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Fast Response Photochromic Textiles from Hybrid Silica Surface Coating

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Abstract: In this study, a hybrid silica sol-gel embedded with a photochromic dye has been applied to wool fabric to form a photochromic coating. The treated wool fabrics showed very quick photochromic response. Five different silanes have been used as the silica precursor, and the resultant coating showed slight differences in photochromic performance, fabric washing fastness, and surface hydrophilicity. However, the silica type had a considerable influence on fabric handle property. The silica matrix from the silane containing a long alkyl chain had a very little influence on the fabric handle and better photochromic performance than those from other different silane precursors.

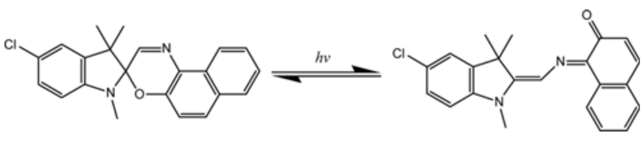
Keywords: Photochromic dyes, Photochromic fabrics, Silica sol-gel, Surface coating, Wool fabrics

Introduction

Photochromic compounds are of interest in both science and industry for their unique characteristic of changing colour reversibly in response to stimulation from light [1,2]. This material has been in use in ophthalmic lenses and potential applications can be found in areas such as rewritable optical recording media [3-7], data memory [8-14], optical switches [11,13,15-17], and sensors [18-21]. The use of photo-chromism in textiles will create new opportunities to develop smart garments capable of blocking UV radiation and/or sensing environmental changes, as well as displaying fancy colour-changing effects [22-25].

Colour changes in photochromic compounds typically come from the shift of optical absorption due to molecular structure or conformation change. For example, spirooxazine dyes open their oxazine ring upon UV irradiation, to form a merocyanine structure that has a larger conjugated molecular system (Scheme 1). As a result, the optical absorption is shifted from the UV to visible region. After the UV exposure, the "ring-open" isomer returns automatically to the "spiro" structure hence decolouration, because the "spiro" isomer is the thermodynamically stable state. The colouration and decolouration of the photochromic dyes is affected by both the physical and chemical environments surrounding the photochromic molecules [26]. A fast optical response can be achieved if the photochromic transformation is free of steric hindrance that requires free volume around the molecules.

Photochromic textiles have been prepared via conventional dyeing techniques to insert photochromic molecules into fibers [27,28] or via applying microcapsules containing photochromic dyes onto textile surfaces [29,30]. The dyeing processes tends to have problems such as low colour-switching speed and poor stability, because the rigid polymer matrix restricts the photochromic transformation [31], while the surface coating of photochromic microcapsules usually imparts harsh handle to the fabrics which adversely affects the comfort characteristics of garments made from the fabric.



Scheme 1. The photochromic effect.

Recently, hybrid organic-inorganic silica with embedded dyestuff in the matrices from a sol-gel process has shown great potential in the preparation of functional coatings for photonic [32-34] and sensor [35-37] applications. The embedded dyes have shown significant improvement in washing fastness [38], and the light fastness is enhanced as well [39, 40]. Using a sol-gel method, different types of substrates like glass, paper or textile can be coated [41-43].

Silica contains a huge number of "nano-sized" tiny pores which provides an ideal host for photochromic molecules [44], as these tiny pores offer sufficient free volume for the photochromic molecules to accomplish the photochromic transformation. Although silica embedded with a photochromic dye has been used to produce functional surfaces on hard substrates, such as glass and plastic film [45-48], its use in textiles is seldom reported. A coating for textile application has special requirements for softness, breath-ability, and durability to withstand repeated surface abrasion and washing cycles.

In this study, we used a spirooxazine and five different silane precursors to produce hybrid photochromic silica coatings on wool fabrics, and examined the effect of silica type on photochromic performance and textile properties. We have found that the photochromic coatings show fast photochromic responses and reasonable bonding strength with the wool substrate and that the silica type affects both the photochromic performance and textile properties.

Experimental

Materials and Measurements

Phenyltriethoxysilane (PhSi), methyltriethoxysilane (MeSi),

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2-(cyclohexenyl)-ethyl-triethoxysilan (CycHSi), tetracetoxysilane (TAS), and 5-chloro-1,3-dyhydro-1,3,3-trimethylspiro [2H-indole-2,3'-[3H]-naphth [2,1-b] [1,4] oxazine] (photochromic dye) were obtained from Aldrich. Vinyltrimethoxysilane (VinSi) and octyltriethoxysilane (OctSi) were provided by Degussa. Ethanol was purchased from Asia Pacific Specialty Chemicals. All chemicals were used as received.

The photochromic effect was recorded based on a purpose-made device consisting of a UV-light source (DH 2000-BAL, wavelength range is 230-2000 nm, continuous), an optical fiber UV-VIS spectrometer (SUB4000 UV-VIS, Ocean Optics), and a personal computer. The differential absorption, $\Delta A=A_{\text{light}}-A_{\text{dark}}$ between the fabric with and without UV irradiation is used in all optical absorption spectra, unless otherwise indicated.

The washing fastness was tested using the washing procedure for Test C described in Australian Standard (AS 2001.4.15). The abrasion fastness was tested by the Martindale method, with 9 kPa loading on the fabric and the abrasion cycle under 100r, 300r, 500r, and 1000r, separately.

The flexural rigidity was measured by a M003B Shirley Stiffness Tester according to BS 3356 BS9073 part 7 and ASTM D1388. In the test, a rectangular fabric strip supported on a horizontal platform of the stiffness tester was extended in the direction of its length, so that an increasing part overhangs and bends under its own mass. When the tip of the specimen reaches a plane passing through the edge of the platform and inclined at an angle of 41.5 °, the bending length is recorded (Scheme 2).

The bending modulus Q (g/cm^2) was calculated according to equations below:

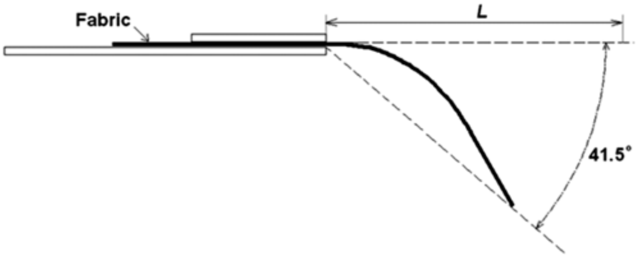
$$Q = \frac{12G \times 10^{-3}}{g^3} \tag{1}$$

$$G = MC^3 \tag{2}$$

Here G (mg·cm) is flexural rigidity of fabric, M (mg/cm^2) is the areal density of the fabric. C (cm) and g (cm) are bending length and fabric thickness, respectively.

Silica Sol Preparation and Fabric Coating

The silica sol gel was prepared typically by mixing alkyloxysilane, tetracetoxysilane (TAS), water, and ethanol with the ratio of 1:1:7:10 (mol) and stirring intensively at room temperature for 24 h. 0.5 % photochromic dye-ethanol solution was then added to equal volume of the sol-gel solution and stirred at ambient temperature for 20 min. to give a homogeneous solution. A piece of wool fabric (20×20 cm^2) was dip-coated with this dye-containing sol solution and dried at room temperature. The coated fabric was then dried and cured at 110 °C for 10 min. This treatment effectively stabilized the photochromic properties but avoided thermal degradation of wool fibers.



Scheme 2. Illustration of the concept for characterizing the fabric bending length.

Results and Discussion

Optical Properties of Photochromic Wool Fabric

The optical absorption of the photochromic dye in ethanol is shown in Figure 1(a). Without UV irradiation, the solution has no apparent absorption in the visible region, 400~750 nm. However, a strong absorption peak occurred with the maximum around 620 nm when the solution was exposed to UV light. A similar result was also found for the wool

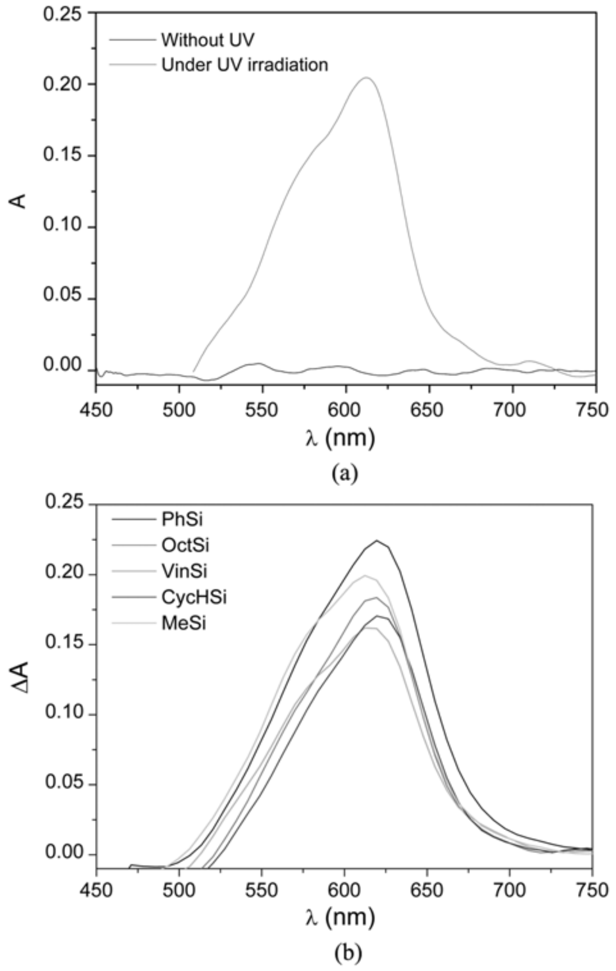
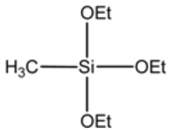
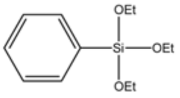
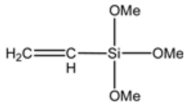
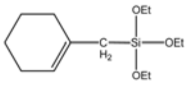
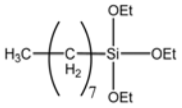


Figure 1. Optical absorption of the photochromic dye in ethanol (a) and photochromic fabrics (b).

Table 1. Photochromic performance and fabric properties of the photochromic fabrics

	Sample	Percursor structure	ΔA^a	$t_{1/2}$ (s)	$t_{1/2}$ (s)	Abrasion fastness (%)^b	Washing fastness (%)	Bending modulus (g/cm^2)		CA (°)
								Warp	Weft	
Silica-coated fabrics	MeSi		0.22	18	22	50.14	29.75	12.9	2.9	139.5
	PhSi		0.24	6	28	57.03	38.16	42.5	8.8	143.7
	VinSi		0.17	5	5	55.00	42.86	20.9	2.8	143.8
	CycHSi		0.20	16	16	63.97	68.27	2.4	0.57	147.9
	OctSi		0.24	3	4.5	55.96	37.31	2.0	0.57	145.1
Control	–		0	–	–	–	–	0.41	0.035	126.5

^{a}The absorption at 620 nm, ^{b}the percentage decrease in ΔA after 1000 abrasion cycles.

fabrics coated with a thin coating of silica containing the photochromic dye, as depicted in Figure 1(b).

After treated with the same concentration of photochromic dye but a different silica sol, the fabrics showed a similar optical absorption spectrum but varied slightly in the absorption intensity. The chemical structures of the silane precursors and the intensity of the absorption peak at 620 nm are listed in Table 1. The photochromic coating using PhSi as the silica precursor showed the strongest optical absorption, while the coating using VinSi has the lowest absorption intensity. The fabrics treated by other silica showed medium absorption intensity between those treated by PhSi and VinSi. The differential absorption intensity based on the PhSi coating was in the range of 0~0.07.

By recording the optical absorption change at 620 nm, the optical response properties can be understood. The optical response curve of the photochromic fabric using OctSi as silica precursor is shown in Figure 2. Starting from the UV irradiation, the fabric took about 28 seconds to reach a saturated absorption, and in the first 20 seconds the absorption increased to 90 % of the saturated absorption. After the UV exposure, the fabric became colourless within 2 minutes, indicating a rapid colour fading. Like in photochromic glass [44], this photochromic switch is reversible and can be repeated for at least 450 cycles, and the fabric still showed the photochromic function after two-year storage in the dark at the ambient conditions.

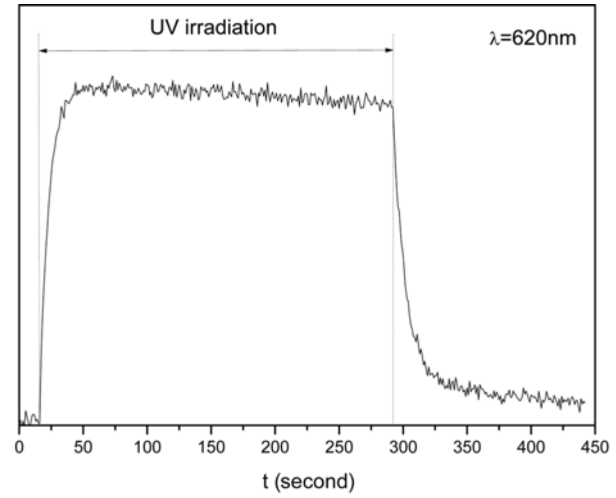
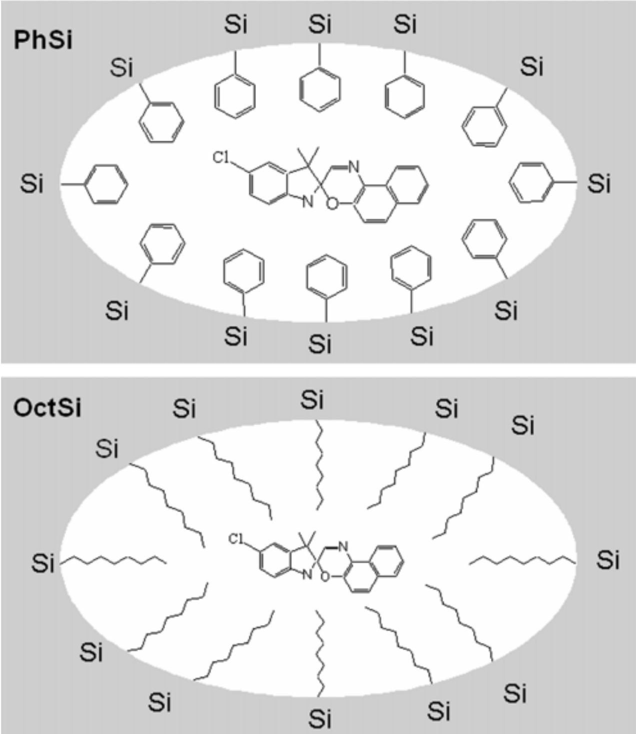


Figure 2. Colouring and decolouring curve of the photochromic fabric (from OctSi).

The optical response and the fading speed can be expressed by the UV exposure period to reach half of the saturated absorption ($t_{1/2}$) and the initial fading period to reduce half of the absorption ($t'_{1/2}$) after UV exposure, respectively. The $t_{1/2}$ and $t'_{1/2}$ data for the photochromic fabric treated with different silica matrices are also listed in Table 1. The quickest responding and fading speeds were found for the photochromic fabric using OctSi as the matrix material. The

MeSi matrix resulted in reduced optical response time and fading speed. By comparison, the PhSi matrix had a comparable coloration speed to the OctSi, but a slower decolouration speed. However, VinySi had a similar coloration speed to PhSi, but the decolouration speed is much shortened.

As with a rigid polymer matrix, the photochromic dye is usually affected by the free volume, the polarity and the glass transition temperature of the polymer matrix. A similar effect could also be found in the silica matrix. The main difference between the precursors is the functional group that covalently connects with the Si atom. As these functional groups normally aggregate on the pore surface forming an organic shell within the silica matrix, their chemical structure affects the pore size and flexibility. A short alkyl group, such as a methyl group, could result in a rigid surface, while a long alkyl chain could form a flexible shell, but have an influence on the pore volume due to the steric effect. As a result, the photochromic molecules in the OctSi matrix showed higher speed in both optical response and colour fading than that in the MeSi matrix. In contrast, phenyl groups normally form rigid pores, and the pores are enlarged because of the steric effect of phenyl plane (Scheme 3) [49,50]. The quick response speed confirms that the pores in the PhSi matrix have a relatively large volume. However, the photo-chromic dyes in the PhSi matrix show a slow decolouration speed, which could be attributed to the interaction between the conjugated "ring-open" photochromic molecules and the phenyl groups of the silica retarding the decolourization process [45,48,51].



Scheme 3. Dye-hybrid silica networks.

Abrasion Fastness

The SEM images of untreated wool fibers and the photochromic wool fibers before and after repeated abrasion are shown in Figure 3. The wool surface became rougher when the surface was coated with a thin layer of silica. The fiber cuticle was removed after repeated abrasion and the optical

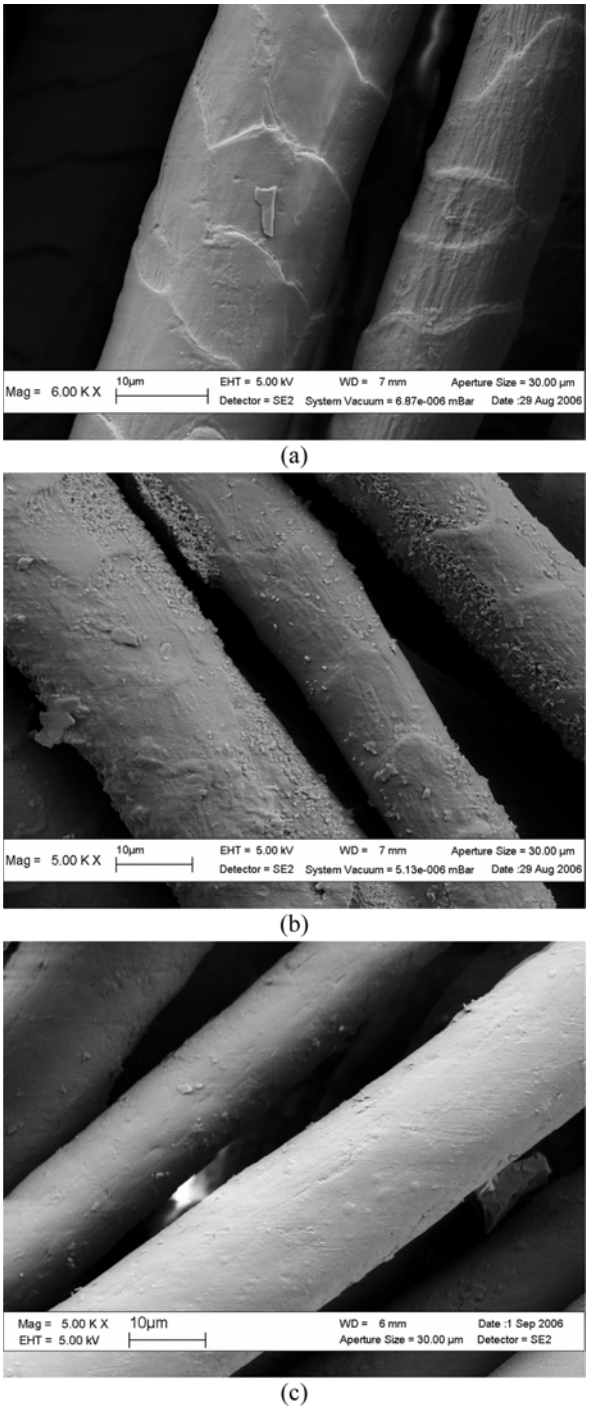


Figure 3. SEM images of (a) untreated wool fibers, (b) photochromic wool fibers, and (c) the photochromic wool fibers after 1000r abrasion (from OctSi).

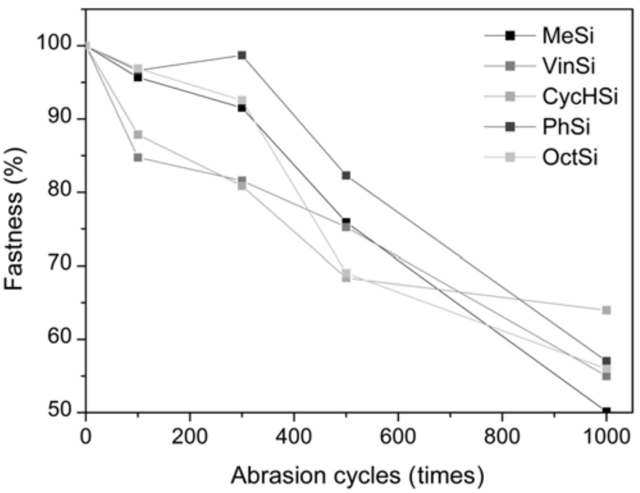


Figure 4. The abrasion fastness verus abrasion cycling.

absorption reduced gradually with the increase in the number of abrasion cycles.

$$\text{Abrasion fastness}(\%) = \frac{\Delta A_2}{\Delta A_1} \times 100\ \% \tag{3}$$

where ΔA_1 and ΔA_2 are the differential absorption intensities of the photochromic fabric before and after the abrasion damage, respectively. As shown in Figure 4, the abrasion fastness is dependent on the number of abrasion cycles. After 1000 cycles of abrasion damage, the fastness for the fabric coated with silica from MeSi, VinSi, OctSi, PhSi, and CycHSi precursors was 50 %, 55 %, 56 %, 57 %, and 64 %, respectively. This indicates that the silica type affects the abrasion fastness.

Washing Fastness

Washing fastness is also a very important factor for evaluating the durability of the photochromic fabric. The optical absorption of the photochromic fabric reduced after a standard repeat washing during the test. This decrease in the absorption intensity can be used to characterize the washing fastness of the photochromic dye.

$$\text{Washing fastness}(\%) = \frac{\Delta A_2}{\Delta A_1} \times 100\ \% \tag{4}$$

where ΔA_1 and ΔA_2 are the differential absorption intensities of the photochromic fabric before and after standard repeat washing, respectively.

The washing fastness data of the photochromic fabrics treated with different silica matrices is listed in Table 1. The silica material affected the washing fastness. The highest washing fastness was the fabric treated with CycHSi as the matrix material.

Fabric Handle

The bending modulus was used to estimate the fabric handle property and the modulus values of the photochromic fabrics are listed in Table 1. The fabrics treated by OctSi and CycHSi have a similar bending modulus to the untreated control fabric. However, the bending modulus was increased considerably when the fabric was treated by PhSi or MeSi. The effect of the silica surface coating on the fabric handle in both warp and weft directions showed a similar trend.

The effect of the silica coating on the fabric handle could derive from the rigidity of the silica matrix, which is affected by the structure of the organic functional groups. The OctSi contains a long alkyl chain that makes the matrix more flexible. As a result, the coating layer has a minimal effect on the fabric handle. When the silica contains a more rigid group, such as phenyl or methyl, the coating layer tends to be more rigid, thus leading to poor fabric handle.

Water Contact Angle (CA)

When the wool fabric was coated with a thin layer of the hybrid silica, the water contact angle was increased and the silica coating prepared from different silica precursors had different contact angle values. As listed in Table 1, the silica containing a vinyl group or a long chain alkyl such as CycHSi and OctSi led to a great increase in the contact angle value, while silica containing methyl or phenyl groups had a smaller increase in the contact angle. The increase in the contact angle value suggests an increase in the fabric surface hydrophobicity.

Conclusion

Results from this study have indicated that hybrid silica containing photochromic dye is a promising coating material to develop photochromic fabric with fast optical response. The chemical structure of the silica precursors used influenced both the photochromic performance and the fabric properties. Photochromic silica coating prepared from a silane precursor bearing a long alkyl chain shows very fast photochromic responses, reasonable abrasion fastness, and minimal effect on the fabric handle. This result can also be used to develop other functional fabrics based on immobilizing the functional compound in silica “nano-porous” matrix.

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