Silica-based solid sensors prepared by the sol-gel method

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Abstract

The scope of the laboratory is the development of silica-based materials, with potential application as catalyst support, polymer additive, sorbents, sensors, preconcentration phases and chromatographic phases. The present text illustrates the development of two solid pH sensors with potential application in the fabrication of intelligent plastics, i.e., packing plastics which may change color in the case of degradation of the food by the alteration of pH or evolving of amines. In the first case study, the nature of the sol-gel route impinges some textural effects on the resulting sensor, which in turn responds differently to the target molecule. In the second case study, the presence of organic groups (coming from organoalkoxisilanes employed in the sol-gel synthesis) within the silica matrix affects the encapsulated content, and therefore the performance of the pH indicator.

Introduction

Sol-gel derived materials have received a peculiar interest as chemical receptor matrices due to their optical transparency, mechanical stability, chemical resistance and flexibility of sensor morphological configurations. Furthermore, the control of textural properties, in the case of pH sensors, enables a rapid response because the sol-gel matrix allows fast proton diffusion, and their ability to respond rapidly makes them desirable for use in pharmaceuticals, foods and chemicals industries [1].

The nature of the encapsulation route

We have investigated the effect of the nature of the indicator molecule and the influence of the sol-gel route on the structural, textural and morphological characteristics of the final sensor and its influence on the response to ammonia gas.[2] Three different pH indicators (alizarin red, brilliant yellow and acridine) were encapsulated by the three different sol-gel routes (the hydrolytic acidic, hydrolytic basic and non-hydrolytic routes), and the resulting systems performance were tested as acid-base sensors. Figure 1 illustrates the resulting sensors and their color change in contact with ammonia vapor. Shorter response times were achieved by the pH indicators encapsulated by acid route (RA). Higher incorporated indicator content was achieved by the non-hydrolytic sol-gel route (RNH).

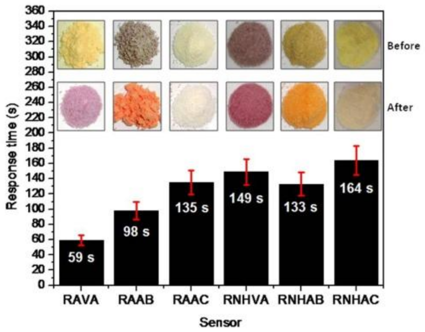


Figure 1. Incorporated content, visual color change and response time to ammonia gas for the synthesized solid sensors. RA = acid route; RNVA = non-hydrolytic route; VA = alizarin red; AB = brilliant yellow; AC = acridine.

Applications for real samples (environmental and industry samples) have shown their application as pH sensor. Figure 2 shows some examples about their pH range. It is worth mentioning that AC (acridine) is a fluorescent molecule.

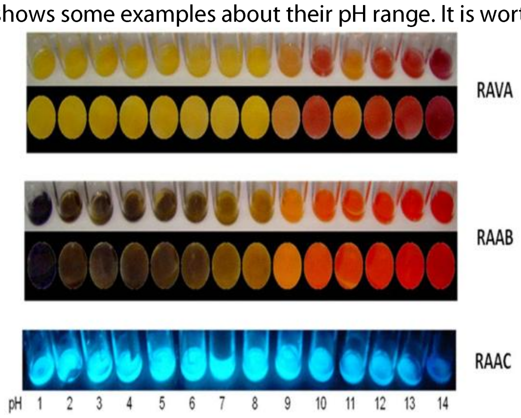


Figure 2. Performance of the solid sensor at different pH in environmental and industrial samples. RA = acid route; Indicators: VA = alizarin red; AB = brilliant yellow; AC = acridine.

The perception of color change of the sensor in the presence of ammonia was investigated by monitoring the perception of color change by 50 subjects. Correspondence analysis has shown statistic significance between females with blue eyes older than 25 years old and the visual perception and the rapid perception of color change of RAVA, for instance, as shown in Figure 3.

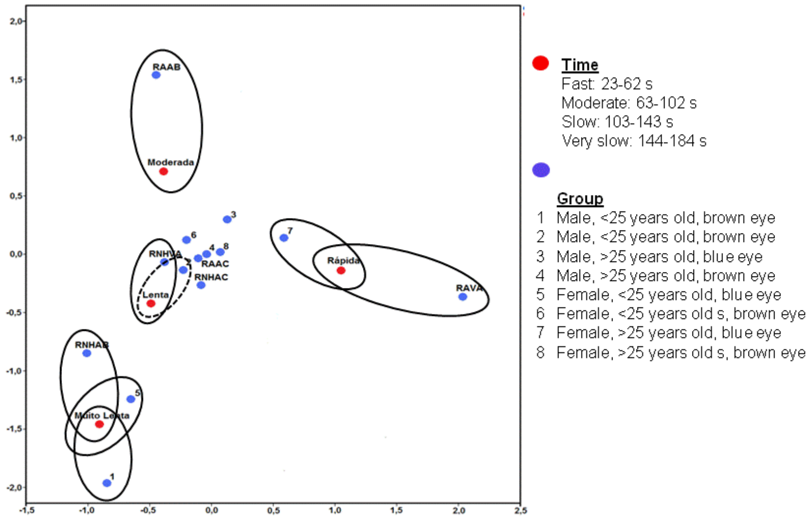
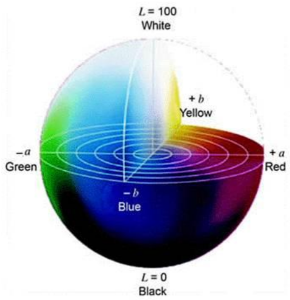


Figure 3. Correspondence analysis of the visual color change perception by the human eye.

Such behaviour can be assigned to delta color in the perception model of color change. Figure 4 provides the data showing the gap of color change of the solid sensors. Measurements were performed by diffuse reflectance in the UV-vis region and data were analyzed by color software.



$$\Delta E^*_{ab} = [\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}]^{1/2}$$

Sensor	Color coordination after NH_3 contact	ΔE^*_{ab}
RAVA		41,19
RAAB		37,23
RAAC		8,39
RNHVA		12,63
RNHAB		28,81
RNHAC		9,81

Figure 4. Correspondence analysis of the visual color change perception by the human eye. N = 50.

According to Figure 4, the acid route (RA) provides the higher color variation (Delta color). Furthermore, one can observe that the sol-route affects the pH indicator performance: compare the same indicator (VA): in the case of acid route (RAVA) and non-hydrolytic one (RNHVA).

The effect of organoalkoxysilane within the silica matrix

Another group of sensor was developed by the use of anthocyanins, pigments responsible for the red, purple, and blue colors of many fruits, vegetables, cereal grains, and flowers, as indicators. Anthocyanins were then efficiently incorporated within hybrid silica matrixes synthesized by the sol-gel method (series A). Silica structure was chemically modified with different organoalkoxysilanes. The presence of anthocyanins is revealed by the absorption band at 520 nm. Series B shows the series of hybrid silica without anthocyanins (Figure 4).

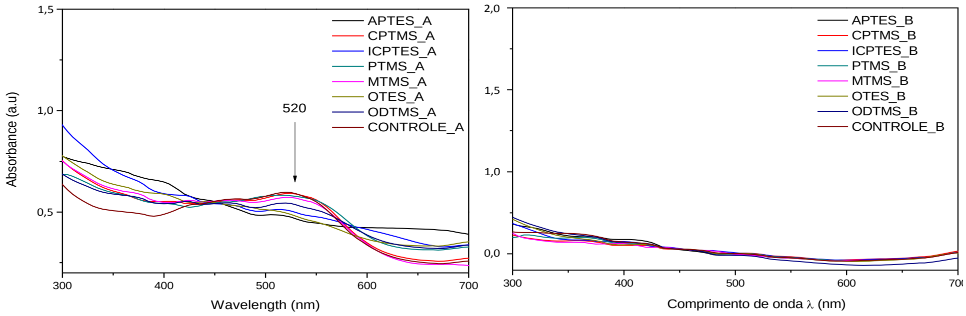
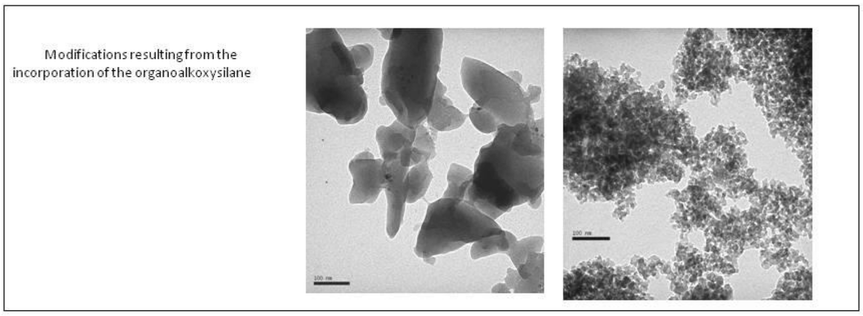


Figure 5. UV-vis spectra of hybrid silicas (serie B) and hybrid silicas containing encapsulated anthocyanins.

According to the results, the nature of the organoalkoxysilane impinges structural modifications in the silica matrix. Furthermore, as shown in Figure 5, the presence of anthocyanins affects textural characteristics of the hybrid matrices, resulting from the reaction between the organoalkoxisilanes and TEOS.



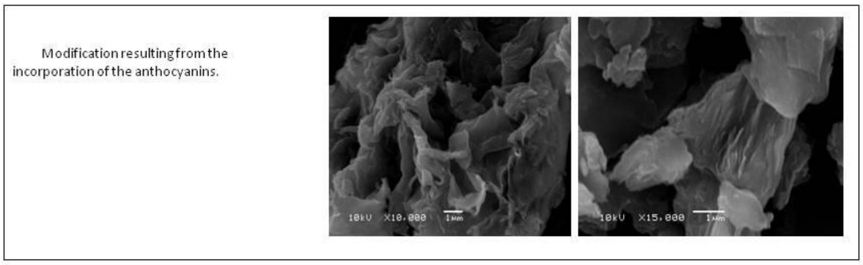
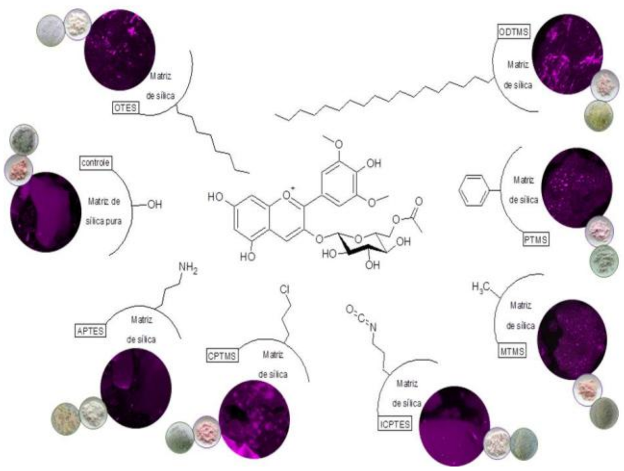


Figure 6 depicts the heterogeneity resulting from the distribution of anthocyanin. Brighter point represents higher anthocyanin concentration. In smaller circles, the sensor behavior vis-à-vis the pH is shown: rose/red (acid medium) – green (basic medium), observed for the neat anthocyanin.



ODTMS_A

Figure 6. Scheme representing the color change and morphological aspects (confocal microscopy) of the anthocyanins encapsulated in hybrid silicas prepared in the presence of different organosilanes.

References

1. L.A. Terry, S.F. White, L.J. Tigwell, The application of biosensors to fresh produce and the winder food industry, *J. Agric. Food Chem.* 53 (2005) 1309-1316.
2. L.B. Capeletti, F.B Bertotto, J.H.Z. dos Santos, E. Moncada, The effect of the sol-gel route on the characteristics of acid-base sensors. *Sensor & Actuators B: Chemical* (2010) (no prelo).

A complete version of the manuscript will be published in Sensor & Actuators B: Chemical (2010)