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Reliable, doped hybrid xerogel-based optical fibre sensor for pH monitoring for industry

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ABSTRACT

A new optical fibre pH sensor has been developed based on incorporating the pH indicator in a hybrid siliceous xerogel. Here the hydrophobic siliceous materials were fabricated using the sol-gel method, employing an optimal percentage of organic precursor moieties, propyltriethoxysilane:tetraetoxysilane, then doping it with three different pH indicators (phenolphthalein, bromophenol blue and cyanidin blue), to create three different optical fibre sensor systems (5pTEOSPH, 5pTEOSBF and 5pTEOSCB). These pH sensors exhibit important features needed by industry: fast response times, minimal dye leaching, good stability, a high level of reproducibility, and reversibility in response. Sensors of this type have a number of important potential uses in different applications in industry today.
Keywords: Xerogel, hybrid xerogel, pH, pH indicator, optic fibre sensor.

1. INTRODUCTION

Porous siliceous xerogels display a wide range of important properties which make them suitable for the development of membrane sensing components for different optical fibre sensors (OFSs), such as good thermochemical stability, a refractive index close to that of the optical fibre itself and transparency across a wide wavelength range. Their porous texture (involving their specific surface area and average pore distribution) and surface chemistry can be fine-tuned by including functional 'guest materials' into the TEOS xerogel matrix (XG) from which the sensor is made.

While sol-gel based techniques for optical fibre sensors for pH monitoring were first reported by some of the authors more than two decades ago[1], the measurement of pH is even more widely required in a range of applications, which include biochemistry, clinical chemistry, and environmental science[2] and many different forms of pH sensor have been developed in recent years[3]. The most widely used device remains the glass electrode, taking advantage of its high accuracy and sensitivity, but accepting the problems of fragility and vulnerability to fouling, with a consequent degradation of the sensor performance and the need for frequent recalibration. As a result, new and better solutions are needed and fibre optic sensor systems for measuring pH present an attractive alternative, exploiting inherent, positive features such as small sensing volume, good flexibility and the facility for remote sensing[4],[5]. The technique uses the fast, reversible change the optical characteristic of the active part of the sensor to external environmental changes, incorporating an optical element attached to the distal end of the optical fibre, to respond rapidly to the physical and chemical changes occurring.[6]

In order to optimize the performance of an optical fibre sensor of this type, work has been done which centred on the monitoring of the change of the pH in a medium forming part of an OFS system. To do so, the key aim has been to optimize the sol-gel itself and so the inclusion of the organic precursor in the matrix was used to reduce its hydrophobic nature and porosity, features which had the positive effect of decreasing the leaching of the pH indicator dye embedded into the xerogel, when the sensor is used inside the measurement medium. As part of the optimization process, three different pH indicators were used: phenolphthalein, bromophenol blue and cyanidin blue, these being chosen based on their different detection ranges and their solubility in an ethanoic medium. With these three different xerogels the following were synthesized: 5pTEOSPH (with phenolphthalein as an indicator), 5pTEOSBF (with bromophenol blue) and 5pTEOSCB (with cyanidin blue). In each case, to optimize their performance in an optical fibre sensor system, the

adsorption/desorption isotherms were studied, to unravel their textural properties when placed at the distal end of an optical fibre. The OFS systems thus prepared show the morphology of an electrode-based system but maintain the advantages of the use of optical fibre-based measurement, as the sensors constructed are easy and convenient to use with, moreover, no reference signal required.

2. METHODOLOGY – XEROGEL PREPARATION

In this work, three different doped hybrid xerogels (XGs) were prepared using a molar relation of 1.00:5.50:4.75 of a mixture of pTEOS+TEOS (5% propryltriethoxysilane and 95% tetraorthosilane, in molar percentage), ethanol (EtOH) and water, with the addition of the appropriate pH indicator. The pH indicators chosen, dissolved in EtOH at a concentration of 70 mM, included disodium; 4-[1-(4-oxidophenyl)-3-oxo-2-benzofuran-1-yl]phenolate (phenolphthalein), 3,3′,4,5,7-Pentahydroxyflavylium chloride (cyanidin chloride) and 3′,3″,5′,5″-Tetrabromophenolsulfonephthalein (bromophenol blue). These solutions were added to the mixture dropwise, resulting in a final concentration of 31.5 mM in the ethanoic media. Milli-Q grade water was subsequently added dropwise, and the final pH was adjusted to 2.0 using a 0.1 M HCl solution added drop-by-drop, with a glass pipette. The doped XGs obtained in this way were designated as 5pTEOSPH (when phenolphthalein was incorporated into the ethanoic media), 5pTEOSCB (when a cyanidin blue solution was added), and 5pTEOSBF (when the bromophenol blue was used in the ethanoic mixture). Figure 1a shows schematically the evolution of the xerogel, along the gelification process from the sol (the initial state) to the monolith (the state seen once the material had dried). After adjusting the pH of the xerogels thus synthesized, the flasks containing them were sealed with paraFILM^{TM} and placed in an oven at 60 °C (Thermo Electron LED T6, Thermo Scientific), until gelation took place.

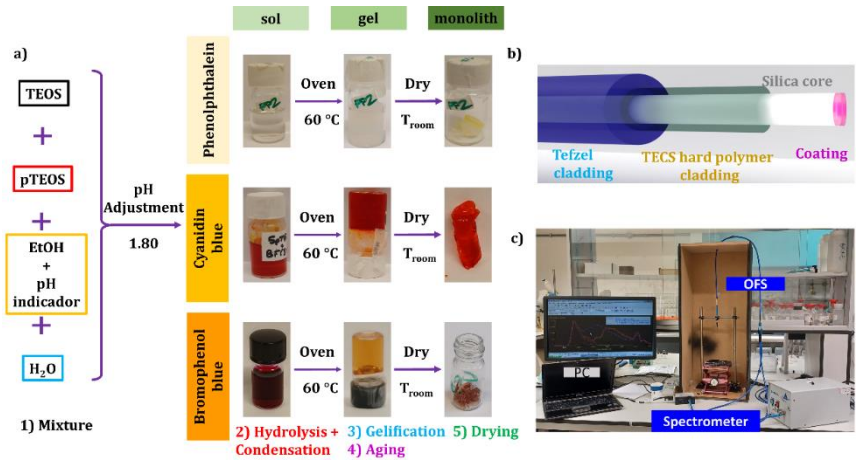

Figure 1. a) Schematic of the synthesis of the hybrid xerogels TEOS:RTEOS (95:5, R=propyl [P]) doped with the following pH-indicators included: phenolphthalein, cyanidin chloride and bromophenol blue, b) OFS coating process, and c) experimental set-up for the measurements made.

To form the OFS from the XGs prepared above, optical fibre pigtails with inner and outer diameters of 200 µm and 225 µm respectively (using SMA connectors) were used to fabricate the sensors themselves. The active sensing layer was coated onto the optical fibre using a process involving 3 immersions into the different, freshly prepared solutions (gelification time equal to 0), enabling the creation of three different probes (with the different indicators), labelled OFS5pTEOSPH (phenolphthalein), OFS5pTEOSPH (bromophenol blue) and OFS5pTEOSCB (cyanidin blue) probes (as seen in Figure 1b). The experimental set up, shown in Figure 1c, consisted of a spectrophotometer (model USB2000, OceanOptics), a halogen light source (model DH-2000-BAL, Mikropack) and a 600 µm UV-vis bifurcated fibre (OceanOptics, Ostfildern) to connect both components to the sensor. The integration time selected was 500 ms, with the scan average time and the boxcar width set to ten, with a sampling rate of 1 min. The sensors developed in this way were characterized using the ratio of the maximum spectral intensities monitored, I_1 and I_2, to obtain a 'self-referenced' measurement from which the pH could be determined.

3. RESLUTS AND DISCUSSION

Figure 2 shows the results of a series of evaluations carried out looking at the adsorption/desorption isotherms with N_2 (at −196 °C), and CO_2 (at 0 °C). All the isotherms show a Type I(b) behaviour (based on the IUPAC classification). They are

mainly microporous with a narrow pore size distribution (PSD). When the pH indicator was added into the xerogel mixture, the value of a_{BET} was seen to decrease (5pTEOSCB (506 m^2 g^{-1})>5pTEOSBF (349 m^2 g^{-1})>5pTEOSPH (61 m^2 g^{-1})). The 5pTEOSPH is mainly a ultramicroporous material because it was seen to hardly adsorb N_2 and showed the narrower distribution in the CO_2 adsorption/desorption isotherm.

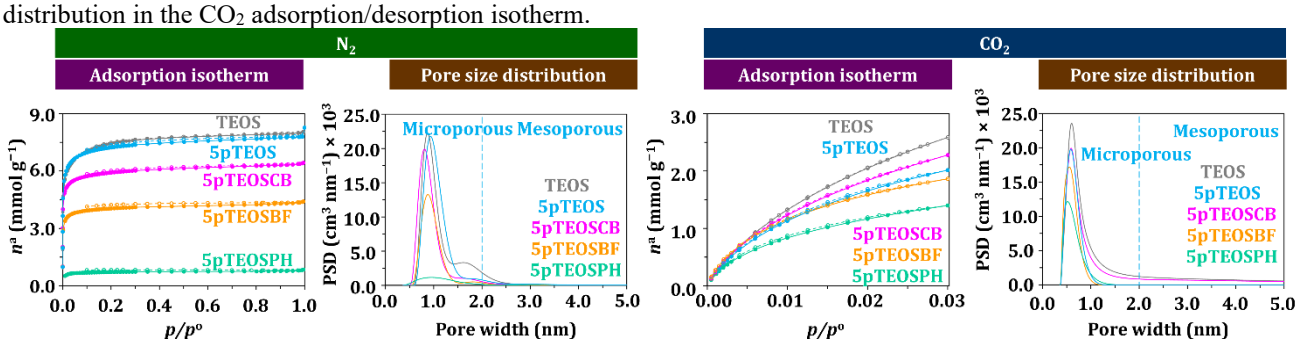

Figure 2. Adsorption/desorption isotherm with N_2 (−196 °C) and CO_2 (0 °C) of 5pTEOS doped with pH indicator xerogels and pore size distributions (lines-markers: adsorption, continuous-filled; desorption, dashed-empty).

The value of E_c calculated using the DR methods increased with the decrease of the a_{BET}, in the same order ((5pTEOSCB (20.5 kJ mol^{-1})>5pTEOSBF (19.3 kJ mol^{-1})>5pTEOSPH (13.6 kJ mol^{-1})). Therefore, it can be concluded that the materials are mostly microporous, which should not be a drawback for their use as pH sensors, since the aim is for the material to interact rapidly with the medium, so that colour changes are produced by the indicators that have been incorporated in the matrix, and this interaction should be labile. The adsorption/desorption isotherms with water vapour reveal that the inclusion of the pH indicator in the silica matrix show a decreasing in the values of a_{BET} and V_{meso}, which together with the incorporation of the propyl group provides evidence of the hydrophobic nature of the surface material.

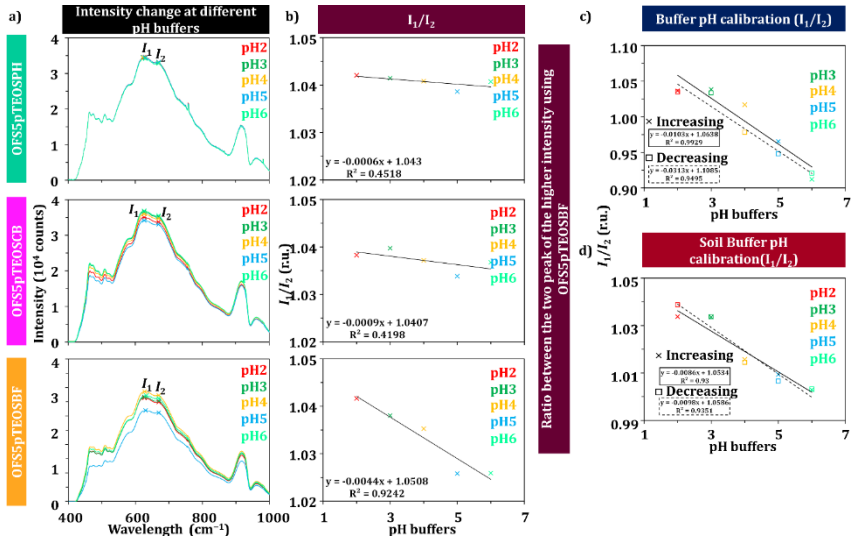

Figure 3. a) Intensity response for different pH buffers and b) the ratio calculated from the indicated points in the intensity graphs, same scale use to make de comparison. c) Calibration curves for the pH buffer and c) the soil pH buffers.

Figure 3a shows the response of these fibre sensors to the different buffer solutions into which they were placed. The OFS thus developed showing the best response is OFS5pTEOSBF, because, on one hand, the linear trend seen has the best fit (R^2=0.9242), and on the other, the highest difference in the intensity ratio was observed (I_1/I_2=1.042 (pH=2) to 1.026 (pH=6), see Figure 3b). The OFS5pTEOSPH sensor changes from non-colour to yellowish at pH=6, whereas the OFS5pTEOSCB goes from red in acid pH to purple in pH=4 and blue for pH=6; finally, the OFS5pTEOSBF sensor changes colour (when the pH=3), from dark orange to dark blue. The last example shows the most drastic change, and this could be because the cyanidin has also a wider range of change. In light of those results, the OFS5pTEOSBF sensor was studied more intensively in terms of calibration, stability, and reproducibility, as discussed below.The reproducibility of the sensor designated 5pTEOSBF (manufactured using 3 dips) was verified by preparing two further probes: one to be

tested again with different buffers and the second one for use in soil pH measurements. Figure 3c shows the calibration graph obtained when the first sensors were immersed into five different pH buffer solutions (pH=2, 3, 4, 5 and 6), while increasing and decreasing the pH value. The responses were noted after a period of 25 minutes of immersion in the pH buffer solutions. This response is better in terms of the behaviour seen than is shown in Figure 3b (better R^2 and higher I_1/I_2), although both sensors show essentially the same behaviour: when the pH increases, the ratio (I_1/I_2) decreases, emphasizing the reproducibility of the sensor response.

Finally, to simulate an evaluation 'in-the-field', a test was carried out using pH-modified soil samples with the second 5pTEOSBF new probe: the pH of the soil tested was set using pH buffers, keeping the moisture value at 50 %. The response, displayed in Figure 3d, was recorded every 25 min. As would be expected, the sensitivity obtained for the soil test was somewhat lower than that for the pure pH buffer solution, but importantly the same behaviour is observed: when the pH increases the ratio decreased, and when the pH decreases the ratio increased, showing both a reversible and linear response. On-going development work using soil samples will continue and further results will be reported.

4. CONCLUSION

The XG matrix discussed in this work (5pTEOS) can be used to form OFS systems with three different pH indicators (phenolphthalein, bromophenol blue and cyanidin blue) embedded, in that way to obtain several different doped hybrid xerogels (labelled 5pTEOSPH, 5pTEOSBF and 5pTEOSCB). Although these pH indicators are large organic molecules, the textural parameters of the XG matrix formed did not suffer major variations, resulting in microporous (5pTEOSCB, 5pTEOSBF) and ultramicroporous (5pTEOSPH) materials. The adsorption/desorption isotherms with water vapour were obtained and show that the materials have a labile interaction with the water molecules.

The resulting sensors created show a behaviour which follows the changes in the pH of the buffers, through a self-referenced characterization (in terms of the ratio between the two maxima of the spectra). The response obtained from the sensors follows a well characterized pattern, with increasing pH the ratio decreases which is also reproducible, reversible, and linear. The observations of the study, and the preliminary results from the simulated 'in-the-field' test on soil samples give confidence in the potential of this sensor design for important environmental monitoring applications.

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