Journal of the European Ceramic Society 20 (2000) 1621–1628

Eriochrome cyanine doped sol–gel coatings. Optical behavior against pH

M.A. Villegas[a,*], L. Pascual[a], S.E. Paje[b], M.A. García[b], J. Llopis[b]

[a]*Instituto de Cerámica y Vidrio, CSIC, Antigua Ctra. de Valencia, Km. 24,300, 28500 Arganda del Rey, Madrid, Spain*
[b]*Facultad de Ciencias Físicas, Universidad Complutense, Ciudad Universitaria s/n. 28040 Madrid, Spain*

Received 23 March 1999; accepted 6 October 1999

Abstract

Sol-gel silica coatings doped with eriochrome cyanine (EC) have been prepared upon soda lime glass substrates by dip-coating. Sols were obtained starting from a silicon alkoxide hydrolysed in acid medium. EC was added to the silica sol dissolved in water and methyl alcohol to reach 1% of the total weight. Dried coatings showed pH-sensitivity (change of optical absorption and luminescence) when dipped into liquids as well as when exposed to aqueous gases at different pH. On this basis, EC doped coatings could be used as optical sensors, for instance, in analytical probes. Coatings have been demonstrated to be stable enough to UV radiation, at least at handling temperature to be used for optical sensors in common analytical instrumentation. Additional tests pointed out the behaviour of coatings to different chemical media at temperatures below 100°C. Adherence of coatings was evaluated by scratching and peeling, as well as dipping the samples into a cleaner solution submitted to ultrasounds. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Coatings; Optical absorbance; Photoluminescence; Sensors; SiO_2; Sol-gel processes

1. Introduction

Sol–gel glass systems have been used in the last decade as the preferred matrices to introduce or to entrap a lot of chemical species such as biomolecules,[1,2] transition metal complexes,[3,4] luminescent molecules,[5,6] liquid crystals,[7] photochromics,[8,9] noble metals nanoparticles,[10] rare earth ions,[11] organic dyes,[12,13] etc. Since sol–gel glassy network of monoliths, fibers or coatings have a residual porosity if densification is not totally achieved, they seem to be ideal for encapsulation. If the links formed between matrix and dopant are weak enough, a wide variety of molecules, ions or elements may be lodged with a very low reactivity inside the sol–gel system, although able to react as a response to some external change for which they are sensitive. This is the case of organic compounds commonly used as indicators for complexometry or for spectrophotometric determinations.

We especially focus on the incorporation of dopants pH- and redox-sensitive and also capable to show any luminescence when excited in the visible and/or UV ranges. It is well known that the entrapment of dyes with acid-basic properties,[11] which optical behavior has been applied for sensing purposes. Less frequent is the incorporation of reagents with electrochemical activity into sol–gel materials. In this case the results[12] show the best response time for coatings, as a consequence of their short diffusion paths. Indeed, the coatings are redox-sensitive and maintain the electrochemical properties of the dopant dye. Incorporation of organic luminescent dyes into sol–gel systems has been widely proved, particularly for rhodamines and related molecules.[14,15] Such luminescence (fluorescence) arises from photostable dyes immersed in sol–gel glasses and can be applied in solid state lasers with high quantum yield.

The interest of this paper is to combine both pH sensitivity and luminescent response in the same sol–gel system. For that purpose the choice of the organic dye will be according to: (1) adequate optical behavior (absorbance and photoluminescence) of the dye in solution; (2) dye ability to be incorporated in to a sol–gel system, i.e. solubility in aqueous–alcoholic media, compatibility with alkoxides, thermal stability enough to warrant the presence of most of the dye concentration after the drying of gels, etc.; (3) photostability of

---

* Corresponding author. Tel.: +34-9187-11800; fax: +34-9187-00550.

E-mail address: mavillegas@icv.csic.es (M.A. Villegas).

0955-2219/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0955-2219(99)00281-2

the dye doped gel and maintenance of the optical reactivity of dye into the sol–gel material.

The eriochrome cyanine (EC) molecule, frequently used in chemical analysis as an indicator for complexometry,[16] has two carboxilic groups, one hydroxyl, one carbonyl and one sulfonic group which ensure compatibility with polar solvents that are commonly used in sol–gel synthesis. On the other hand, EC shows optical absorbance and luminescence in the visible range with pH sensitivity. Thus, that dye seems to be adequate in order to obtain doped sol–gel coatings with the tailor-made optical properties stated above.

The main objective of the present work was to introduce EC molecules into sol–gel silica based coatings without loss of their optical pH-sensitive properties, as long as possible.

2. Experimental

Doping solution was first prepared by dissolving 1 g EC ($C_{23}H_{15}Na_3O_9S$) in 100 ml of distilled water–methyl alcohol mixture (50 vol%) (intense red color). Sols were prepared starting from tetramethoxysilane ($Si(OCH_3)_4$, TMOS) prehydrolysed with concentrated HCl in methyl alcohol medium. Molar ratio TMOS:H_2O:CH_3OH was 1:4:8. Final sol concentration was calculated to be about 100 g silica per l. EC solution was added to the prehydrolysed TMOS sol, so that the EC content was 1 wt% of the total. After addition while stirring drop by drop, sols showed an intense orange color. Sols were stirred for 30 min at room temperature and then were kept for 15 min before the deposition on substrates. A dip-coating technique was used to obtain thin homogeneous coatings upon common glass slides. The drawing rate from sols varied between 5 and 30 cm min^{-1}.

Coatings were dried at 60°C for three days, and then the thickness was measured by an interference fringe method, since the values are of the same order of magnitude as the wavelength of visible light. The refraction index was measured ($n_D = 1.5124$) by Abbe refractometry using CH_2I_2 as contact liquid and a light source of $\lambda = 589$ nm. Thicknesses of the EC doped coatings studied here were in the 260–310 nm (± 15 nm) range depending on the drawing rate used to prepare the samples. Thicker coatings appeared cracked or peeled indicating that a critical thickness was exceeded.

Optical characterization of EC in solution and EC doped coatings was performed recording absorbance spectra in the 200–800 nm range with a Perkin–Elmer spectrophotometer, model Lambda 9. Luminescence response was monitored in a fluorescence spectrometer Perkin–Elmer LS5 attached with a red sensitive photomultiplier (corrected emission and excitation spectra in the ranges 250–720 and 230–700 nm, respectively). Isothermal photostability of samples was tested by means of exposures to an UV source (300 W) at a distance of 20 cm, as a function of time.

Mechanical behavior of coatings was evaluated with a Leco hardness tester and a Leitz Wetzlar microdurometer by using a hemispheric pin (12.5 mm radius of curvature). The tests were performed following Etienne et al.,[17] in order to create sliding friction damage at the coating surface, which gives information about the adherence to the glass substrate. Other tests to point out the adherence of coatings were carried out by using an ultrasounds bath (frequency 50 kHz) at 30°C that allows the evaluation of the peeling limits of coatings.

3. Results and discussion

All of the as-prepared coatings dried in air at 60°C showed a transparent pink color that changes towards yellowish orange with increased pH from 0 to 14 and independently of the thickness. In fact, Fig. 1 shows the spectra of a doped coating successively immersed into solutions of pH = 0 and pH = 14, together with the corresponding spectra of the prepared EC solution for the two extreme pH. Main acid absorption peak for EC solution was at about 514 nm whereas the basic peaks were located at 434 and 582 nm. Absorption spectra of the EC doped coatings seem similar to those of the EC solutions but less intense, worse defined and slightly shifted to higher wavelengths. As Fig. 1 shows, the spectra display a peak at about 517 nm for acid conditions whereas for the basic ones they show two peaks at 450 and 480–485 nm. In this latter case, the shape of

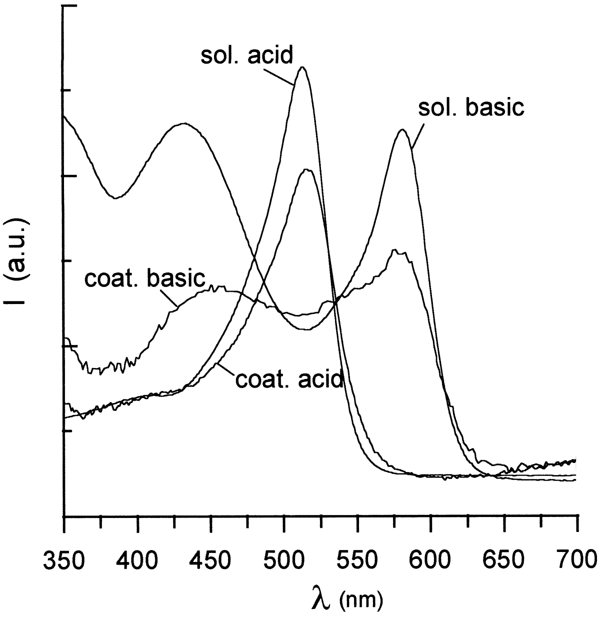

Fig. 1. Optical absorption spectra from EC in solution and EC doped coatings at pH 0 and 14. Spectra are normalised in intensity to clarify wavelength shifts.

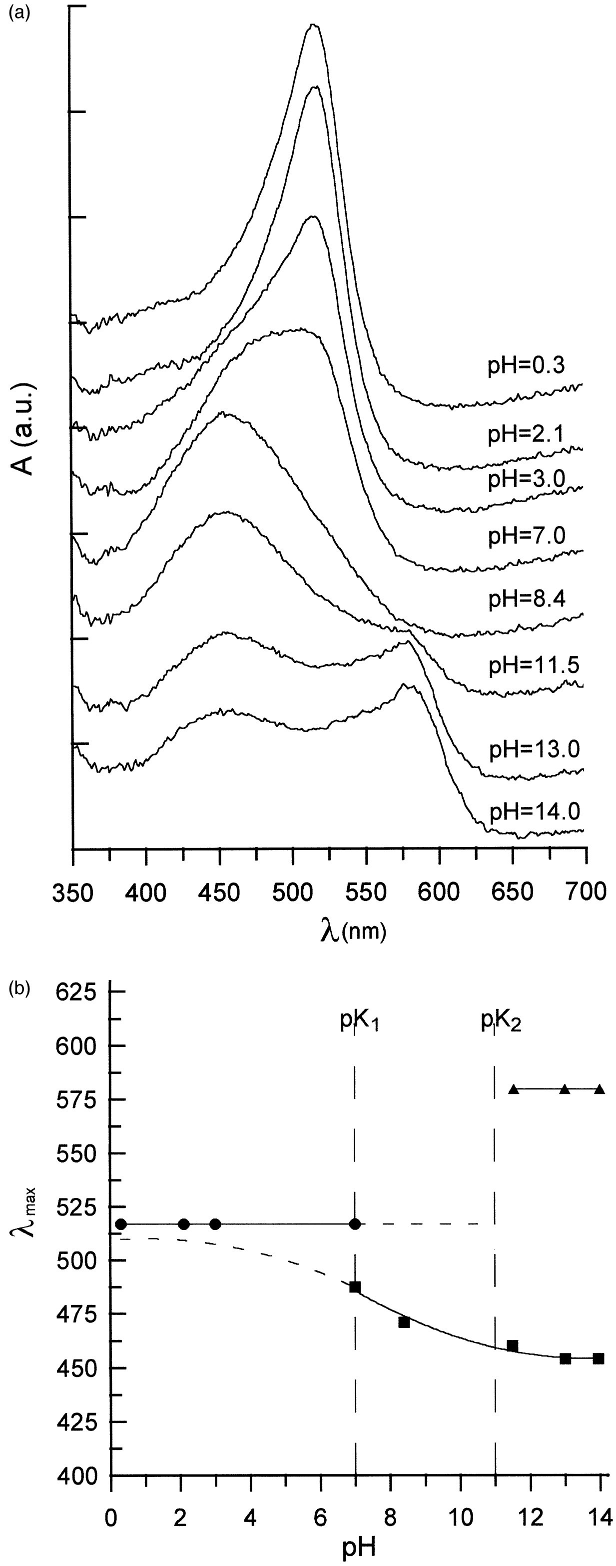

Fig. 2. (a) Absorption spectra from EC doped coating dipped into liquid media with different pH, (b) Evolution of wavelength and intensity of bands from the former spectra as a function of pH.

spectra suggests that some spectral component (at about 514 nm) due to residual acid EC species overlapped the bands observed in basic media.

Changing pH from acid to basic, a series of absorption spectra were recorded after dipping doped coatings during 15 min into buffered solutions. Fig. 2a shows the evolution of the absorption spectrum as a function of pH. Peak positions and relative intensities from the spectra depicted in Fig. 2a were also plotted in Fig. 2b, in order to illustrate the pH sensitivity of EC doped coatings in a similar way as a calibration curve does. At acid and neutral pH, the absorption peak at about 517 nm predominates with decreasing intensities as the pH increases. As Fig. 2a shows, in the $7 < \text{pH} < 11$ range the spectra display peaks at about 480 nm for the lower pH values and move their position progressively to 454 nm as pH increases. With increasing pH above 11, the 454 nm absorption intensity diminishes progressively and a new band peaking at about 580 nm is developed. Following the absorption spectra evolution versus pH depicted in Fig. 2b and bearing in mind the theory of chemical indicators, two relative or apparent constants could be proposed for EC doped coatings. Since pH = 7 and 11 seem to be the limits between which the change of optical absorption spectra is maximized, we define the first EC doped coating constant as $K_{1\text{EC}} = 10^{-7}$ and the second one as $K_{2\text{EC}} = 10^{-11}$. Then, the two ranges for color change (pH sensitivity ranges) are estimated to be around pH = 6–8 and 10–12. At $\text{pH} < 6$ the color visually observed is pink, which corresponds to coordinates (0.524,0.412) (related to illuminant A,[18] calculation as a coating), with dominant $\lambda_d = 591$ nm and purity percentage of 56. At $\text{pH} > 12$ the color is light yellow yielding coordinates (0.484,0.400), $\lambda_d = 606$ nm and 18% of purity. In the range $8 < \text{pH} < 10$ the appearance of coatings is pale orange with intermediate color coordinates, dominant wavelength and purity.

Following a similar procedure to that for the absorption experiments, the EC doped coatings were successively immersed first for 15 min into buffered solutions with pH ranging from 0 to 14, dried at room temperature by a soft paper tissue and then examined in the fluorometer. Fig. 3 shows the evolution of PL spectra (excitation and emission) as a function of pH for an EC doped coating. As can be seen in Fig. 3b, for acid pH in the $0 \leqslant \text{pH} \leqslant 3$ range the emission spectra of EC doped coatings were dominated by a broad emission band peaked between 560–580 nm with an excitation peak at 520 nm. The excitation spectra regard those reported above for the absorption spectra peaked at 517 nm. As the pH of the buffered solution increases from 0 to 14, the emission peak shifted to longer wavelengths (see Fig. 4) and the excitation spectrum showed a progressive decrease in the intensity of the 520 nm component. As Fig. 4 shows, the major variations of the emission peak shift occurred in the $0 \leqslant \text{pH} < 4$ range, while for $\text{pH} \geqslant 4$ there was approximately a linear dependence. Experimental points in Fig. 4 were tentatively fitted by using a sigmoidal function with a linear background, as an

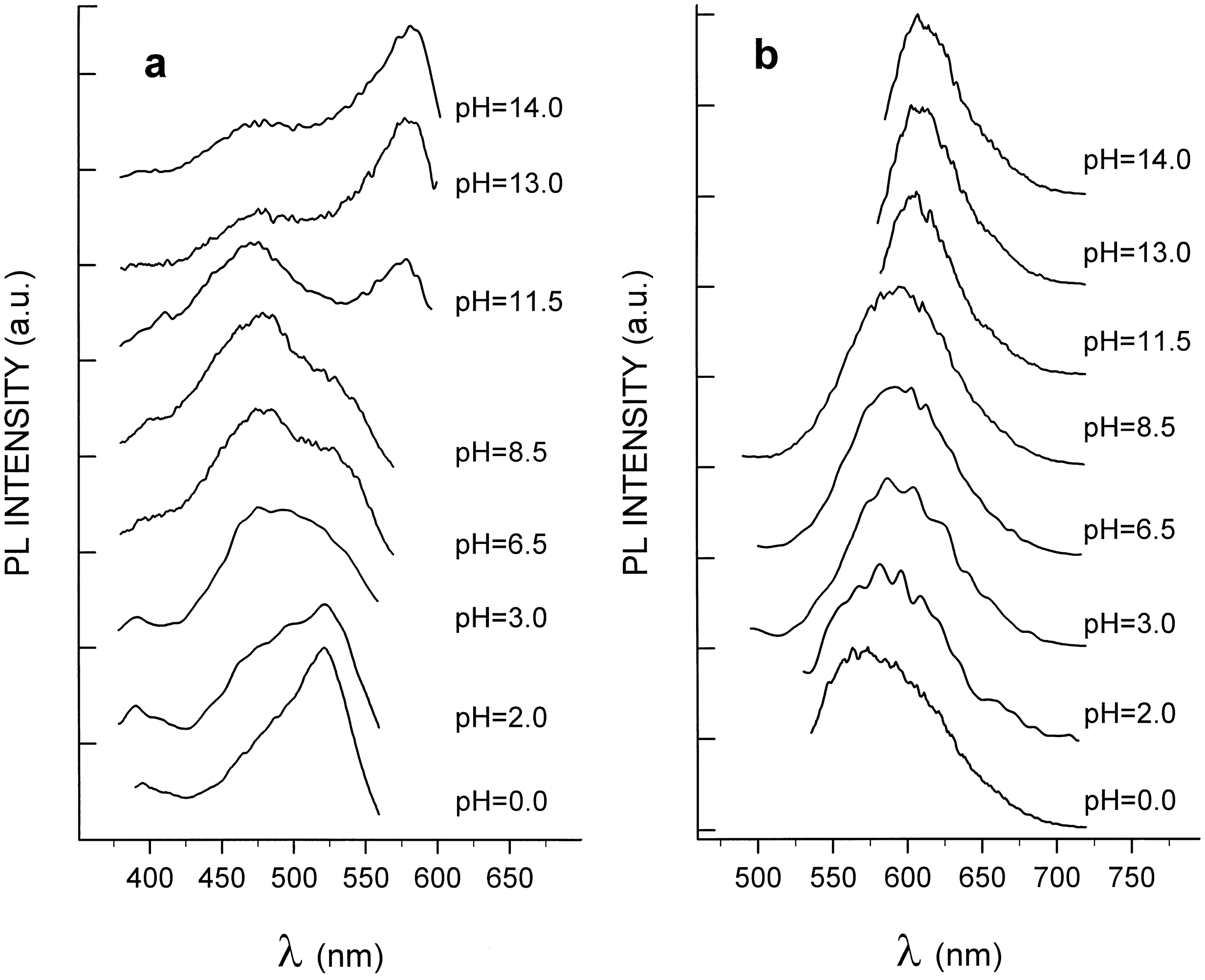

Fig. 3. Normalised spectra of an EC doped coating after being immersed into different buffered pH solutions: (a) excitation spectra and (b) emission spectra.

attempt to evaluate interpolated pH values for experimental emission data from the coating sensor.

Excitation spectra for intermediate values of pH, that is, pH between 6 and 9, exhibited composed shapes with two peaks: the main at 475 nm and the less intense at 520 nm. Then, the I(475 nm)/I(520 nm) ratio increased with increasing the pH up to 10, since for $\mathrm{pH} > 10$ the 520 nm peak is not clearly defined in the excitation spectra (because it was likely hidden in the broad shape of the 475 nm band as is shown in Fig. 3a). This situation is comparable to that described above for the evolution of the absorption peaks at 517 and 454 nm against pH. For $\mathrm{pH} \geqslant 11.5$ the emission spectra displayed the peak between 600 and 610 nm, with excitation spectra exhibiting two well defined peaks: the dominant at 585 nm and the secondary one at 475 nm. The former appeared practically at the same position as those observed in the absorption spectra of EC coatings immersed in buffered solution with $\mathrm{pH} \geqslant 11.5$. Therefore, the results indicate that there are some similitudes in the evolution against pH between the following absorption and excitation pair of peaks: $\lambda_{\mathrm{abs}} \cong 454$ nm and $\lambda_{\mathrm{em}} \cong 475$ nm, $\lambda_{\mathrm{abs}} \cong 517$ nm and $\lambda_{\mathrm{em}} \cong 520$ nm and, finally, $\lambda_{\mathrm{abs}} \cong 582$ nm and $\lambda_{\mathrm{em}} \cong 585$ nm, respectively.

Emission and excitation spectra of the EC coatings immersed in different pH solutions were reproducible after consecutive cycles, being independent of the order of pH changes selected.

An attempt to understand the behaviour of EC molecules versus pH changes could be as follows: the sulphonic group of EC should be the first to be deprotonated, due to the strong acidity of sulphonic acids compared to the other carboxilic acids. That will occur at about $\mathrm{pH} = 7$ ($\mathrm{p}K_{1\mathrm{EC}} = 7$), which is consistent with the known data (7.25) for the sulphonic H^+ equivalent in violet pyrocathecol (indicator molecule similar to EC with one sulphonic group and without carboxilic groups). When pH increases up to 11, the H^+ of the two carboxilic groups of EC should be dissociated ($\mathrm{p}K_{2\mathrm{EC}} = 11$). Since their position in the EC molecule is almost equivalent, both H^+ could be released at the same time. Nevertheless, a decarboxilation of the

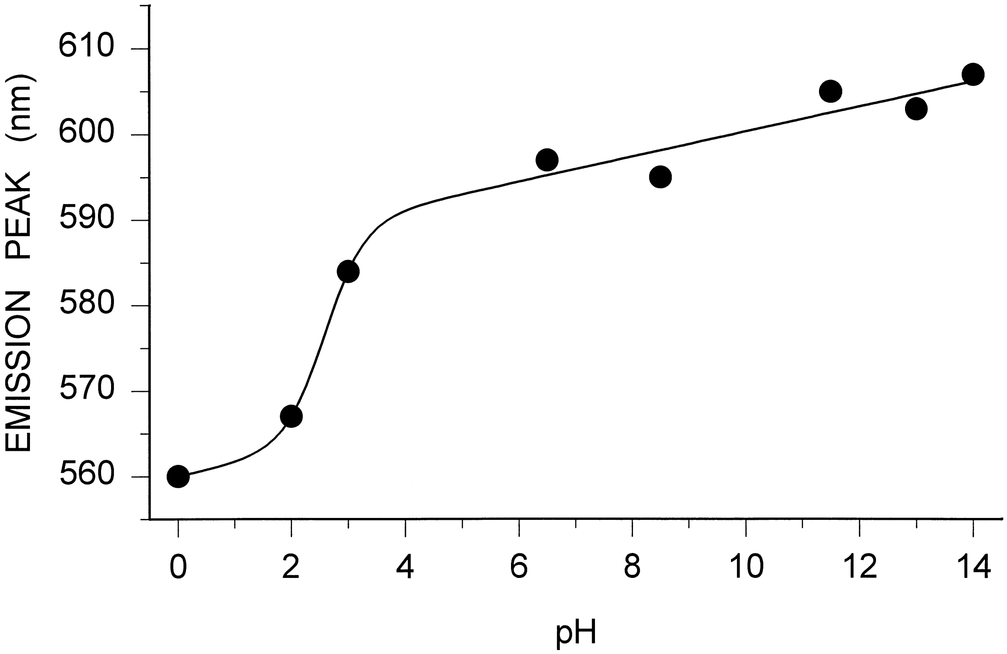

Fig. 4. Peak position of emission as a function of pH at which the EC doped coating was exposed. The full line represents the fit of experimental values to the function

$$P(\mathrm{pH}) = 559.98 + 1.47\mathrm{pH} + \frac{25.73}{1 + \exp\left[-\left(\frac{\mathrm{pH} - 2.59}{0.35}\right)\right]}.$$

β-keto-COOH of EC cannot be discarded, because the drying temperature of samples was just 60°C and the pH during the sol preparation was acid, which favours the well known acid-catalysed decarboxilation of β-ketoacids at 50–60°C (by means of the enolic form of the carbonyl group of EC as an intermediate).[19] Bearing in mind the previous discussion, the absorption band at 517 nm (and the excitation peak at 520 nm) could be attributed to neutral EC species dominant at $\mathrm{pH} \leqslant 7$. In the $7 \leqslant \mathrm{pH} \leqslant 11$ range the mean band at about 500–450 nm (and excitation peak at about 475 nm) could be due to the anionic form of the deprotonated sulphonic group of EC. Finally, at $\mathrm{pH} \geqslant 11$ the anionic form of EC resulting from the deprotonation of carboxilic acid(s) would be responsible for the new absorption band developed at about 580 nm (or excitation at 585 nm) and emission at about 620 nm.

When coatings were exposed to an aqueous vapour at a given pH, the optical absorbance changed. Coatings were maintained for 5 min under aqueous ammonia atmosphere and then removed in order to immediately record the optical spectrum. Further measurements were performed to monitor the spontaneous evolution of coating absorption in air. Fig. 5 resumes the results for an overall time of 6 h, for which the wavelength $\lambda_{\max}$ shifts from 454 to 467 nm, while the intensity remains unchanged. The small shift of $\lambda_{\max}$ means a spontaneous pH regain from 9 to 7 approximately (see Fig. 2b). This allows to conclude that, on the contrary with the reactivity observed in liquid media, the optical absorption of EC doped coatings is not stable when pH-sensitised under an aqueous atmosphere.

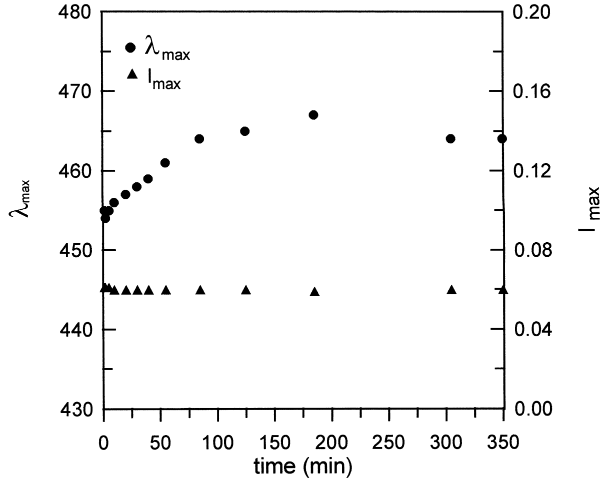

Fig. 5. Spontaneous evolution in air of $\lambda_{\max}$ and $I_{\max}$ of optical absorption for EC doped coatings previously exposed to ammonia atmosphere during 5 min.

As is said above, EC sensitive coatings show stable optical absorption in liquid media with different pH. On the other hand, the process is reversible as Fig. 6 demonstrates, at least for 32 consecutive cycles during a

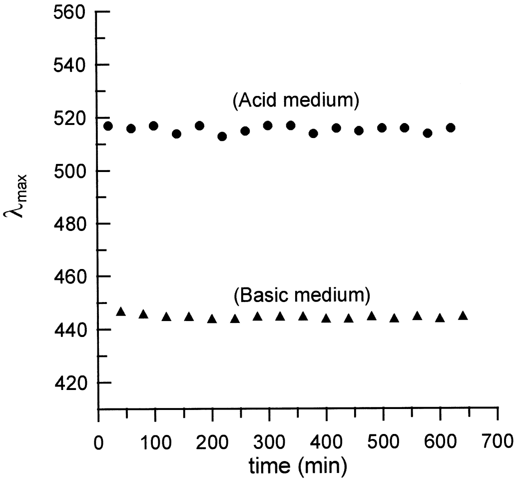

Fig. 6. Evolution of λ_{max} at 445 nm (pH = 14) and 515 nm (pH = 0) during consecutive cycles tested in EC doped coatings.

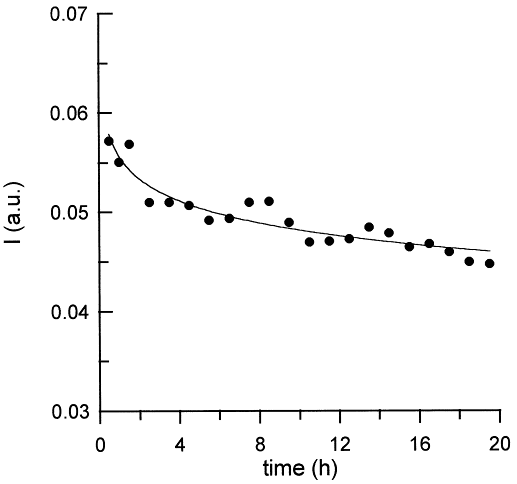

Fig. 7. Photostability of an EC doped coating after UV exposures for different lengths of time.

total time of 10 h. Tests were performed in two extreme acid and basic pH (0 and 14) by using buffered solutions. During that cycles the maximum intensities, which correspond to wavelength points in Fig. 6, remain practically constant. This points out the ability of EC doped coatings to be used as a pH optical sensor for application in instrumentation devices submitted to abrupt pH changes, with neither loss of sensitivity nor fatigue in the optical response.

Photostability of coatings against UV radiation is shown in Fig. 7. After an exposure as long as 20 h, the intensity of the 516 nm band (typical absorption at pH = 0) decreases at about 20%. A decreasing in intensity of the emission at 520 nm was also observed. These decreases in intensity are indicative of partial photodegradation of the EC molecules introduced into the sol–gel system. In particular, that loss of optical absorption (emission) must be exclusively attributed to the UV effect, since the sample temperature during tests

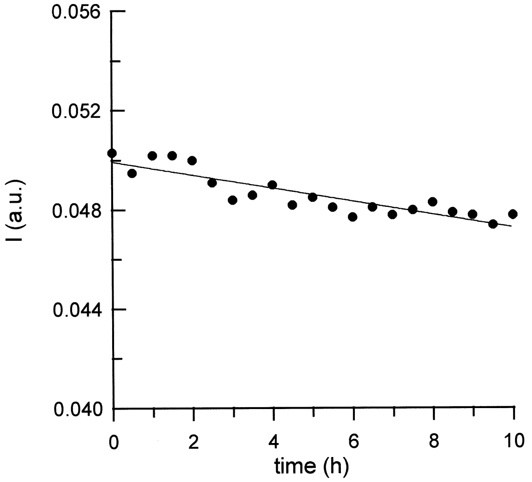

Fig. 8. Optical absorption intensities of an EC doped coating submitted to ultrasounds versus treatment time.

was always controlled to be below 30°C and, hence, thermal decomposition of EC can be discarded.

A first experiment to evaluate adherence of the doped coatings was performed by dipping them into a cleaner solution (pH = 8) at 30°C submitted to ultrasounds, during different lengths of time. Fig. 8 shows the evolution of the intensity of the wide absorption band (λ_{abs} = 446–452 nm) as a function of ultrasounds treatment time. The decreasing observed (about 5%) could be derived from the experimental handling. Together with the absence of cracks or peeling in the coating surface, it demonstrates the good adherence of the coating to the glass substrate. The presence of ≡Si–OH groups in the coatings (from the alkoxide hydrolysis), ensures the linkages with the substrate surface, even when the thermal densification was as soft as the treatment carried out up to 60°C during 3 days.

Therefore, adherence of coatings to the soda lime glass substrates used has proved to be good enough to be handled and even cleaned with different conventional glass cleaners, detergent for tableware wash machine, lye and several organic solvents (alcohols, acetone, benzene, toluene and halo-alkanes) and concentrated chemical reagents all over the pH range. Coatings show no superficial damage, corrosion, peeling or cracking after dipping into the liquids above mentioned at room temperature. Obviously, EC molecules and other organic matter are progressively burned off from coatings when heated at temperatures higher than 100°C. So that, at approximately 180°C coatings appear colorless and their absorption spectrum shows no bands in the visible range, which is in agreement with EC release. On the other hand, the use of the coatings here produced as optical sensors to perform pH measurements at temperatures higher than 100°C is unlikely, since pH is concepted for liquid media at the temperatures at which the solvents do exist (usually below 100°C).

Mechanical tests carried out with a doped coating 260 nm thickness by application of charges ranging from 4.9 to 98.0 N pointed out the absence of cracking and peeling at the coating surface. When a load higher than 9.8 N was applied, some superficial scratches were observed. This is probably due to residual defects (micro pin holes) of the coating creeped by the hemispheric indenter or to very small irregularities of the indenter surface.

The width of the scratch path for 49 N of charge is 650 μm, whereas for 98 N is about 950 μm. These results are consistent with the value found by Etienne et al.[16] (800 μm for 5 N) in organic–inorganic silica coatings upon a transparent plastic. It is noticeable that, in the present case, although the path width is of the same order of magnitude, the charge is about one order of magnitude higher, which indicates the good adhesion of the EC doped coating to the glass substrate. This difference is easily explained on the basis of the similar inorganic glassy nature of the coating and the substrate that favours the formation of stable chemical links between both of them. Moreover, EC doped coatings appear to be more stiff and solid than sol–gel coatings upon plastics.

4. Conclusions

Eriochrome cyanine (EC) doped silica coatings have been produced by sol–gel method upon soda lime glass substrates. The as prepared thin films (≈300 nm) dried at 60°C show reversible pH sensitivity in liquid and gaseous media. Their optical absorption spectra as well as their photoluminescence change as a function of the pH of the medium at which the coatings were exposed. EC molecules were introduced into the silica sol–gel coating in such a way that they are accesible to aqueous H_3O^+ and OH^-, i.e. in the residual pores of the silica network partially condensed. The pH sensitivity ranges in which EC doped coatings change λ_{max} and I_{max} are determined to be around 7 and 11, i.e. pH = 6–8 and pH = 10–12. A correlation of the evolution of λ_{max} and I_{max} of optical absorption with the pH is given. That correlation could be used as a calibration curve. No fatigue is found in the reversible optical response of EC doped coatings.

In the same way, the luminescence is found to be sensitive to pH at which the coating is exposed. Thus, the emission peak shifts to longer wavelengths with increasing pH. The excitation spectra show a similar behavior against pH than those of absorption spectra. For $0 \leqslant pH \leqslant 4$ the excitation appears dominated by a peak at about 520 nm, for $6 \leqslant pH \leqslant 9$ the spectra consists in two components at 475 and 520 nm, which contribute with different weight. Finally, for $pH \geqslant 11.5$ the 475 nm component coexists with the characteristic alkaline component at 585 nm. Coatings have demonstrated to be photostable enough, chemically resistant and mechanically suitable to be applied as a pH sensor in optical devices.

Acknowledgements

We would like to thank Professor J.M. Fernández Navarro for his valuable advice and suggestions. Authors wish to thank to EC-FEDER-CICYT project 2FD97-0141 and to DGESIC project PB97-0287 for financing support.

References

1. Shabat, D., Grynszpan, F., Saphier, S., Turniansky, A., Avnir, D. and Keinan, E., An efficient sol–gel reactor for antiboby-catalyzed transformations. *Chem. Mater.*, 1997, **9**, 2258–2260.
2. Bronshtein, A., Aharonson, N., Avnir, D., Turniansky, A. and Altstein, M., Sol-gel matrixes doped with atrazine antibodies: atrazine binding properties. *Chem. Mater*, 1997, **9**, 2632–2639.
3. Dulebohn, J. I., Haefner, S. C., Berglund, K. A. and Dunbar, K. R., Reversible carbon monoxide addition to sol–gel derived composite films containing a cationic rhodium (I) complex: toward the development of a new class of molecule-based CO sensors. *Chem. Mater.*, 1992, **4**, 506–508.
4. Matsui, K. and Momose, F., Luminescence properties of tris(2,2′-bipyridine)ruthenium(II) in sol–gel systems of SiO_2. *Chem. Mater*, 1997, **9**, 2588–2591.
5. Dunn, B. and Zink, J. I., Optical properties of sol–gel glasses doped with organic molecules. *J. Chem. Mater*, 1991, **1**, 903–913.
6. Ingersoll, C. M. and Bright, V. F., Toward sol–gel processed chemical sensing platforms: effects of dopant addition time on sensor performance. *J. Sol–Gel Sci. Technol.*, 1998, **11**, 169–176.
7. Levy, D., Pena, J. M. S., Serna, C. J. and Otón, J. M., Glass dispersed liquid crystals for electro-optical devices. *J. Non-Cryst. Solids*, 1992, **147–48**, 646–651.
8. Mennig, M., Krug, H., Fink-Straube, C., Oliveira, P.W. and Schmidt, H., SPIE 1758. *Sol–Gel Optics II*, 1992, 387–394.
9. Fachet, R., Müller, M., Bürger, H. and Kriltz, A., Photochromic materials via sol–gel process. *Glatech. Ber. Glass Sci. Technol.*, 1998, **71**, 243–246.
10. Villegas, M. A., García, M. A., Llopis, J. and Fernández Navarro, J. M., Optical spectroscopy of hybrid sol–gel coatings doped with noble metals. *J. Sol–Gel Sci. Technol.*, 1998, **11**, 251–265.
11. McDonagh, C., Ennis, G., Marron, P., O'Kelly, B., Tang, Z. R. and McGilp, J. F., Characterisation of sol–gel glasses using optical probes. *J. Non-Cryst. Solids*, 1992, **147–148**, 97–101.
12. MacCraith, B. D., Ruddy, V., Potter, C., O'Kelly, B. and McGilp, J. F., Optical waveguide sensor using evanescent wave excitation of fluorescent dye in sol–gel glass. *Electronics Lett*, 1991, **27**, 1247–1248.
13. Leventis, N. and Chen, M., Electrochemically assisted sol–gel process for the synthesis of polysiloxane films incorporating phenothiazine dyes analogous to methylene blue. Structure and ion-transport properties of the films via spectroscopic and electrochemical characterization. *Chem. Mater*, 1997, **9**, 2621–2631.
14. Reisfeld, R., Eyal, M. and Brusilovsky, D., Luminescence enhancement of rhodamine 6G in sol–gel films containing silver aggregates. *Chem. Phys. Lett.*, 1988, **153**, 210–214.
15. Reisfeld, R., The state of the art of solid state tunable lasers in the visible. *Optical Materials*, 1994, **4**, 1–3.

16. Jarosz, M. and Marczenko, Z., Study of the formation of vanadium (IV) complexes with some triphenylmethane reagents and cationic surfactants. *Analyst*, 1984, **109**, 35–38.
17. Etienne, P., Denape, J., Paris, J. Y., Phalippou, J. and Sempere, R., Tribological properties of ormosils coatings. *J. Sol–Gel Sci. Technol.*, 1996, **6**, 287–297.
18. Bamford, C.R., *Colour Generation and Control in Glass*. Elsevier, Amsterdam, 1977, pp. 16–32.
19. Allinger, N.L., Cava, M.P., Jongh, D.C. De, Johnson, C.R., Lebel, N.A. and Stevens, C.L., *Química Orgánica*. ed. Reverté S.A., Barcelona, 1976, pp. 768–769.