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Sensitive glasslike sol–gel materials suitable for environmental light sensors

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Abstract

New sol–gel based sensitive materials able to detect moderate doses of UV, Vis and near IR radiations have been designed, prepared and characterised. These glasslike detectors are respectively composed by four different sols of inorganic and hybrid organic–inorganic silica matrixes. The sols were prepared from alkoxide (TEOS) and alkylalkoxide (GLYMO) precursors with molar ratios 1:0, 1:1, 1:4 and 0:1, respectively. All the sols were doped with an organic photochromic dye (spiropyran). The detectors characterisation was carried out by means of exposures to natural light under different light intensities (100–3000 lx). The highest sensitivity against the light radiation was found for sols with molar ratio TEOS:GLYMO of 1:1. The time response of detectors is found at about 10 min and their life time is roughly 4 months at least. Moreover, the detectors show good optical reversibility. These sensitive glasslike materials have been designed to be applied for preservation of historical goods. They can detect and evaluate dangerous light doses for the proper conservation conditions of historical materials, which are sensitive or moderately sensitive against light radiation (<600 lx).

Keywords: Sol–gel processes; Spectroscopy; Colour; Glass; Sensors

1. Introduction

During the last decade sensitive materials based on sol–gel technology have demonstrated to be suitable for production of transductors, dosimeters, detectors and sensors.[1–4] Such sol–gel materials can be obtained as small monoliths, thin coatings, fibres, soft gels and even liquid sols. Chemical response, and especially optical response, seems to be the most common way of operation of sensitive sol–gel materials,[5,6] which is attained by doping polysiloxane networks with organic dyes, coordination complexes, lanthanide ions, luminescent species, etc.

The conservation of historical and cultural goods needs the implementation of innocuous protection systems, which are technologically useful during long time for the preservation of the materials that compose such objects. One general protection procedure widely applied to evaluate and control the environment (both indoor and outdoor) is the use of sensors. The sensors show two important advantages: (i) they do not interact directly with the object to be protected and (ii) they give an anticipated response related to the possible damage to be submitted by the object. Over the last decade several studies on the monitoring of indoor environments were carried out. In these cases the concentration of atmospheric pollutants is lower than those of outdoor environments (CO, NO_x, SO_2, O_3, HCHO, etc.).[7,8] The presence in museums and galleries of other environmental parameters, as the light radiation, is an important factor to be taken into account, due to the sensitivity of some of the historical materials exhibited.

A lot of photodegradable objects from the historical and cultural heritage, such as textiles, graphic documents, image supports, statues, stained glass windows, archaeological remains, etc. are exposed in museum halls to natural and/or artificial light. The long exposure to natural light or to high doses of artificial UV, Vis and/or near IR is an environmental parameter that affects negatively the proper conservation of the materials which constitute such objects and art works. The exact limits of lighting, to which these valuable pieces and objects are exposed, must be considered in order to avoid their deterioration.

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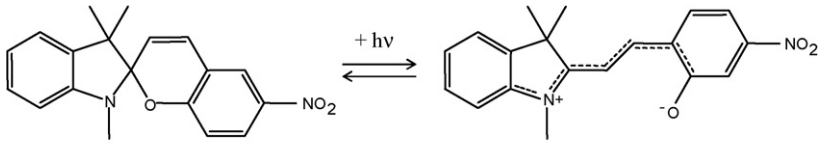

Fig. 1. Chemical structures of the 6-nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyrane-2,2′-indoline] (SP) molecule.

Lighting criteria and its maximum recommended values vary depending on the kind of material to be preserved and on the exposure or conservation conditions outdoor or indoor, respectively. For instance, although for museums a lighting standard is lacking, some determined lighting thresholds are suggested, depending on the sensitivity or photostability of the materials exposed or stored. The materials are usually classified according to their response against lighting: sensitive (lighting resistance threshold up to 50 lx), moderately sensitive (up to 200 ± 50 lx) and moderately resistant (up to 600 lx).[9,10] The object's deterioration due to lighting is estimated by means of the lighting level multiplied by the exposure time. Actually, accumulated lighting doses are the most important cause for photodegradation of the majority of sensitive materials.

The development of chemical sensors for conservation of historical materials, based on optical response against critical lighting levels, is the most adequate strategy to perform a fast, accurate and comfortable evaluation of environmental lighting conditions. This kind of sensors informs not only the lighting for a given moment, but also detects more or less intense lighting changes. Another added value of these sensors is the reversibility, which ensures their reusing.

During the last 20 years, sol–gel procedure has been developed as a synthetic route to obtain glassy and glasslike matrixes at low temperature, making possible the incorporation of different kind of dopants.[11] Among them organic dyes[12–14] and photochromic substances[15,16] should be mentioned, since light sensitive materials with interesting properties can be prepared. Probably, spiropyranes are the most known organic photochromic compounds, which produce merocyanines when irradiated by UV light (Fig. 1).[17,18] The use of organic photochromic compounds as light sensitive dopants in the corresponding sensors or detectors is possible by means of the sol–gel procedure.[19–22] The spiropyranes encapsulation into a glassy sol–gel matrix is an interesting starting point to prepare specific light sensors.[23–25]

The main purposes of the present work are: the design, preparation and characterisation of sol–gel glasslike materials sensitive against light radiation in the visible range and, as far as possible, the production of a reversible and reusable device. Such a sensitive material should modulate its optical response inside the light intensity range allowed for the correct conservation of historical objects exposed or stored in museums. In other words, the goal is the preparation of a detector or sensor to notice quickly and efficiently the environmental lighting with a reasonable response time, in such a way that the information about the risk to which the cultural goods materials are submitted is given as soon as possible, i.e. before the damage is caused. This is a noticeable innovation in comparison with dosimeters (they are not reversible sensors) nowadays used for indoor lighting control. The most known light dosimeters are the *Blue Wool Standard*[26] and those developed by Roemich et al.[27] These dosimeters evaluate the lighting effect due to the exposure of a coloured material to the radiation source and then the decolouring process is studied. In this case exposure times must be as long as those to which the historical objects are submitted and when the detector degradation occurs, the damage of the historical object would be already produced. Finally, in the present research the effect of inorganic and hybrid organic–inorganic sol–gel glasslike matrixes on the sensors properties have been studied (response time, sensitivity, optimal radiation range to observe the sensor change of colour, etc.).

2. Experimental

Four different sols were prepared starting from tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS) and 3-glycidoxypropyl-trimethoxysilane ($Si(OCH_3)(C_5H_{11}O_2)$, GLYMO) as precursors for a polysiloxane glasslike matrix. Such sols were doped with 2.6 wt.% 6-nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyrane-2,2′-indoline] (SP), as a photochromic substance. Molar ratios GLYMO:TEOS:EtOH are shown in Table 1. The precursor's hydrolysis was carried out under acid (HCl) hydro-alcoholic medium. The light sensitive sols (sensors) obtained were homogeneous, transparent and showed pale yellow colour. They were stirred for 30 min to accomplish hydrolysis and favour partial polycondensation reaction. As a reference, a hydro-alcoholic solution containing 0.5% SP was prepared.

Optical response of the sensors prepared and the hydro-alcoholic solution (all of them containing SP) against different natural light doses under room temperature was recorded with a Shimadzu 3100 spectrophotometer. Light intensities were measured by using a luxometer Promax model IL-185. Optical regain (reversibility) of sensors after the exposures was reached submitting the sensors to the darkness. The optical reversibility was studied by recording the corresponding spectra before and after

Table 1
Experimental parameters used for the sensors preparation

Sensor name	GLYMO/TEOS ratio	Molar ratio		
		Alcoxides	Ethanol	Water
GT 1:4	1:4	1	16	4
GT 1:1	1:1	1	16	4
GT 1:0	1:0	1	16	3
GT 0:1	0:1	1	3	4

successive cycles of exposures to 3000 lx for 5 and 15 min under darkness.

3. Results and discussion

Fig. 2 shows the visible absorption spectra of sol GT 1:1 (Fig. 2a) and of the reference hydro-alcoholic solution containing SP (Fig. 2b). The spectra were recorded after exposures to 250 lx for different periods of time (from 0 to 60 min). In both cases the absorption maximum is located in the 535–522 nm range, which corresponds to an intense pink colouring. Such an absorption band is exclusively attributed to the SP dopant molecule, since under its absence no absorption band was recorded throughout the visible range. The optical sensitisation ability of SP when incorporated into the sol as a function of lighting time (Fig. 2a) is higher than when incorporated into the hydro-alcoholic solution (Fig. 2b). This fact can be exclusively attributed to an interaction as a function of exposure time of SP molecules with the polysiloxane network formed after the hydrolysis of the silica matrix precursors and its further polycondensation. However, under the hydro-alcoholic medium, SP photosensitivity is drastically reduced. This may be due to an interaction between water and/or ethanol with SP molecules, which is practically independent of the lighting time. These results confirm the glasslike silica matrix ability as a host for photoactive SP molecules. Such glasslike matrix is not only innocuous for the SP photochromism, but also increases and improves its optical response respect to those from the hydro-alcoholic solution doped with SP.

The lighting intensity influence on the optical response of SP-doped sols as a function of exposure time is shown in Fig. 3. On the ordinate axis the corresponding reduction percentage of absorbance (apparent optical sensitivity, OSa), referred to the intensity of the main absorption maximum (λ = 535 nm), is plotted. Initially, sols GT 1:4, GT 1:1 and GT 1:0 show an intense pink colouring, while sol GT 0:1 shows an orange hue under absence of light. When these sols are irradiated, they become pale pink, salmon and finally clear yellow, depending on the intensity and time of lighting. As can be observed in Fig. 3 (from 100 up to 3000 lx), the higher is the lighting, the higher the optical response of sensors. This means that the sensor changes its colour from intense pink to yellow the more quickly, the higher is the lighting intensity. Furthermore, under such conditions of higher light intensity, the optical response occurs faster (shorter response time). For low intensity lighting (for instance, 100 lx) the sensor colour changes from intense pink to pink (small reduction of absorbance), during a relatively long exposure time (∼45 min). However, for high intensity lighting (for instance, 2000 lx) the sensor colour changes from intense pink to yellow (high absorbance reduction or *bleaching*), with a short response time (∼5 min). Related to the sensors with different molar ratio of inorganic and hybrid organic–inorganic precursors (sols GT 1:4, GT 1:1, GT 1:0 and GT 0:1), their optical response is faster and stronger change of colour occurs when the sol contains GLYMO. In Fig. 3a the optical response of GT 0:1 indicates that exposure times longer than 40 min and intense lightings (3000 lx) are needed to reach a colour reduction at about 80%. On the other hand, in Fig. 3b the corresponding response of

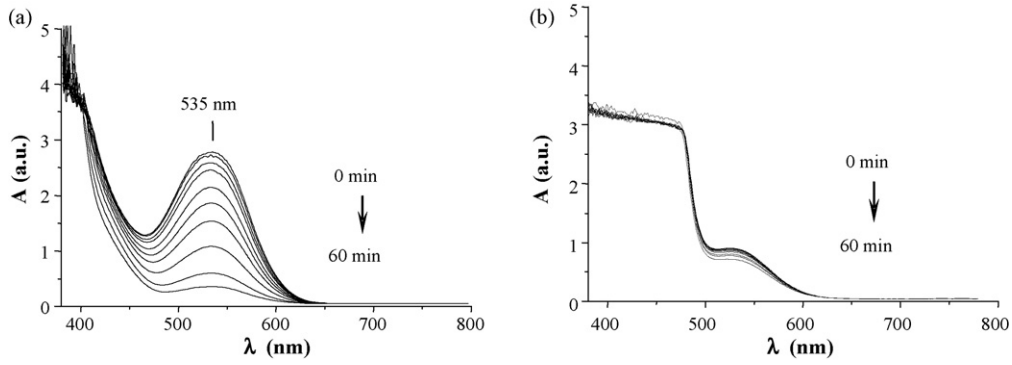

Fig. 2. Optical absorption spectra recorded after different exposure time (0, 1, 3, 5, 10, 15, 20, 30, 45 and 60 min) to a light source of 250 lx. (a) Sensor GT 1:1 and (b) reference hydro-alcoholic solution containing SP.

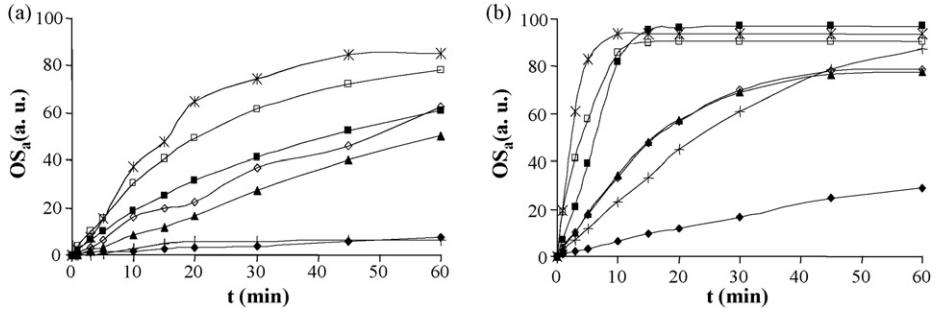

Fig. 3. Apparent optical sensitivity (OSa) measured at the intensity maximum (λ = 535 nm) of the corresponding spectra of sensors: (a) GT 0:1, (b) GT 1:1, as a function of exposure time, for different lighting intensity: (♦) 100 lx, (+) 250 lx, (▲) 350 lx, (◊) 500 lx, (■) 1000 lx, (□) 2000 lx and (×) 3000 lx.

GT 1:1 shows the same colour reduction when the sensor is exposed for 10 min (or even shorter time) to lighting in the 1000–3000 lx range. Therefore, sensors containing GLYMO are more sensitive against the light radiation (sols GT 1:4, GT 1:1 and GT 1:0), in comparison with sensors containing only TEOS as silica precursor (sol GT 0:1). This phenomenon can be explained bearing in mind the three-dimensional polymeric structure of sol–gel glassy matrixes where SP molecules remain encapsulated. Hybrid matrixes TEOS:GLYMO have higher pore radius due to the organic group of GLYMO molecules, which cannot be hydrolysed nor polycondensed. In this case SP molecules encapsulated into the sol–gel hybrid network would have higher functionality. In the TEOS containing glassy matrix as a unique silica precursor, the pores are smaller and the three-dimensional network formed after hydrolysis/polycondensation is more rigid, hindering partially the quick sensitisation of SP molecules to yield merocyanine under light radiation. These results indicate that glasslike materials containing GLYMO doped with SP (sols GT 1:4, GT 1:1 and GT 1:0) can be used as light sensors with response times shorter than 20 min and light doses between 350 and 3000 lx, approximately. Such a lighting range corresponds to that recommended for moderate sensitive historical objects exhibition in museums and other indoors.[9,10]

The optical behaviour of the sol–gel system doped with SP would not be completely suitable if the sensor were not reversible. Optimisation of materials for sensors technology assumes reusable and time durable transductors. Reversible photosensitivity (photochromism) of the SP-doped sol–gel materials was analysed by means of the following experiment: the sensors (initial colour was intense pink) were exposed to 3000 lx lighting for 5 min (the colour became yellowish) and the absorption spectra were immediately recorded. The corresponding absorption spectra of the same sensors under absence of light were successively recorded for different times, after the previous lighting exposure. Fig. 4 shows the intensity average measured in the spectral maximum at $\lambda = 535$ nm for sol GT 1:1. It can be observed that a spontaneous regain of the optical absorption from yellow to intense pink during a maximum time of ~100 min takes place. This means that the SP-doped material behaves as a reversible and reusable sensor against light.

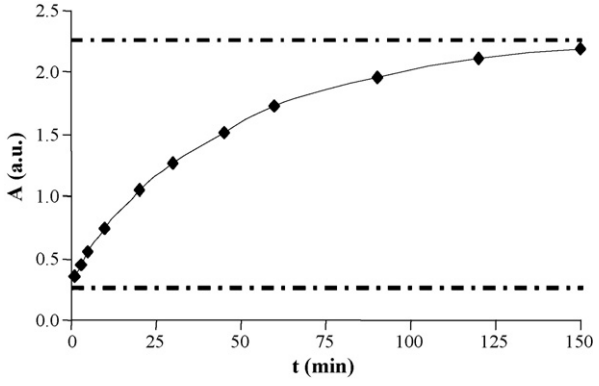

Fig. 4. Spontaneous optical absorption regain of sensor GT 1:1 after exposure to 3000 lx for 5 min and further darkness period. Each experimental point corresponds to the intensity measured at the spectral maximum ($\lambda = 535$ nm).

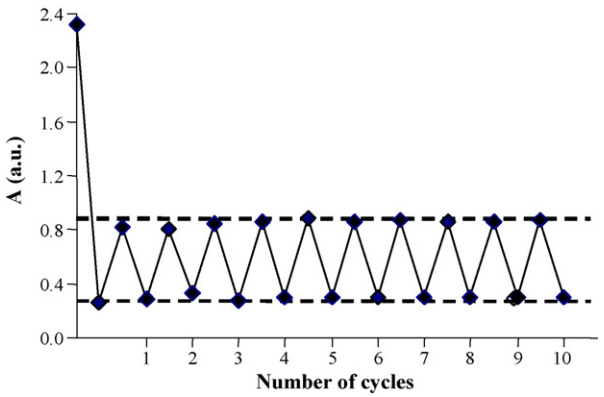

Fig. 5. Variation of the intensity at the optical absorption maximum for sensor GT 1:1 ($\lambda = 535$ nm) as a function of cycles of lighting (3000 lx for 5 min)/darkness (15 min).

With the aim to know better the photochromic properties of the sensors designed, a study about their possible optical fatigue was carried out. Several lighting/darkness cycles were tested as the experimental section indicates. Fig. 5 is a scheme of the GT 1:1 sensor response for successive cycles. It shows the intensity average measured in the spectral maximum at $\lambda = 535$ nm. Dotted horizontal lines were plotted as a guide for the eyes and demonstrate that the sensor optical response is constant, at least during 10 complete cycles, showing fatigue absence. Probably the sensor life time is longer than the tested cycles, which assume a continuous total time service of 180 min.

Finally, calibration curves to co-relate the sensors optical response (in terms of the absorption reduction measured at $\lambda = 535$ nm, sensor *bleaching* from pink to yellow), with the lighting intensity in the 100–3000 lx range were built. In Fig. 6 the results obtained for constant lighting times (10 min) are shown. Such lighting time was selected according to the needs and preferences connected with the particular use to which the sensor will be applied (e.g. environmental lighting evaluation in museums for preventive conservation of historical objects). Fig. 6 indicates that the four sensors prepared are sensitive throughout the lighting range studied, unless for very high light intensities (between 2000 and 3000 lx), due to a saturation of the

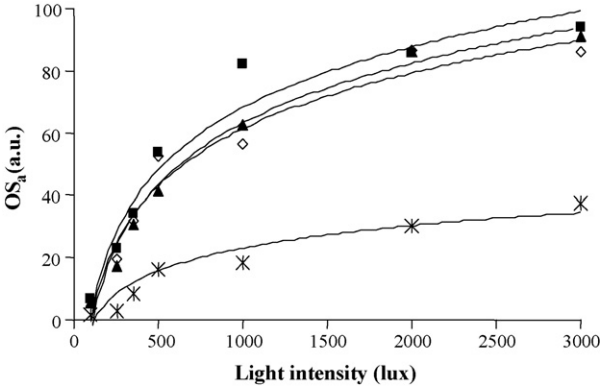

Fig. 6. Calibration curves of the sensors for 10 min exposure time. Evolution of the absorption reduction percentage at $\lambda = 535$ nm (spectral maxima), as a function of lighting intensity: (◊) GT 1:4, (■) GT 1:1, (▲) GT 1:0 and (×) GT 0:1.

optical response. In other words, for lighting above 2000 lx the sensor takes the corresponding yellow colour and the increasing of light intensity does not *bleach* such yellow colour. On the contrary, for low and moderate intensity lighting (between 100 and 1000 lx) the sensor GT 0:1 is the less sensitive, in comparison with the others containing GLYMO. For sensors GT 1:4, GT 1:1 and GT 1:0 the absorbance reduction is higher than for GT 0:1. Molar ratio TEOS:GLYMO seems to be an independent parameter concerning the optical response of the SP molecules encapsulated. Thus, the optical response of the three glasslike materials containing GLYMO (*bleaching* from pink to yellow) is very similar in the 0–500 lx range. Even though all three doped sols behave as useful light sensors, sol GT 1:1 was chosen to accomplish the present optical study, since it clearly shows higher sensitivity, compared with GT 1:0 and GT 1:4.

Optical reversibility (photochromic ability) of the sensor GT 1:1, doped with SP under the conditions expressed above, indicates its special suitability for the application intended. Environmental light monitoring using this sensor can be carried out by two methods: (i) recording the initial visible absorption spectrum of the sensor, sensor exposure, recording the sensor spectrum after exposure and quantitative evaluation of results using the calibration curve; (ii) elaboration of a qualitative colour scale where the relationship colour/light intensity is included and comparison of the sensor colour before and after the exposure.

4. Conclusions

Four sol–gel systems doped with a photochromic spiropyrane (SP) have been designed and prepared. The glasslike materials are sensitive against lighting in the 100–2000 lx range, showing response times between 5 and 30 min. Calibration curves of the *bleaching* percentage of sensors as a function of the lighting intensity have been elaborated. The SP-doped sol–gel systems have demonstrated to be optically reversible without fatigue after several cycles. The sensors optical sensitivity vary depending on the sol–gel matrix developed, which encapsulate the SP molecules. Sensor GT 0:1 (obtained from TEOS) has an inorganic silica matrix and shows lower sensitivity than sensors GT 1:4, GT 1:1 and GT 1:0 (obtained from TEOS and GLYMO) containing a hybrid organic–inorganic silica matrix. For the formulations tested, molar ratio TEOS:GLYMO does not affect in a great extent the sensors sensitivity (especially when TEOS content is not much higher than GLYMO content). Optical response of the three sensors obtained with a hybrid glasslike silica matrix is quite suitable for evaluation of environmental lighting in museums, for preventive conservation of the historical objects exhibited.

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