Spectroscopic studies and evanescent optical fibre wave sensing of Cu^{2+} based on activated mesostructured silica matrix

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This paper report on the synthesis and test of eriochrome cyanine R (ECR) doped mesostructured silica films as Cu^{2+} sensing without prior removal of the surfactant. ECR activated mesostructured silica (via sol-gel technique) coated optical fibre core were used to Cu^{2+} sensing by evanescent wave method. The sol was prepared via acidic hydrolysis-condensation of tetraethoxysilane (TEOS) in the presence of cetyltrimethylammonium bromide (CTAB:$C_{16}H_{33}NCH_3Br$) as the structure-directing agent. Spectrophotometric investigations using doped sol-gel thin films dip-coated on glass slides were reported. Heat treatment temperature effect (optimum temperature 150°C), absorption dependence on the pH of the aqueous phase (pH = 8 seems to be the optimal absorption pH), sensitivity, reversibility and response range (0.05 mmol/l) were reported.

1. Introduction

Evanescent wave sensing using optical fibre is a useful method in the field of chemical sensing [1–3]. When light propagates in an optical fibre, a fraction of the radiation extends a short distance from the guiding region into the medium of lower refractive index that surrounds it. This is the evanescent field that decays exponentially with distance from the core-cladding interface, thus defining a short range sensing volume within which the evanescent energy may interact with measurands that attenuate it by means of refractive index changes, absorption, or scattering. In order to increase the sensitivity of the sensor by evanescent wave method, MacCraith *et al.* [2] used an annular beam mask at launch to block low order modes. In this work, the incident beam at the input end of fibre has to be adjusted to the adequate angle until total internal reflection occurs and evanescent wave propagation take place. Using the same approach as previously [4] (mesostructured silica were used as host matrix for a pH dye), the evanescent wave optical fibre Cu^{2+} sensor is prepared by immobilizing a dye doped mesostructured silica detection layer on the surface of unclad fibre using sol-gel technique.

1.1. Evanescent wave sensing theory [5]

When a transverse electric field is applied to a planar wave guide, the transmitted, reflected and transmitted wave were solutions of wave equations:

$$\nabla^2 \vec{E} + n^2 k_0^2 \vec{E} = 0 \tag{1}$$

where: $\vec{E}$ is the electric field vector, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, $k = n\frac{\omega}{c} = nk_0$ with n index refraction of media, c velocity of light and k_0 the free-space constant related to free-space wavelength $\lambda = \lambda_0/n$ and ω is the angular frequency of the wave.

If the electric field is entirely parallel to the interface, then it only has a y-component; The vector wave equation therefore reduces to a single scalar equation:

$$\frac{\partial^2 E_y}{\partial x^2} + \frac{\partial^2 E_y}{\partial z^2} + n^2 k_0^2 E_y = 0 \tag{2}$$

When total internal reflection does not occur ($\theta_i < \theta_c$ where θ_c is the critical angle), we dispose of two

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equations:

$$\frac{\partial^2 E_{y_1}}{\partial x^2} + \frac{\partial^2 E_{y_1}}{\partial z^2} + n_1^2 k_0^2 E_{y_1} = 0 \quad \text{in medium 1 (core of fibre)} \quad (3)$$

$$\frac{\partial^2 E_{y_2}}{\partial x^2} + \frac{\partial^2 E_{y_2}}{\partial z^2} + n_2^2 k_0^2 E_{y_2} = 0 \quad \text{in medium 2 (clad of fibre)} \quad (4)$$

When field in each region is assumed to be a combination of plane waves, then the solution is:

– In optical fibre core of refractive index n_1:

$$E_{y_1} = E_1 \exp(-jk_0 n_1 (z \sin\theta_1 - x \cos\theta_2)) + E_R \exp(-jk_0 n_1 (z \sin\theta_1 + x \cos\theta_1)) \quad (5)$$

– In optical clad of refractive index n_2:

$$E_{y_2} = E_T \exp[-jk_0 n_2 (z \sin\theta_2 - x \cos\theta_2)] \quad (6)$$

where E_I amplitude of incident wave, E_R amplitude of reflected wave and E_T amplitude of transmitted wave, θ_1 angle of incident wave, θ_2 angle of transmitted wave.

We consider the case when θ_1 greater than θ_c which is given by $\theta_c = \sin^{-1}(n_1/n_2)$. In this regime total internal reflection occurs in the optical fibre core of refractive index n_1 and we cannot satisfy Snell's law equation ($n_1 \sin\theta_1 = n_2 \sin\theta_2$) with a real value of θ_2. Its turns out that we can satisfy it with a complex value instead:

$$\cos\theta_2 = \pm j\{(n_1/n_2)^2 \sin^2\theta_1 - 1\}^{1/2} \quad \text{for } \theta_1 > \theta_c, \quad (7)$$

and solution in optical clad have the form:

$$E_{y_2} = E_T \exp[-jk_0 n_1 z \sin\theta_1] \exp[+k_0 n_2 x \times \sqrt{\{(n_1/n_2)^2 \sin^2\theta_1 - 1\}}] \quad \text{with } k_0 = 2\pi/\lambda \quad (8)$$

The first exponential term in Equation 8 is responsible for the shift of the reflected wave in the direction of its propagation. The second term accounts for the exponential decay of the field intensity in the direction normal to the interface. The reflected beam combines with the incident beam to form a standing electromagnetic wave at the interface. The electric field, which penetrates the optically rare medium, is the evanescent field. The depth of its penetration d_p is then defined as the distance at which the initial intensity decays to its $1/e$ value. Thus from last expression d_p is defined as

$$d_p = \frac{\lambda}{2\pi}\left(n_1^2 \sin^2\theta - n_2^2\right)^{-\frac{1}{2}} \quad (9)$$

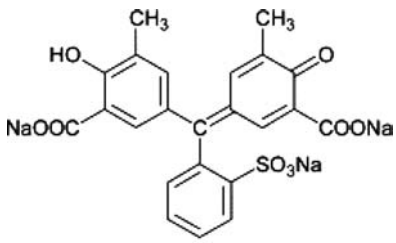
It is important to note that the depth to which the evanescent wave penetrates depends on several parameters, but above all on the evanescent wavelength of the incident beam. This consideration will be important in sensing application in which the interaction of a chemical species with this field can be enhanced if the interrogating wavelength coincides with an absorption band of the species.

1.2. ECR doped mesostructured silica

The recent discovery of mesostructured silica formed by the cooperative self-assembly of silicates and surfactants has opened up a new range of possibilities. The highly porous nature of these materials makes them excellent hosts for sensing molecules, since the species to be sensed can easily diffuse towards the sensing centre [6–8].

Until now, three approaches [6–20] were used to dye doped mesostructured materials. The first one consists to impregnation after the calcinations (pores of host matrix were opened by calcination), the second by a direct self-organization of the surfactants followed by its extraction and recently, the surfactant is not removed and has been exploited for the low temperature synthesis of optical materials and acts as a barrier. Furthermore, surfactant seems help trapping of the dye and limits the leaching.

The metal-complexing dye ECR has been shown to be selective for Cu^{2+} when entrapped in a silica sol–gel matrix, whereas it is selective for aluminium when used in free aqueous solution [21–26].



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For the determination of aluminium, Ahmed and Narayanaswamy [21] use ECR immobilised on XAD-2 as a sensitive opto-sensor. Using sol-gel route, Sommerdijk *et al.* [23] studied sensitivity of ECR doped glass matrix (gel) to Cu^{++}. They noted that complexation with aluminium(III) ions was not observed and showed for Cu^{2+} that pH of carrier solution optimise the sensing properties of sol-gel composites. In the goal to detect scandium(III) (Sc(III)), Park and Cha [24] conclude that the complex between ECR and Sc(III) in the presence of surfactant (CTAB) is very stable and more sensitive than in the absence of surfactant. They interpret this mechanism by formation of Sc(III)-ECR-CTAB ternary complex. In a recent paper, John D. Wright and Higginson [26] examine the effects of pH on a gel prepared by sol-gel route using various values of the water-alkoxide (tetramethoxysilane) ratio and showed that ECR sensitivity increase.

In this work, the mesostructured silica sol was doped with ECR and the spectrophotometric capability of ECR dye doped mesostructured silica matrix deposited

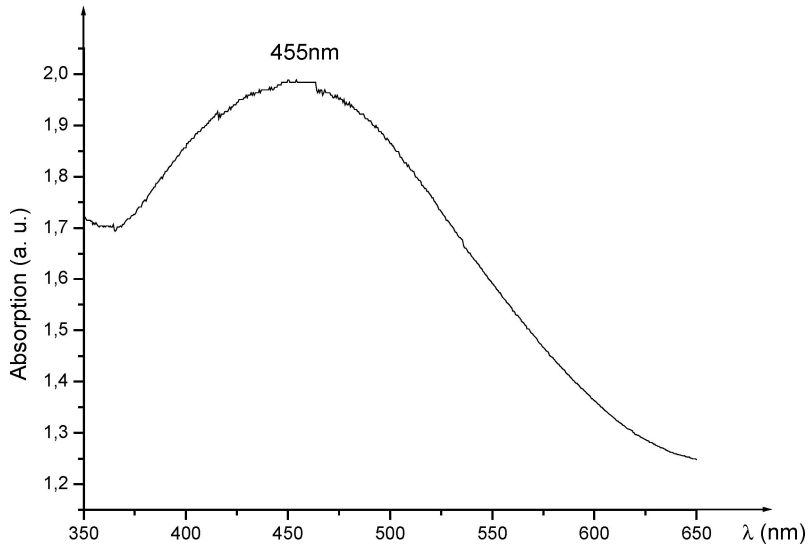


Figure 1 Absorption spectra of a pellet of a mixed ECR-KBr powder.

by dip-coating onto glass slides for Cu^{2+} sensing applications was tested. To achieve this, temperature and pH effect were firstly investigated before using these materials for Cu^{2+} detection.

2. Experimental

2.1. Preparation of mesostructured silica matrix [4]

Using the same sol-gel method as previously [4], the pH of the initial mesostructured silica sol was around pH = 2. The dye (ECR, 1 mmol/l of sol) is then introduced in the sol and left under stirring for four days at room temperature. The resulting solution has a red coloration and the pH of ECR doped sol was around pH = 4 and this pH value accelerate solidification of the sol (two days). Stabilisation of the sol was achieved by bringing back pH of the sol to pH = 2 by adding one drop of HCl 2 M. Sol has now a yellow coloration.

2.2. Preparation of coating

Coating of glass slides and core fibre coating were made as previously [4]. After coating and before use, in order to remove solvent and to get a hard enough thin film, glass slides and optical fibre were successively left in oven for one night at 30°C, heated for four hours at 60°C followed by three steps at 100°C respectively during one, two and three hours and finally for one hour at 150°C. Films exhibit a good transparency with yellow coloration.

3. Optical measurements

3.1. Absorption spectra

Characterisation of mesostructured film doped ECR deposited on glass slides were recorded by optical absorption on UV-VIS spectrophotometer (UV-1201 Shimadzu). The absorbance of dip-coated doped films relative to solution of various pH and solution containing Cu^{++} was measured at 350–650 nm against a dip-coated slide film with un-doped mesostructured silica

4. Results and discussion

4.1. Absorption spectra of ECR doped mesostructured silica dip-coated on glass slides

4.1.1. Heat treatment temperature effect

The optical spectrum of a pellet of a mixed ECR-KBr powder exhibits a maximum absorption band at 455 nm (Fig. 1).

The variation of the optical absorption spectra of the ECR doped mesostructured silica film dip-coated on glass slides as a function of heat treatment temperature (as described in Section 2.2) is shown in Fig. 2a. One hour under 150°C was found to enhance sufficiently sensitivity of films. At 200°C, absorption was tested and absorbance intensity decreased. Absorption band of ECR (Fig. 1) was shifted of 50 nm when ECR was immobilised on mesostructured silica films dip-coated on glass slides and heat treated as described previously, this mechanism is well known when an indicator was immobilised on sol-gel matrix [27].

Fig. 2b shows a plot of absorption intensity versus temperature at λ = 516 nm and it's clear that a steady state is reached. The heat treatment temperature proposed here seems increase absorbance of films and can be resumed to the following steps after dip-coating process:

- One night at 30°C,
- Four hours at 60°C,
- Three hours at 100°C,
- Finally for one hour at 150°C

4.1.2. pH effect

The response of doped film was optimised by studying the effect of pH. This effect was analysed as a function of the pH of carrier solution (distilled water) in the range (pH = 5 to pH = 9). Acetic acid (CH_3CO_2H)

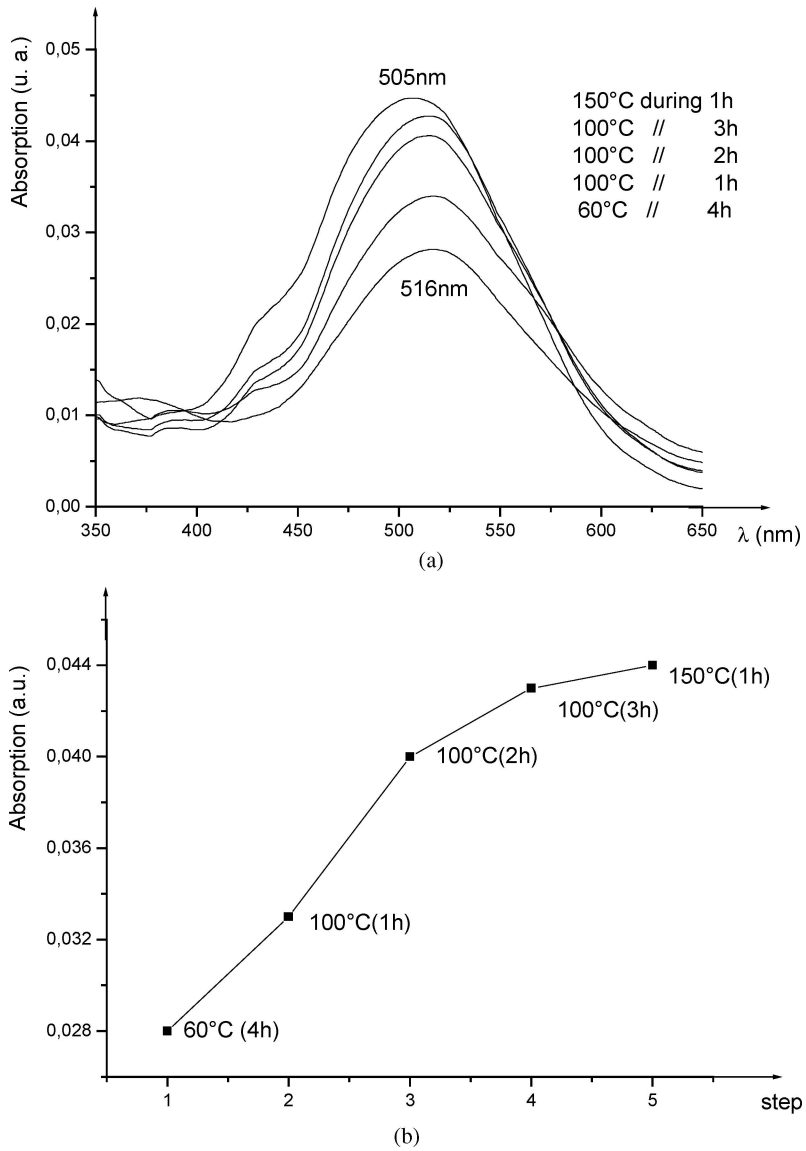


Figure 2 (a) Absorption spectra of ECR activated mesostructured silica dip-coated on glass slides for various heat treatment temperature and (b) Plot of absorption intensity versus temperature at $\lambda = 516$ nm.

and ammonia (NH_3) were used to adjust the pH of the solution. Each glass slide was immersed in a solution at a given pH and then dried at an oven. The response time of colour changing of the mesostructured films when the pH is changed is quite fast, in the range of a few seconds. Fig. 3a shows the absorption spectra at different pH. ECR doped mesostructured silica films is specially sensitive between pH = 6.5 to pH = 8. and in this range of pH, an isobestic point is observed at 468 nm. The absorption intensity versus pH was plotted at $\lambda = 440$ nm (Fig. 3b), pH = 8 seems to be the optimal absorption pH.

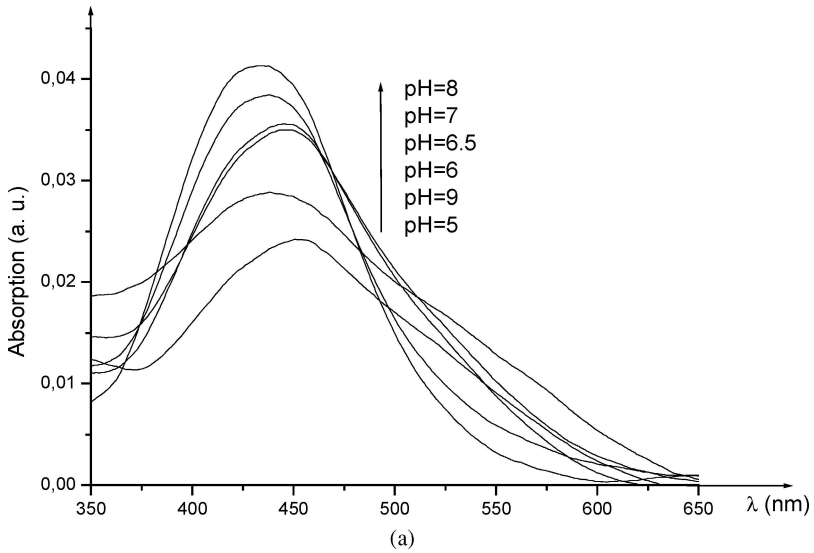
4.1.3. Sensitivity of doped films to Cu^{2+}

ECR Doped mesostructured silica dip-coated on glass slides were used to detect Cu^{2+} in solution. A series of carrier solution (distilled water) buffered at pH = 6.5, pH = 7 and pH = 8 were used, Cu^{2+} was then added (5 mmol/l) and pH was again readjusted. Fig. 4 shows absorption spectra of ECR doped films after exposure (5 min) to different buffered Cu^{2+} solutions. Sensitivity of ECR doped mesostructured silica films to Cu^{2+} buffered at pH = 8 is confirmed. Maximum wavelength was around 580 nm. Therefore, the following experiments were performed with an aqueous solutions buffered at pH = 8.

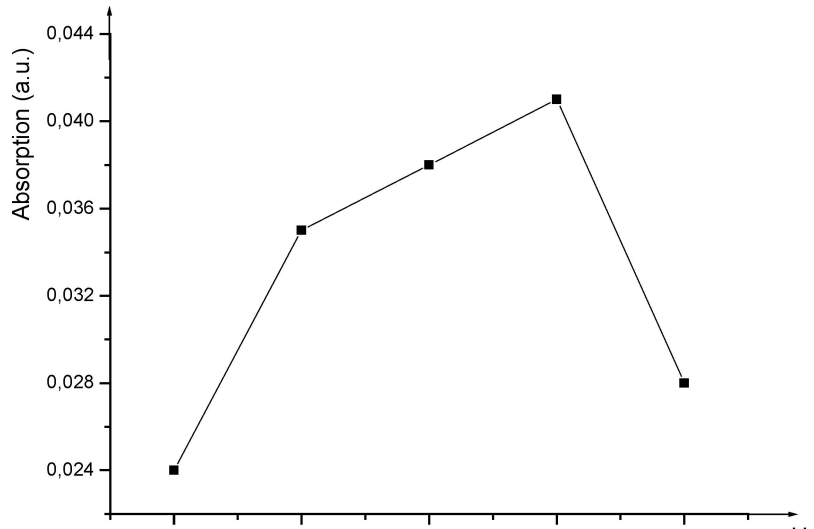
Another series of absorption spectra was made to asses the performance of ECR immobilised on sol-gel film to detect Cu^{2+} versus time and response were reported on Fig. 5a. Until five minutes of exposure time, absorption increase and Cu^{2+} seems not yet totally recovered. This can be result by the fast surface interaction (rapid use of the surface active sites) followed by the slowly depth one (slowly deeper penetration into the sol-gel matrix). Beyond, a little increase of absorbance is observed and a steady-state seems reached (Fig. 5b).

4.1.4. Detection reversibility

Fig. 6 shows absorption reversibility of Cu^{++} detection by ECR doped sol-gel films. Dip-coated slide was first exposited to Cu^{++} buffered solution (5 mmol/l,



(a)



(b)

Figure 3 (a) Absorption spectra of films dip-coated on glass slides for various pH of carrier solutions (pH range 5–9) and (b) Plot of absorption intensity versus pH at $\lambda = 440$ nm.

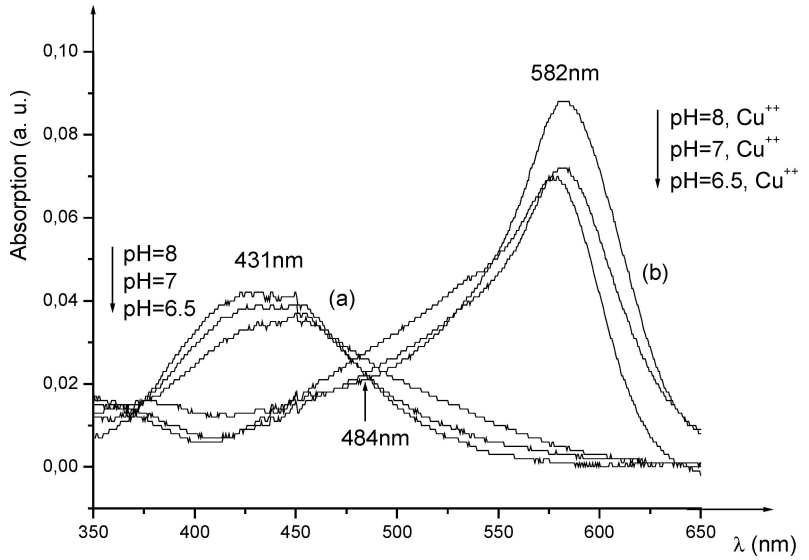
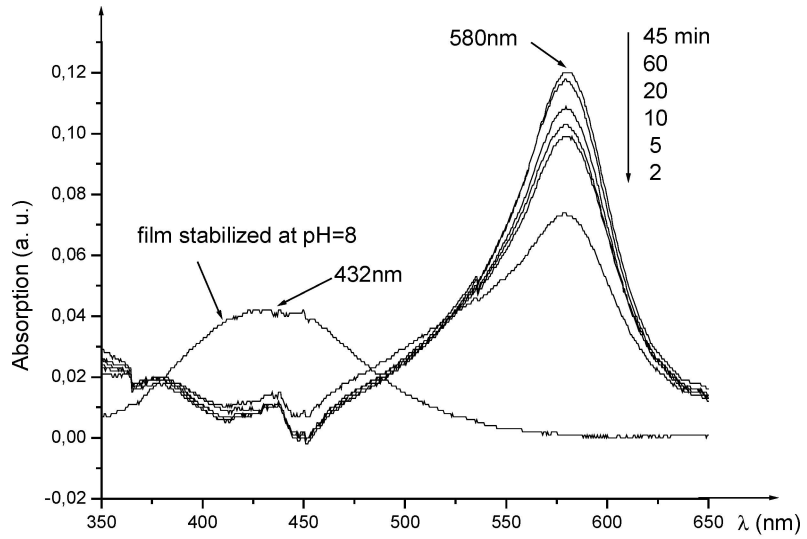
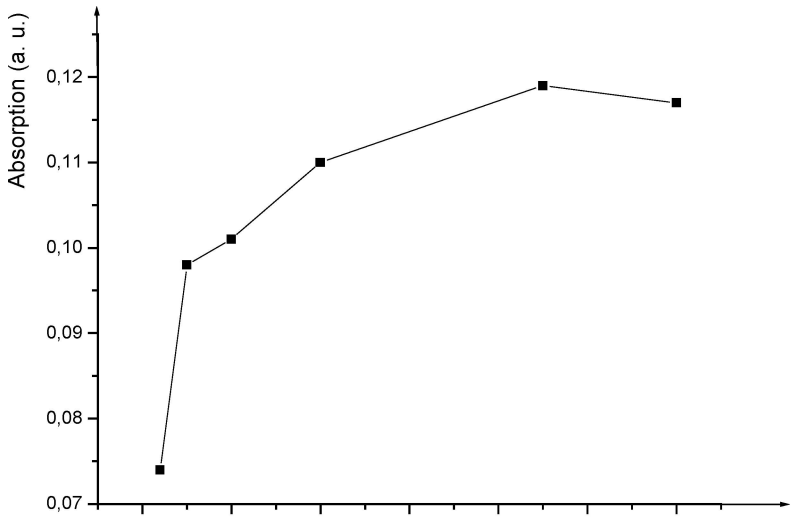


Figure 4 Sensitivity of ECR doped films to Cu^{2+}. pH = 8 seems enhance sensitivity: (a) before exposition to Cu^{2+} and (b) After exposition to Cu^{2+}.



(a)



(b)

Figure 5 (a) Absorption performance of ECR to detect Cu^{++} after exposure for various time (in minutes) to a pH = 8 buffered solution containing 5 mmol/l of Cu^{2+} and (b) Absorption intensity of ECR to detect Cu^{++} versus time at $\lambda = 580$ nm.

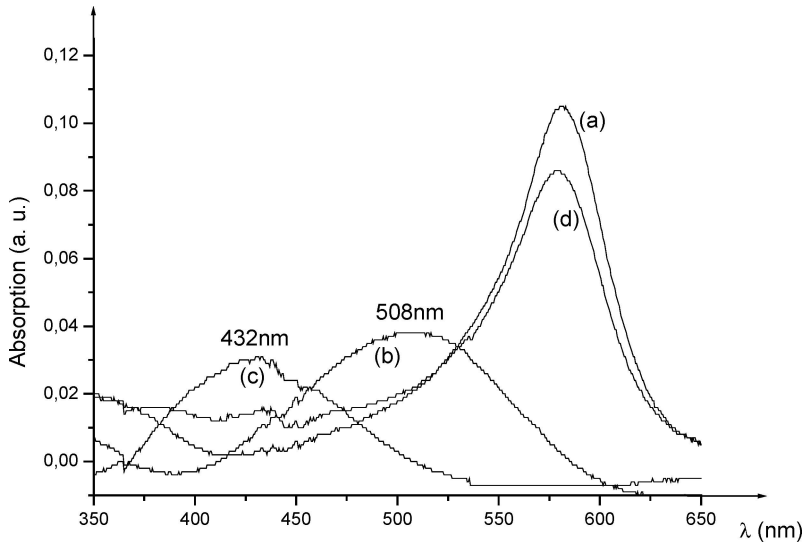


Figure 6 Reversibility of detection of ECR doped films dip-coated on glass slides: (a) First exposition of slide to Cu^{2+} followed by (b) Regeneration of film by a brief exposition to 2M HCl (few seconds), (c) Stabilisation on buffered solution pH = 8 and and (d) Re-exposition to Cu^{2+}.

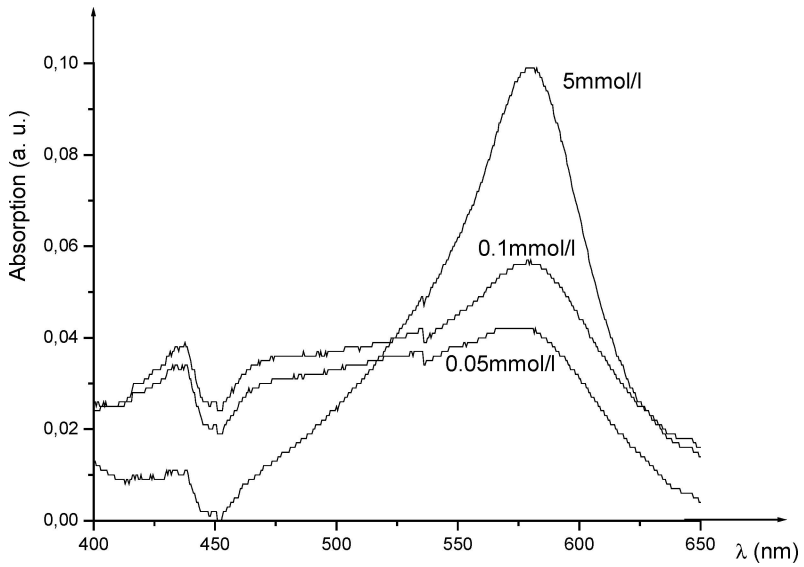


Figure 7 Response range of ECR doped films after contact during five minutes with various concentrations of Cu^{2+}.

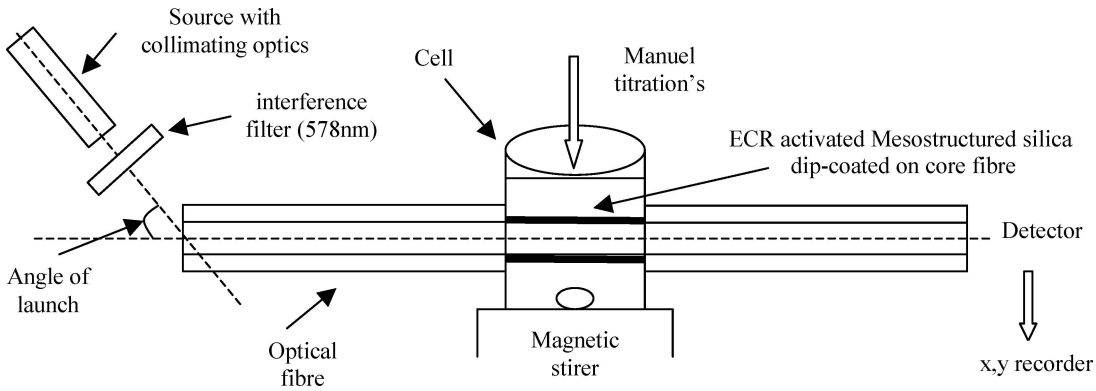


Figure 8 Experimental set-up of evanescent wave optical fibre Cu^{2+} sensing

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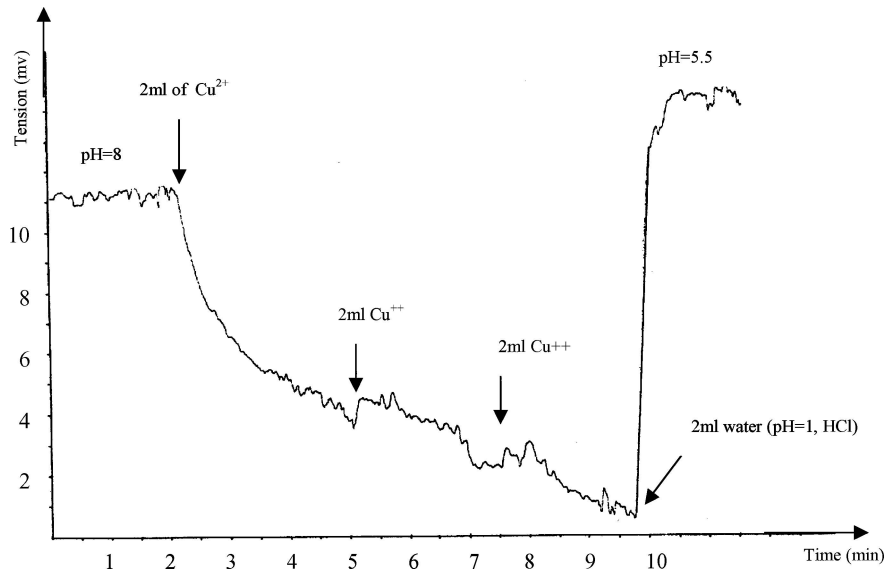

Figure 9 Optical fibre evanescent wave sensor: transmitted signal versus time (min).

pH = 8) during 5 mn (Fig. 6a) followed by a briefly (few seconds) exposure to 2 M HCL (Fig. 6b), stabilisation on buffered distilled water (pH = 8) (Fig. 6c) and finally, re-exposition to Cu^{++} (Fig. 6d). Regeneration of the Cu^{2+} sensing layer by HCl treatment was successful.

4.1.5. Response range

Absorption spectra of ECR doped mesostructured silica dip-coated on glass slides recorded as a function of wavelength after contact with various concentrations of Cu^{2+} during five minutes is shown in Fig. 7. Cu^{2+} was detected at a lower limit of 0.05 mmol/l which

confirm the highly porous nature of mesostructured silica matrix as excellent hosts for sensing molecules.

4.2. Evanescent wave optical fibre Cu^{2+} sensing

The optimum operating absorption wavelength of ECR doped mesostructured silica films is around 580 nm, therefore the experimental set-up includes a source (spectral lamp Hg) with collimating optics followed by an interference filter (578 nm). The incident beam at the input end of fibre has to be adjusted to the adequate angle until total internal reflection occurs and evanescent wave propagation take place. The fibre goes through a cell containing the solution to be analysed. The input end of the fibre is placed in the centre of rotation. The optical power transmitted with the output end of the fibre was detected with a photodiode PIN linked to a x-y recorder (Fig. 8). A cell containing 60 ml of water (under stirring) was buffered at pH = 8 and was titrated manually with a Cu^{2+} solutions of concentrations of 5 mmol/l. At the beginning, 2 ml was added to the cell followed by two another same titration's, the response is shown on Fig. 9. Since the first drop, the response of the fibre confirm clearly fast surface interaction (rapid use of the surface active sites) followed by the long depth one (deeper penetration into the sol-gel matrix). During the following drops, no response of sensor was noted. Regeneration of the optical fibre sensor with an aqueous solution drop (2 ml) adjusted with HCl to pH = 1 was rapid.

5. Conclusion

Absorption studies and evanescent optical fibre sensing of thin films deposited respectively on glass slides and on optical fibre core shows that ECR incorporated in mesostructured silica matrix without prior removal of the surfactant is sensitive with adjusted pH to Cu^{2+}. Cationic surfactant (CTAB) seems to favour the trapping of dye in host matrix limiting at the same time the leaching of the dye. This phenomena was already noted by Park and Bull [24] about Sc(II)-ECR-CTAB solution. To gain further mechanistic insight into films, experimental studies of ECR doped mesostructured silica are under investigations.

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