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Integration of New Sol-Gel Films Into Optical Chemical Sensors

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Abstract

CSEM has developed new sol-gel based sensitive layers enabling the optical detection of volatiles and dissolved analytes with enhanced performances. These sol-gel films exhibit a hierarchical nanoporous structure. Dedicated optical readers have been developed to interrogate the optical signal of the sensitive sol-gel patches. Applications of this technology, focusing yet on O₂, CO₂, and pH detection, are illustrated with practical cases in aeronautics and environmental, health, and process monitoring.

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Keywords: chemical sensors; sol-gel nanoporous films; optical readers; O₂; CO₂

1. Introduction

The miniaturization of sensors together with the dramatic increase in portable computational power is currently generating a whole range of new applications for chemical sensors. These sensors can be used for applications related to the environmental monitoring, health, aeronautics, or even food safety just to name a few. In order to be used with portable devices, sensitive materials must be small, cost effective, and reliable. Sensors based on luminescence change in presence with a specific molecule are promising candidates for this type of applications as they can be interrogated by standalone compact optical readers with wireless communication capabilities. CSEM has developed new optical sensitive patches based on a sol-gel nanoporous layer. These luminescent films are read with specifically designed readers for O₂, CO₂, and pH detection.

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Nomenclature

| | |
|-------|---|
| PSD | Power Spectral Density (Pa ² /Hz) |
| RMS | Root Mean Square |
| CCIFS | Chambre de Commerce et de l'Industrie Franco-Suisse |

2. Sol-gel nanoporous sensitive layers

To overcome the disadvantages of optical sensors based either on microporous or meso- and macroporous sensitive layers embedding photosensitive dyes, new functionalized thin films deposited on various substrates such as steel, glass, and flexible plastic sheets have been developed [1]. The host film is made of a double matrix: a microporous sol-gel network encapsulating the active species, which is embedded in a mesoporous coating (fig. 1-A). This hierarchical nanostructure brings to the sensitive layers enhanced performances, such as higher optical signal, sensitivity, robustness, mechanical resistance, transparency, selectivity, and a faster response (fig. 1-B).

Mesoporous matrix made of metal oxide (e.g. silica, Al oxide) are typically prepared by deposition of waterborne nanopowders dispersions using bar-, dip-, slot die, or curtain coating processes. The resulting thickness can be adjusted from a few to a few tens of microns.

The sol-gel microporous matrix is prepared from a mixture of hydrolyzed in ethanol organo-silanes and a dye. The resulting sol (also called the ink) is then printed on the mesoporous matrix by dip-coating, blading, inkjet printing techniques. These processes are fully up-scalable for a future industrial transfer.

3. Oxygen sensing

The technology of optical O₂ sensors is typically based on the encapsulation of a luminescent dye (e.g. ruthenium complexes, metalloporphyrins) in an inert matrix. In the presence of oxygen, the excited state of the dye is non-radiatively deactivated leading to a decrease in the intensity and also in the lifetime of the luminescence.

In a typical ruthenium-based experiment, the ink is prepared by mixing methyltriethoxysilane (MTES) and (3,3,3-trifluoropropyl)trimethoxysilane (FTP-TMOS) in ethanol. The mixture is hydrolyzed with HCl acidified water. Finally, Ruthenium(diphenylphenanthroline) chloride complex (Ru(dpp)₃) dissolved in ethanol is added to the mixture. The Ru(dpp)₃ complex is the fluorophore which phosphorescence is quenched in the presence of oxygen.

3.1. Pressure sensitive paint (PSP)

Oxygen sensitive paints are used to measure surface pressure as long as oxygen fraction in air remains constant. The fundamental operating principle of PSP is the quenching by oxygen of the luminescence from luminophores dispersed in the paint. Light intensity emitted by the paint is measured by a photodetector, providing a global map of pressure distribution over the probed surface [2]. The extension of the PSP technique to unsteady measurements is a new challenge that require the development of new paints with response time of several orders of magnitude below the one of conventional PSP. Among the several ways to reduce the response time of the paint while maintaining a high sensitivity to pressure and a high intensity of luminescence, the most efficient is based on the introduction of porosity within the coating to increase the diffusivity of O₂.

An innovative pressure sensitive paint has been developed in collaboration with ONERA for the observation of aerodynamic disturbances in wind tunnel [3]. In the present case, the shock wave fluctuations over the wing of an aircraft model has been investigated (fig. 1-D). First, a silica mesoporous layer was deposited on metallic inserts by dip-coating (fig. 1-C). Then, this mesoporous matrix was printed with a Ru(dpp)₃ ink. As a result, this new PSP enabled a low response time (< 100 μs), a high pressure sensitivity (> 0.75%/Pa) while maintaining a high emission intensity (three to five time higher than state-of-the-art PSP), and a good stability during the measurements.

Useful results as RMS, PSD, and coherence maps were obtained and compared favorably with those of pressure sensors (fig. 1-E-F). PSP measurements provide a high density of spatial information over a large area that is difficult to achieve with local pressure sensors. These outstanding results were awarded by the 2016 Innovation Prize of CCIFS.

Further developments will focus on process consolidation enabling the application on larger 3D surfaces.

3.2. Oxygen sensitive patches and DEMOX reader

Commercially available mesoporous silica-based layers deposited on transparent plastic sheets have been printed by the $\text{Ru}(\text{dpp})_3$ ink using a blading process (fig. 1-A). An oxygen optical reader called Demox was developed to determine rapidly, efficiently, and non-invasively the oxygen concentration in cell cultures (fig. 1-G). The Demox reader determines oxygen concentration by measuring the fluorescence lifetime of $\text{Ru}(\text{dpp})_3$ dye in CSEM's oxygen sensitive patches using phase shift. The reader has a format very similar to a microscope objective so that it can be directly mounted on the inverted microscopes used routinely in biology (fig. 1-H). The microscope facilitates alignment between sensor and reader while ensuring a stable and constant optical environment for reliability. The Demox oxygen sensor was awarded the BioInnovation-Ecllosion prize 2015. The solution is highly customizable.

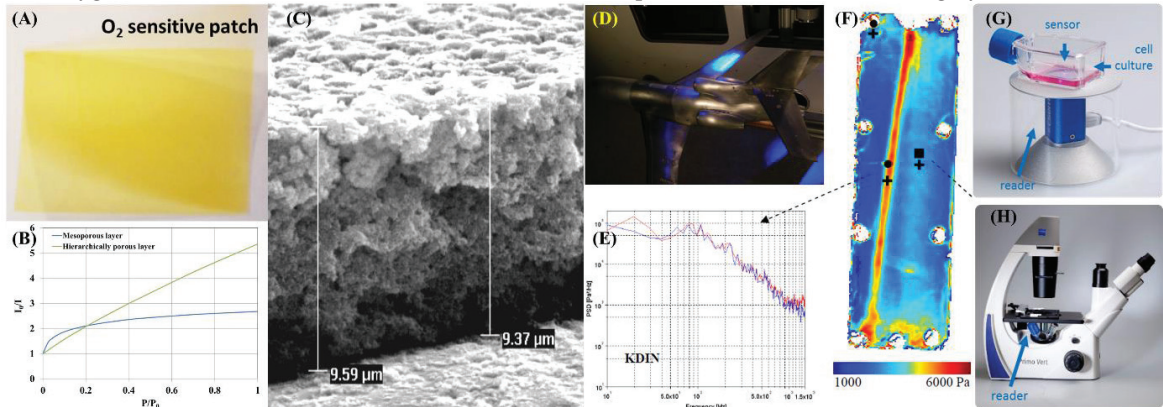


Fig. 1: (A) Pictures of O₂ sensing patches; (B) Stern-Volmer curves of O₂ (0-21% range); (C) SEM micrograph of the nanoporous silica layer cross-section of a PSP deposited on a metallic support; (D) Photograph of the illuminated PSP on a model in wind tunnel; (E-F) PSD and RMS map from nano-PSP, acquired @5000 Hz, demonstrating the perfect fit with local electronic pressure sensors and the fast response compared to conventional PSP ($F < 2000$ Hz); (G) Demox reader on its support for non-invasive oxygen measurement in cell culture and, (H) mounted on an inverted microscope.

4. CO₂ and pH sensing

A similar approach has been used for the detection of CO₂ and pH. For gaseous CO₂, the mechanism is based on a local pH change upon reaction with a quaternary ammonium base selective for CO₂. This event is monitored with a pH indicator dye that can be luminescent or colored (Fig. 2-A-B).

A miniaturized optical device for the detection of CO₂ is currently under development for air quality monitoring in buildings (Fig. 2-C). A disposable and low cost sensitive patch is interrogated in a closed module containing LEDs, lenses, and photodetectors (Fig. 2-D). Data processing based on artificial neural networks has been designed to limit the signal deviation ($< 0.05\%$). Once integrated into a system comprising humidity and temperature sensors, the device has a low detection limit (yet down to 1 ppm) enabling the monitoring of air quality and other sensor calibration.

In parallel, compact colorimetric readers of pH have also been developed for health monitoring applications based on similar detection schemes. pH sensitive patches have been prepared using silica mesoporous layers printed with an ink containing pH indicator dyes (without any quaternary ammonium base). The microporous matrix was designed in order to prevent any dye leaching during measurements. The pH sensitive patches remain stable after more than one month soaked into water with pH values ranging from 3 to 9 (Fig. 2-F). The designed pH reader consists in an optical light guide, so-called optical bridge, connecting optically the light source, the sensing patch and the detector (Fig. 2-E). A pH indicating patch is placed on top of one of the optical bridges emerging from the top part of the device. The technology allows to measure skin pH or to monitor breath quality and any liquid environment, beyond commercial system performances (Fig. 2-G).

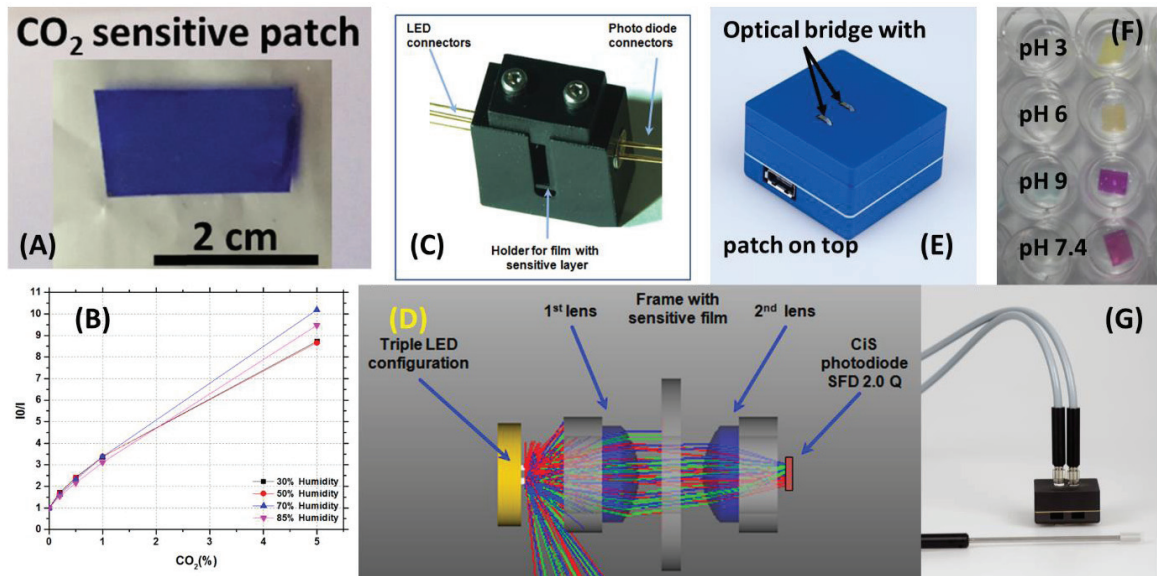


Fig. 2: (A) Pictures of CO₂ sensing patches; (B) Stern-Volmer curves of CO₂ at various humidity values; (C) micro-optical light emitter-receiver module for the CO₂ sensitive films; (D) Optical design of the sensor head; (E) Picture of the Colorimetric wearable pH reader device; (F) pH sensitive patches in water at various pH values after 1 month soaking; (G) Picture of the optical pH-meter.

5. Conclusion

The development of new and low cost O₂, CO₂, and pH sensitive patches with enhanced performances has enabled their integration into miniaturized systems. In addition, the transfer of O₂ sensitive layers onto metallic model parts open up new perspectives for the development of fast PSP for the optimization of aerodynamic profiles in unsteady conditions.

Specific associated readers have demonstrated promising performances for environmental quality monitoring, healthcare, and bioprocess monitoring among others. Further development will be dedicated to the improvement of the performances regarding to environment changes (e.g. humidity) and the scale-up of the fabrication processes.

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