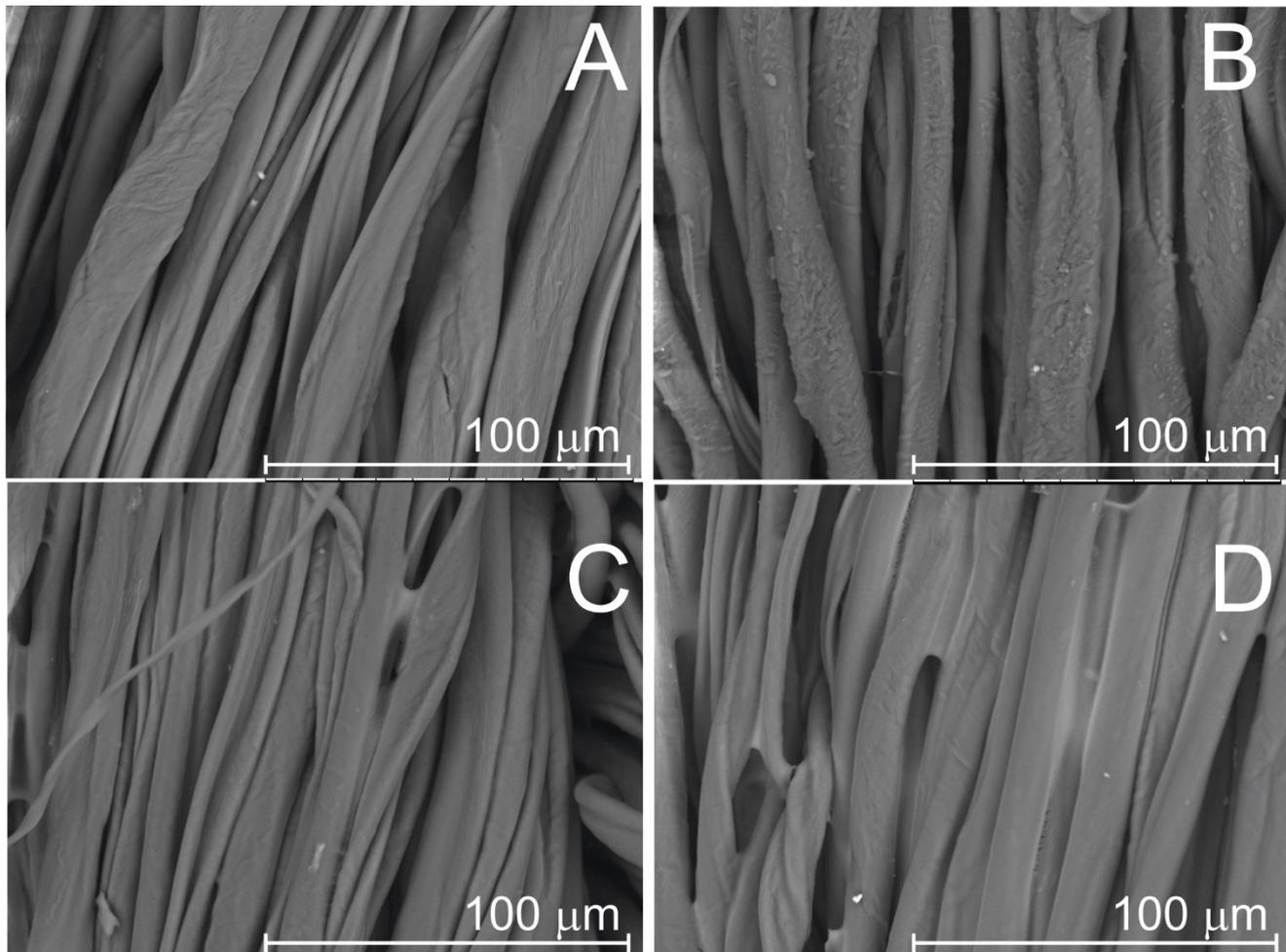


Fig. 3 Microscopic images of cotton samples taken by scanning electron microscopy (SEM) – the following samples are shown: (A) untreated cotton reference; (B) cotton sample after application of Rhodamine B 3 wt-% from aqueous solution); (C) cotton sample after application of Rhodamine B with 3 wt-% in mixture iSys HPX:water; (D) cotton sample after application of Rhodamine B with 3 wt-% solved in pure iSys HPX.

3.2 Optical appearance under illumination

The optical appearance of prepared textile samples is documented for all samples under two different types of illumination (Figures 5 to 7). First illumination is done with a D65 lamp, which is related to a daylight illumination. Second, an illumination with a UV-A lamp is performed.

By comparing the color impression of the finished fabrics under different illuminations (Figures 5 to 7), some differences can be observed. Using D65 illumination samples finished with aqueous solutions show only a slightly less intense coloration than the ones finished with iSys HPX based liquors. This difference is much more prominent under UV illumination where the iSys HPX based finishing exhibit a much stronger fluorescence than the water-based finishing. Furthermore, under both illuminations the color strength or fluorescence intensity seems to be decreasing with the dye concentration in the recipe.

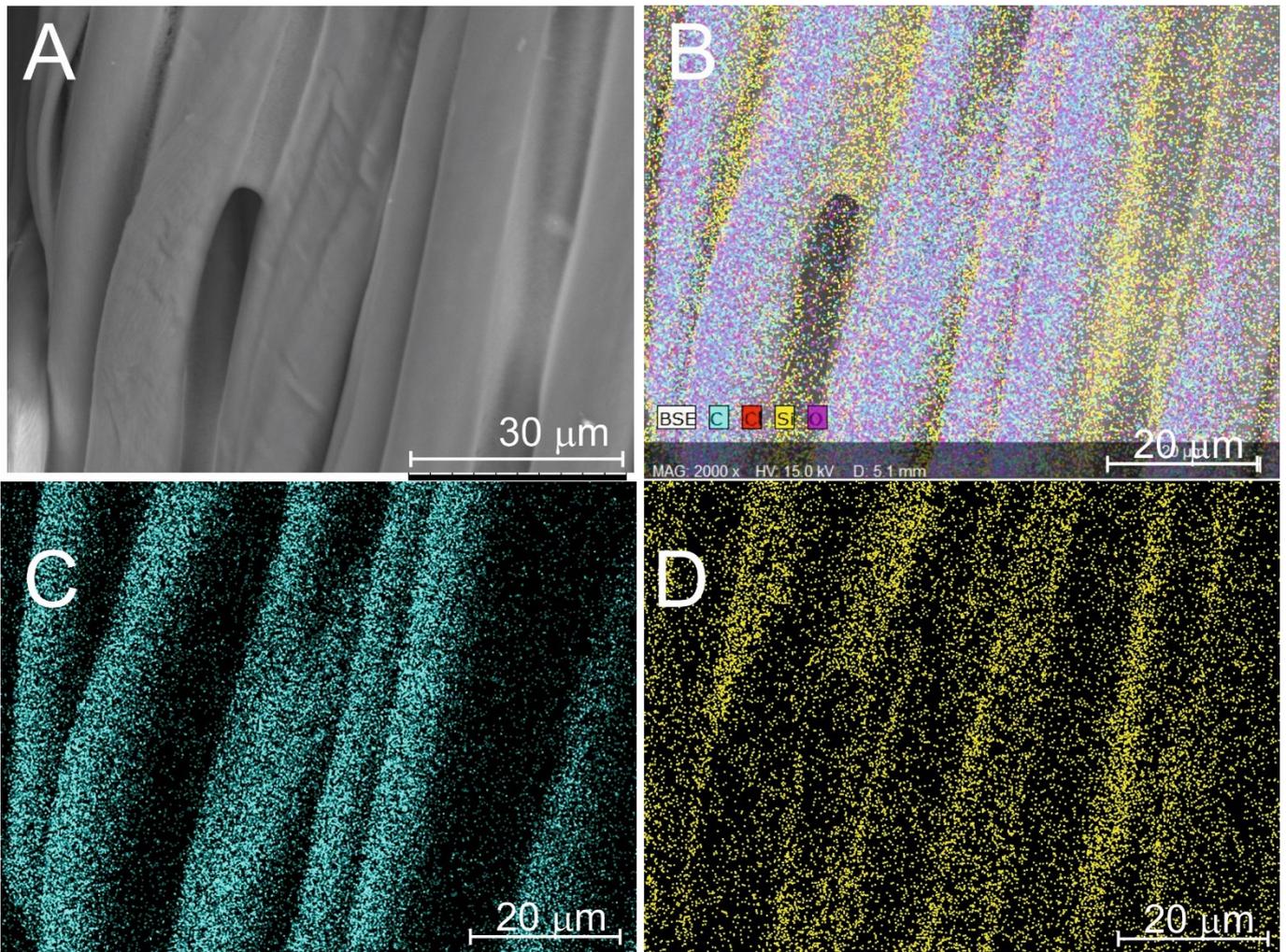
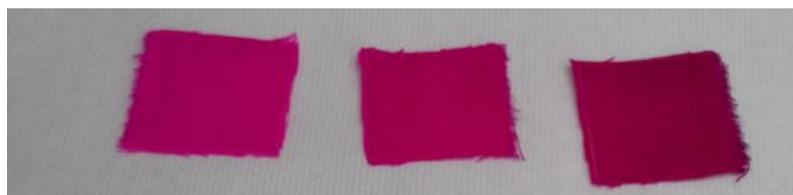


Fig. 4 SEM image recorded in higher magnification and EDS mappings of a cotton sample treated with a Rhodamine B solution 3 wt-% in iSys HPX – the following images are shown: (A) SEM image; (B) EDS mapping with all detected chemical elements as mixed map; (C) EDS mapping for carbon; (D) EDS mapping for silicon.

Daylight illumination



UV light illumination

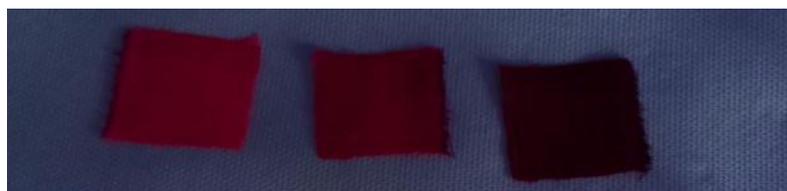


Fig. 5 Photographs of Rhodamine B containing cotton samples under different illumination (top: daylight; bottom: UV light). The Rhodamine B is applied on the fabrics from aqueous solution with increasing dye concentration – from left to right (0.5 wt-%; 1 wt-%; 3 wt-%).

Daylight illumination

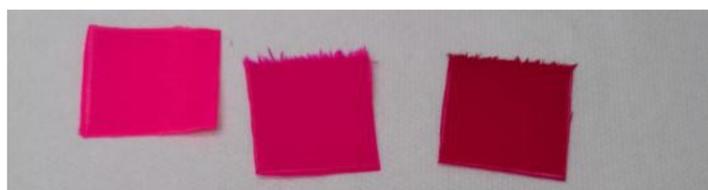


UV light illumination



Fig. 6 Photographs of Rhodamine B containing cotton samples under different illumination (top: daylight; bottom: UV light). The Rhodamine B is applied on the fabrics from a solution containing water and iSys HPX in a ratio 1:1. The dye concentration is increased from left to right (0.5 wt-%; 1 wt-%; 3 wt-%).

Daylight illumination



UV light illumination



Fig. 7 Photographs of Rhodamine B containing cotton samples under different illumination (top: day light; bottom: UV light). The Rhodamine B is applied on the fabrics from the chemical iSys HPX with increasing dye concentration – from left to right (0.5 wt-%; 1 wt-%; 3 wt-%).

3.3 Fluorescence properties

To support a general overview on the fluorescence properties, a two-dimensional fluorescence mapping of the aqueous solution of Rhodamine B is recorded (Figure 8). This mapping shows the intensity of fluorescence emission in the visible spectral range from 410 nm to 800 nm for excitation with UV light in the range from 400 nm to 800 nm.

The main fluorescence effect is gained for an excitation around 350 nm, leading to a main emission of light around 590 nm. However, also the excitation with UV light around 380 nm leads to significant fluorescence emission. This sensitivity for UV light at 380 nm is especially important for practical application, because of the high content of this type of UV light in the sun light.

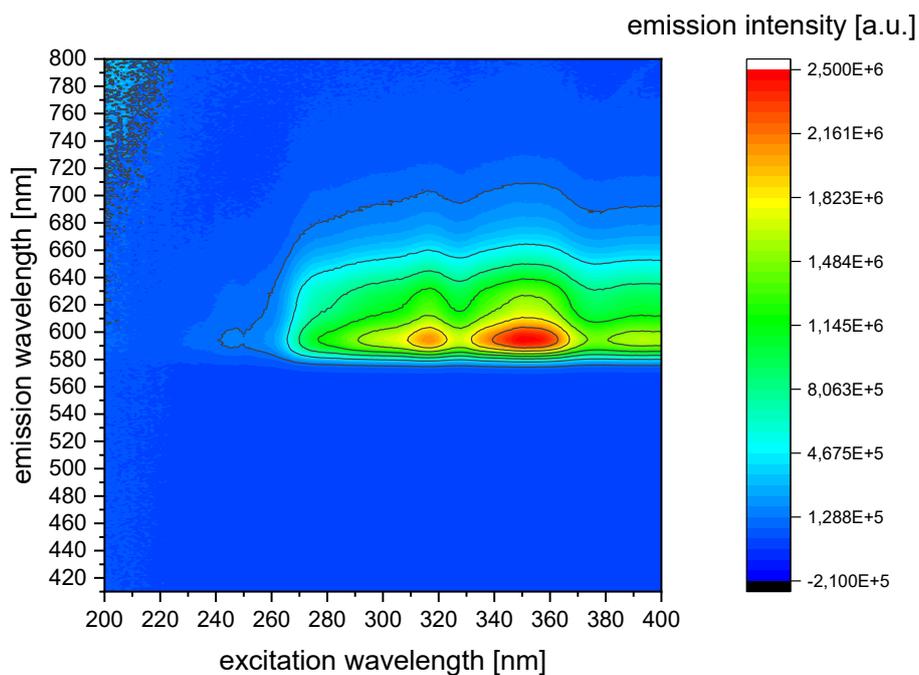


Fig. 8 Two-dimensional fluorescence mapping of the dye Rhodamine B in aqueous solution; with 0.05 g/L dye concentration.

The fluorescence mapping of a cotton fabric after application of Rhodamine B from the sol-gel recipe is presented in Figure 9. Here, a maximum emission is determined for a wavelength of around 620 nm if excitation is done with UV light from 350 nm to 390 nm. For this, the fluorescence properties of Rhodamine B on textile application are different compared to the fluorescence of the dye in aqueous solution.

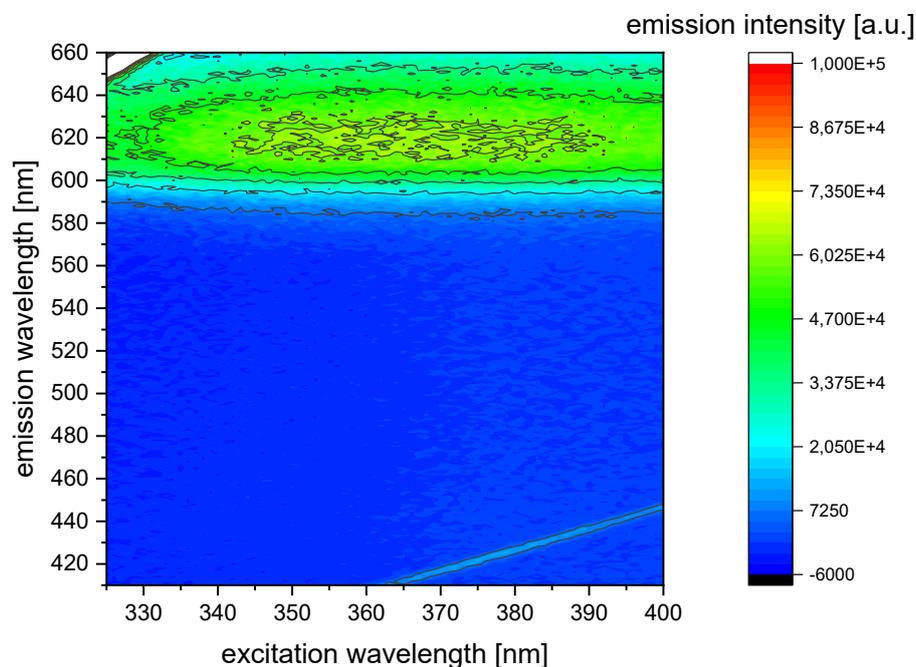


Fig. 9 Two-dimensional fluorescence mapping of a cotton fabric with applied Rhodamine B from iSys HPX; with dye concentration of 0.5 wt-% in the applied recipe.

To evaluate the different fluorescence properties, fluorescence spectra of differently prepared Rhodamine B solutions and all textile samples are recorded. These fluorescence spectra are taken from an excitation at 380 nm, because of the practical relevance of UV light from this spectral area.

Figure 10 presents the fluorescence spectra of Rhodamine B in water. The strong influence of dye concentration on the intensity of fluorescence is obvious. Also, the position of maximal fluorescence emission in the spectra is significantly influenced by the dye concentration. Rhodamine B, like other polymethine dyes, is known for forming compounds like dimers, trimers and also larger aggregates in solutions. In such molecular composites, absorption coefficients differ in their size and spectral distribution as well as the fluorescence emission and respective quantum yields. These effects are explained by the exciton theory, which was introduced by Kasha and others [59]. Depending on the orientation of the transition dipole moments μ of the aggregated monomers in an oligomer, the electronic ground state is lowered in energy due to an additional intermolecular perturbation potential caused by the van der Waals interactions between the molecules. In the excited state a case distinction is made in such, that the perturbation term in the Hamiltonian is constructed as y'^*y or y^*y' for the different excited states y' in each one of the involved molecules. This leads to an energetical splitting of the excited states. As a result, the excited state of a dimer consists of two energy levels; one is of lower and one of higher energy than the original excited state of a monomer.

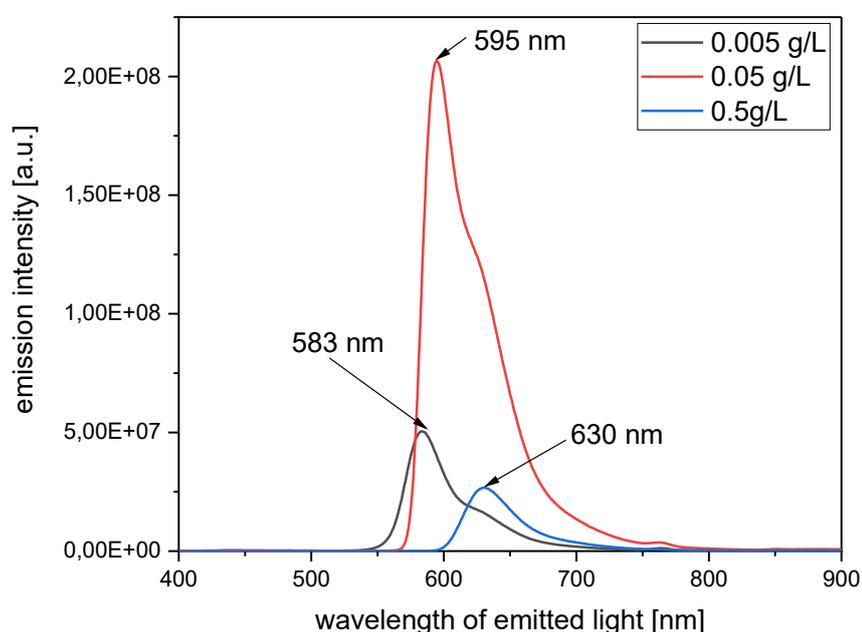


Fig. 10 Fluorescence emission spectra water-based solutions of Rhodamine B with different concentrations (0.005 g/L, 0.05 g/L or 0.5 g/L). The excitation is performed with light of 380 nm.

Such construction of the di- and oligomeric states suggests a linear combination of molecular orbitals. However, in fact the model is a vector-based approach, combining the different (vectorial) transition dipole moments. Depending on the orientation of these transition dipole moments, the aggregates can be classified: For parallel oriented μ , H-aggregates are found, and for linear arrangements of μ , the composites are called J-aggregates. In H aggregates only parallel μ vectors (in contrast to the antiparallel ones) lead to a non-zero oscillator strength, which corresponds to the higher energy level. Therefore, H-aggregates show a hypsochromic absorption and fluorescence. However, fluorescence from that level is forbidden, so H-aggregates lead to fluorescence quenching. DFT calculations suggested a quenching mechanism based on internal conversion of the intramolecular excited state to a charge transfer state in the dimer. The relaxation of the latter is non-radiative [60].

In J-aggregates the situation is vice versa: The antiparallel arrangement is of higher energy, so only the lower energy level offers a non-zero oscillator strength leading to a bathochromic shift of absorption and fluorescence in such aggregates.

Since Rhodamine B carries a carboxy group, one could estimate that pH may influence fluorescence and absorption behavior too. For this, Rhodamine B fluorescence spectra were recorded in the liquid phase at different pH 4-7. These spectra do not show an influence of the pH value on the absorption behavior of investigated dye solutions. For this, pH variations in the finishing liquor or at the fabrics themselves can be excluded as origin for the spectral properties of the materials. This finding is backed by the literature, where above pH 5 and 4×10^{-3} mol/l 70% of the dye dimer and above 2×10^{-2} mol/l 60% trimer was found in the solution [61].

The fluorescence spectra of prepared textile samples are presented in Figures 11 to 13. Figure 11 shows the spectra of the pure aqueous finishing at different Rhodamine B concentrations. A strong correlation of the fluorescence intensity with the dye concentration is visible, as well as a concentration dependent bathochromic shift of the peak emission wavelength. Similar effects can be seen in iSys HPX finished fabrics (Figure 12), but the fluorescence intensity in these spectra is significantly higher compared to the water-based finishing (Figure 11). This increase is even higher for fabrics with pure iSys HPX finishing (Figure 13).

Furthermore, the dependency of the fluorescence intensity and the dye concentration was found not to be linear and the intensity ratios between the different treatments at any given dye concentration was also not constant (Figure 14). More precisely, at higher dye concentrations the influence of the iSys HPX additive on the fluorescence intensity was found to be decreasing.

The bathochromic shift of the emission maximum exhibited a strong positive correlation with the dye concentration. Although the data accuracy seems not to be sufficient to judge if a linear dependency does exist in particular, a trend to larger shifts of the water based finished samples seems to be detectable (Fig. 15).

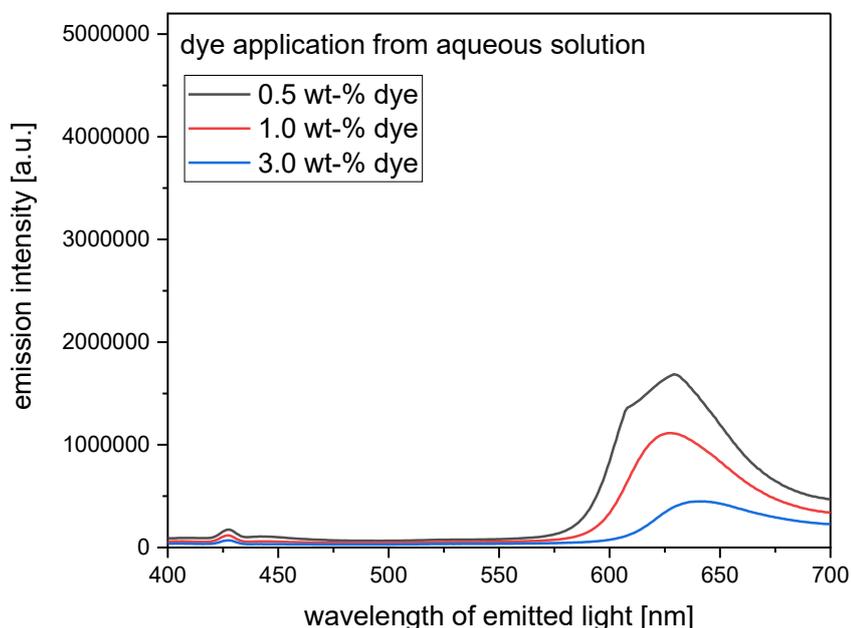


Fig. 11 Fluorescence emission spectra of cotton fabrics with Rhodamine B applied from aqueous solution with increasing dye concentration – (0.5 wt-%; 1 wt-%; 3 wt-%). The excitation is performed with light of 380 nm.

The observed spectral and intensity fluorescence variations in the study can be explained by the formation of aggregates in solution and on the samples. The addition of iSys HPX may further influence the aggregation behavior of the dye on the fabrics. The decreasing fluorescence intensity with the applied dye concentration is therefore originated by increasing aggregation of the dye molecules. It is assumed that H- and J-aggregates are formed which leads to a decrease in overall quantum efficiency and to a red shift of the emission spectrum, probably due to combined fluorescence of few monomers

and J-aggregates. Also, a contribution of the absorption spectra is possible, since the absorption maximum by the aggregate formation so less of the excitation of 380 nm used in this study is absorbed, leading to a lower fluorescence signal.

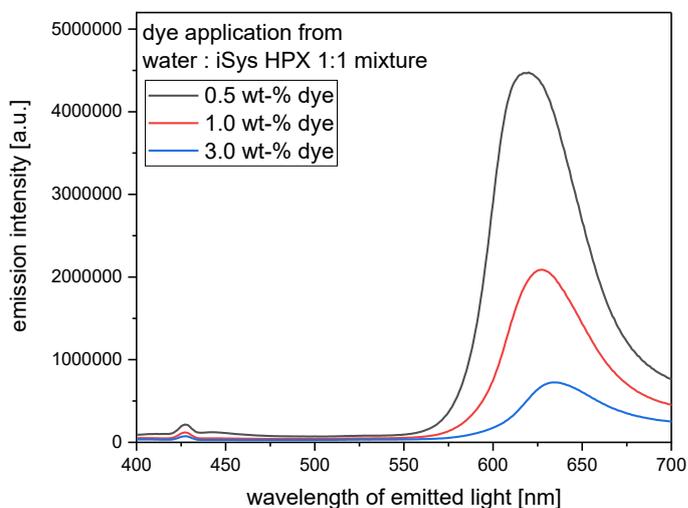


Fig. 12 Fluorescence emission spectra of cotton fabrics with Rhodamine B applied from mixture of water and iSys HPX (ratio 1:1) with increasing dye concentration – (0.5 wt-%; 1 wt-%; 3 wt-%). The excitation is performed with light of 380 nm.

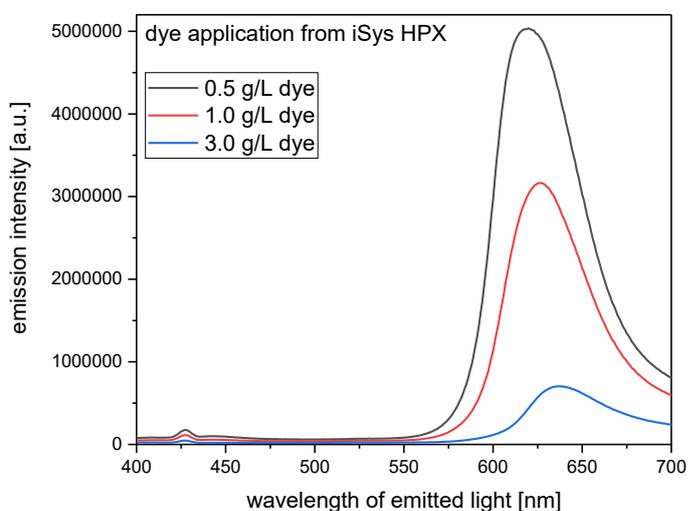


Fig. 13 Fluorescence emission spectra of cotton fabrics with Rhodamine B applied iSys HPX with increasing dye concentration – (0.5 wt-%; 1 wt-%; 3 wt-%). The excitation is performed with light of 380 nm.

Interestingly, in the present study the addition of iSys HPX increases the fluorescence intensity significantly, while the red shift of the fluorescence seems to be altered less. However, Figure 15 may show a trend to a less extended bathochromic shift. Since the iSys-HPX is a sol-gel product it can be suggested that formation of aggregates is significantly reduced by incorporating monomeric dye molecules into the sol-gel matrix, which would prevent the buildup of H-aggregates and therefore less quenching is observed. Such a reduced dimerization of dyes embedded in sol-gel matrices is earlier reported for materials used in optical applications [62, 63].

In the recent investigation on coated textile substrates, the effect vanishes at higher dye concentration because the available interstitial space in the so-gel network may be saturated and additional dye

molecules would form H-aggregates again. Furthermore, in H-aggregates the fluorescence is quenched by internal conversion, but absorption is more or less unaltered. Therefore, at higher dye concentrations less excitation intensity is available to be absorbed by the assumed monomers incorporated in the sol-gel matrix.

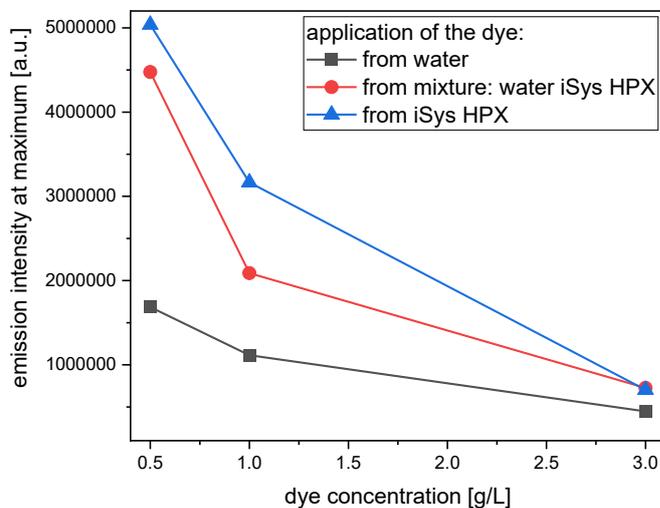


Fig. 14 Emission intensity at the maxima of fluorescence spectra of cotton fabrics with Rhodamine B as function of applied dye concentration. The image compares the three different types of dye recipes.

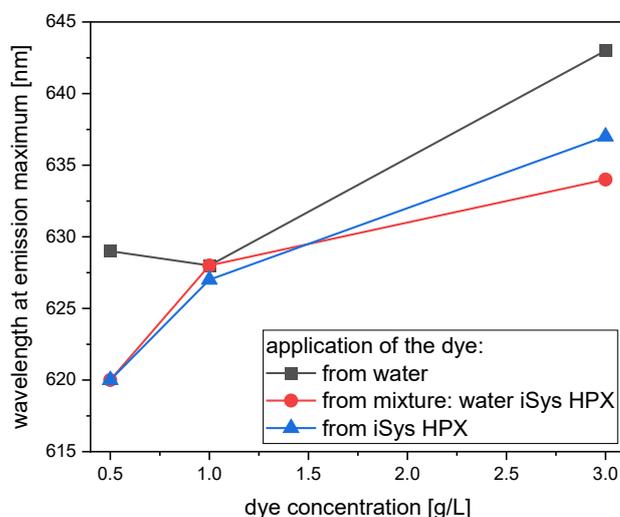
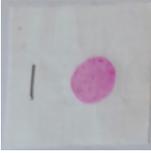
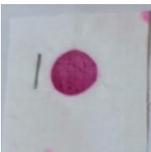


Fig. 15 Wavelength at the emission maxima of fluorescence spectra of cotton fabrics with Rhodamine B as function of applied dye concentration. The image compares the three different types of dye recipes.

3.4 Rubbing stability

The rubbing stability of prepared colored textile samples is determined as dry and wet rubbing fastness. The results of rubbing tests are presented in the following Tables 1 to 3. Samples prepared from Rhodamine B solution without any addition of the sol-gel agent exhibit the lowest fastness grade of 1 – even for dry rubbing test and preparation with lowest dye concentration. Probably for those samples a significant amount of dyestuff is not properly fixed on the fibers and instead deposited on top of the fibers. This deposited dyestuff can be easily removed by the rubbing test.

Table 1. Rubbing fastness of Rhodamine B containing cotton samples. Shown are cotton test fabrics after the rubbing test. The Rhodamine B is applied on the fabrics from aqueous solution with increasing dye concentration.

Concentration of Rhodamine B (wt-%)	Dry rubbing fastness		Wet rubbing fastness	
	Rubbed cotton test fabric	Fastness grade	Rubbed cotton test fabric	Fastness grade
0.5		1		1
1.0		1		1
3.0		1		1

Significantly better rubbing fastness is reached with the combined application of Rhodamine B and the sol-gel product together (Tables 2 and 3). For all samples, the dry rubbing fastness is significantly better compared to the wet fastness. Also, lower applied dye concentrations lead to better rubbing fastness, resulting even in highest fastness grades of 4 to 5.

Table 2. Rubbing fastness of Rhodamine B containing cotton samples. Shown are cotton test fabrics after the rubbing test. The Rhodamine B is applied on the fabrics from mixture of iSys HPX and water 1:1 with increasing dye concentration.

Concentration of Rhodamine B (wt-%)	Dry rubbing fastness		Wet rubbing fastness	
	Rubbed cotton test fabric	Fastness grade	Rubbed cotton test fabric	Fastness grade
0.5		5		2
1.0		2		1
3.0		1		1

The improved rubbing stability can be explained by the embedding of the dye molecules inside a sol-gel matrix which is deposited on the cotton fabric [29-31]. By this, embedding a certain protection against rubbing is introduced. This statement is especially valid for low dye concentrations, because here the

ratio of embedding sol-gel matrix to embedded dye molecules is higher. Advantageous is here, that with the lower applied dye concentration the higher fluorescence emission is recorded.

Table 3. Rubbing fastness of Rhodamine B containing cotton samples. Shown are cotton test fabrics after the rubbing test. The Rhodamine B is applied on the fabrics solved in iSys HPX with increasing dye concentration.

Concentration of Rhodamine B (wt-%)	Dry rubbing fastness		Wet rubbing fastness	
	Rubbed cotton test fabric	Fastness grade	Rubbed cotton test fabric	Fastness grade
0.5		4		2
1.0		3		1
3.0		1		1

4 Conclusions

The combination of fluorescence dyes and commercially available sol-gel recipes for treatment of textile materials is possible. However, the application of Rhodamine B as fluorescent dye in textile finishing is challenging due to the formation of aggregates at relevant dye concentrations which leads to a visible deterioration of the color impression, with respect to the fluorescence spectra. This effect can be mitigated by the use of sol-gel additives, which seem to inhibit the aggregation behavior to some extent. Nevertheless, advantageous is that by combination with sol-gel recipes the fluorescence intensity is improved even for low dye concentrations. Also, the fastness to rubbing is improved by the sol-gel application. By this, the current study can be an interesting starting point for the development of a new kind of fluorescent textile material.

Author Contributions

Wang Yuan: sample preparation, investigation and spectroscopic measurements in the frame of her master thesis at Hochschule Niederrhein; Thomas Grethe: supervision, writing, review and editing; Boris Mahltig: supervision, writing, review, editing, spectroscopic and microscopic measurements. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

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