

Supporting information for

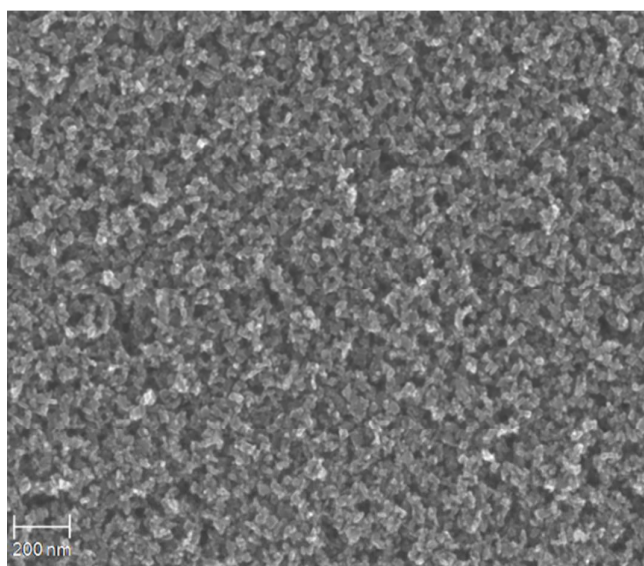
“An optical dosimeter for the selective detection of gaseous phosgene with ultra-low detection limit”

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Experimental section

Films preparation

The Harrison's reagent (a 0.37 μM equimolar mixture of diphenylamine and 4-((dimethylamino) benzaldehyde from Sigma-Aldrich) is infiltrated in nanocrystalline TiO_2 films made with Dyesol[®]18NR-T (Dyesol[®], Queanbeyan, Australia) by a simple screen printing procedure in which we make consecutively two layers through a 90T mesh screen to form a transparent TiO_2 film of 0.16 cm^2 active area. Before infiltration, the substrates were sintered for 30 min at 500 $^\circ\text{C}$. The average thickness of these films was found to be about 3 μm according to Scanning Electron Microscopy measurements (GeminiSEM 300, Zeiss, Germany). As can be seen in Figure S1, the matrix owns a high porosity with a homogeneous porous distribution that favours the interaction between the TiO_2 matrix and the sensing molecules, and later, with the analyte.¹ The infiltration time was fixed at 15 min after checking that longer times lead to saturation of the absorbance.



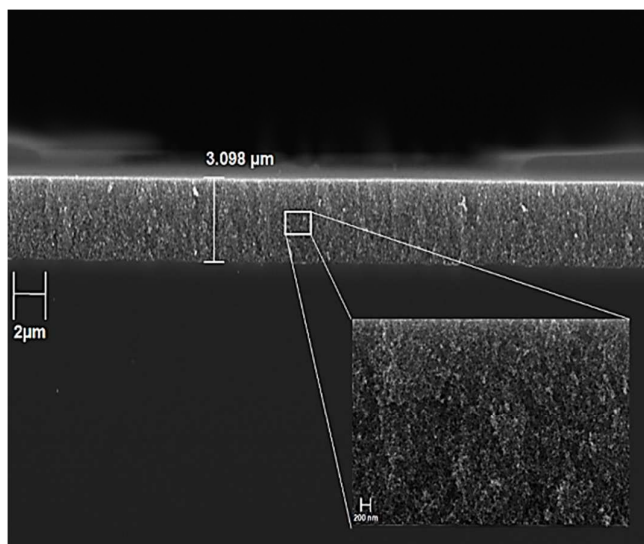


Figure S1. Scanning electron microscope images of nanocrystalline TiO_2 films. Top: top view; Bottom: side view.

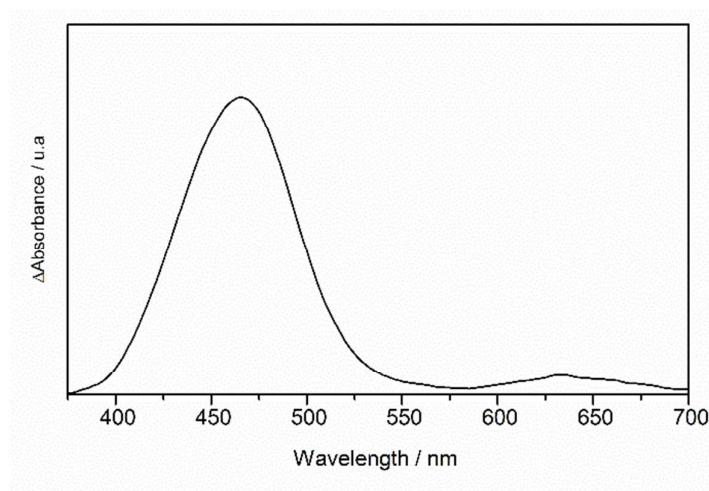


Figure S2. Spectral variation of the infiltrated TiO_2 films after exposure to gaseous phosgene at a local concentration of 1200 ppm. The appearance of a band at 650 nm is apparent.

Gas exposure system

The UV-vis spectra were recorded in both an Agilent Cary-100 spectrometer and in a purpose-built gas testing chamber. Briefly, it consists of a gas inlet and an outlet, a Peltier heating-cooling device and housings for two optical fibers that deliver and collect the light for the optical measurements. The fibers were connected to an Ocean Optics USB4000 spectrophotometer and allowed the determination of the absorption spectra in the UV-vis range. Gaseous phosgene streams were obtained by flowing dry nitrogen through the head-space of a bottle immersed in an ice bath that contained a predetermined toluene-phosgene (from Sigma Aldrich, 15 % in toluene) solution to obtain the desired gaseous phosgene concentration calculated through its vapor

pressure at the corresponding temperature. The desired concentration was finally obtained by dilution with a second nitrogen stream. Both nitrogen streams were controlled by two Bronkhorst F-201FV mass flowmeters. To neutralize the toxicity of phosgene, the gas outlet was passed through a water filter. Additional experiments employing phosgene diluted in synthetic air led to identical results as those obtained with N₂ streams. This method for evaluating the phosgene concentration in the gas phase leads to reliable results when comparing with experimental data.² Details of the experimental set-up can be found elsewhere.³ The increase of the absorption band peaking at 464 nm (ΔA_{464}) is used to evaluate the sensitivity of the infiltrated films. The parallel monitorization of the signal at 800 nm is used to subtract the background signal coming from the detector drift. The instant response of the sensor to 8 ppm of phosgene was obtained by opening the gas stream containing phosgene and immediately recording the UV-Vis spectrum, as fast as an operator can perform this procedure, which was below two seconds in all cases.

Laser desorption ionization experiments

Finally, Laser Desorption Ionization mass spectrometry (LDI-MS) and Matrix-Assisted Laser Desorption Ionization (MALDI) experiments were performed in reflection mode with an UltrafleXtreme MALDI-a-TOF-MS (Bruker-Daltonics). The ion source was operated in the conventional pulsed extraction mode at 25 kV. Given the self-matrix effect of TiO₂, no additional chemical additive is needed for obtaining the LDI spectra. In order to identify peaks that are already presented in the Harrison's reagent before infiltration, MALDI experiments were performed over this mixture with 2,5-dihydroxybenzoic (DHB) acid as MALDI matrix. As it was expected the protonated aldehyde and amine adducts are presented in the low mass region of the MALDI spectra. The results for the m/z region of interest are shown in the bottom panel of Figure S3 with a main peak at $m/z=301$. A peak with a slightly smaller m/z value is present in the infiltrated films before exposure (data not shown for the sake of simplicity), where other additional peaks appear at 266, 336 and 503 m/z and are attributed to the formation of analyte-matrix adducts upon the laser heating, and hence are not related with the specific reaction between phosgene and the probe. These experiments confirm that there is peak at $m/z\sim 301$ in the LDI spectrum of the infiltrated films before exposure that comes from the colorimetric reagent and is discussed in main text. Briefly, it corresponds to condensation product between the reagents. It should be remarked that the use of an acidic organic matrix may have enhanced the condensation, whereas in the case of the infiltrated films, the surface titanol groups confers an acidic environment to TiO₂ surfaces. After exposure to low concentrations of gaseous phosgene, the formation of the molecule 3 in the mechanism detailed in Figure 1c is evident. We have included an inset in the region 300.5-301.5 m/z where a double peak is observed around 301 m/z . The adduct coming from the reaction with phosgene is marked with an asterisk. At high phosgene concentration (or exposure times) a new peak appeared at 468 m/z that can be related to the formation of HCl as an additional product of the sensing reaction. This peak can be attributed to a new specie whose formation is mediated by the accumulation of HCl. This is supported by the appearance of a coincident peak when the films are exposed to saturated vapours of HCl.

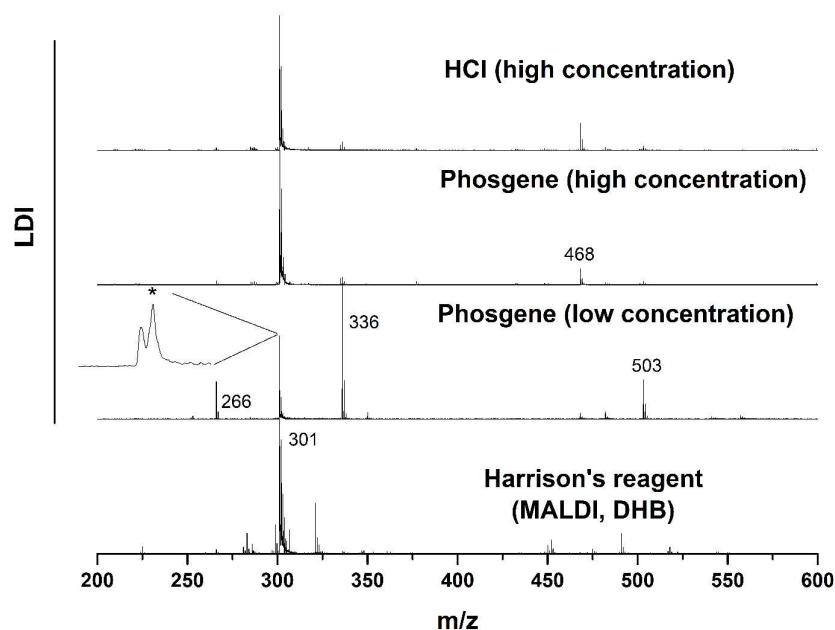


Figure S3. From bottom to top: MALDI spectrum of the Harrison's reagent with DHB as organic matrix; LDI spectrum of the reagent upon exposure to low (in the ppb region) phosgene concentration (the inset highlights the region around 301 m/z , see text for details); LDI spectrum of the reagent upon exposure to high (in the ppm region) phosgene concentration; LDI spectrum of the reagent upon exposure to saturated HCl vapor.

Other additional figures

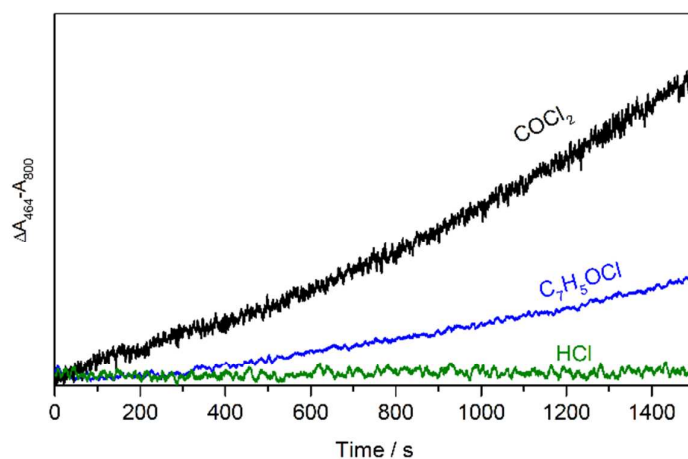


Figure S4. Temporal evolution of the background corrected absorbance of the films at 464 nm under different interfering atmospheres. Notice that the analyte interferent concentration is fixed at 0.75 ppm for all the curves.

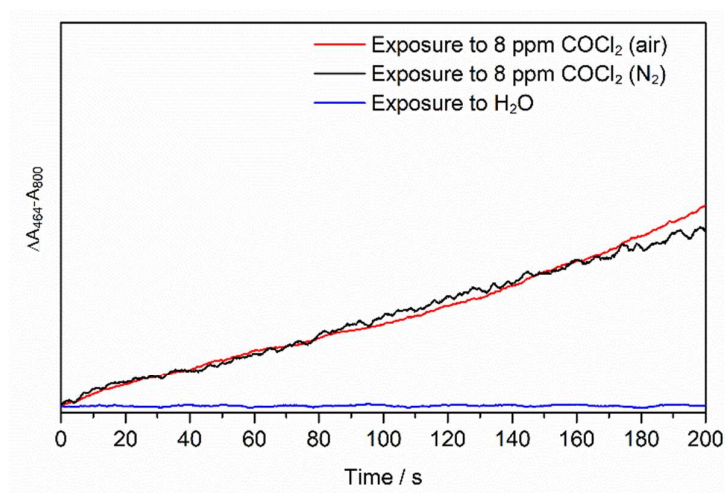


Figure S5. Temporal evolution of the background corrected absorbance of the films at 464 nm under different interfering atmospheres.

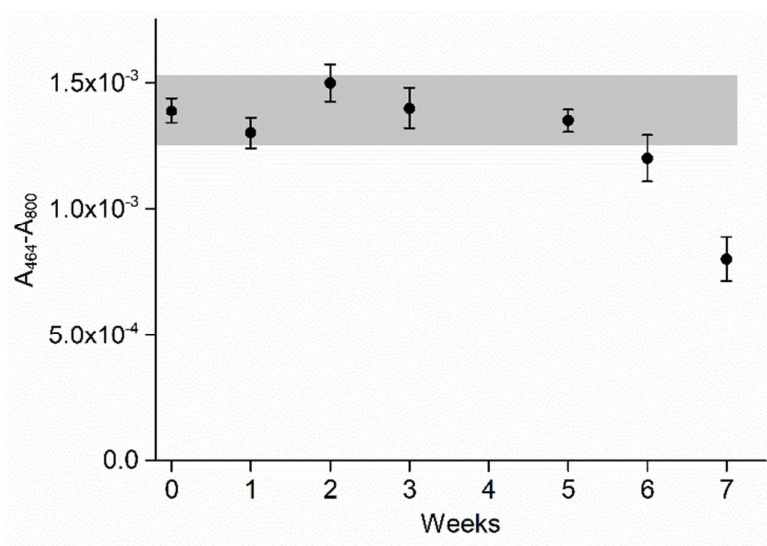


Figure S6. Temporal evolution of the background corrected absorbance of the films at 464 nm for 49 days when stored in an enclosed space below 10 °C. The gray area indicates a range of $\pm 10\%$ of the initial calibration signal averaged over triplicate independent samples.

References

- [1] Zhu, K.; Kopidakis, N.; Neale, N. R.; van de Lagemaat, J.; Frank, A. J. Influence of Surface Area on Charge Transport and Recombination in Dye-Sensitized TiO₂ Solar Cells. *J. Phys. Chem. B.* **2006**, *110*, 25174-25180.
- [2] M. Hirata, S. Ohe and K. Nagahama, in *Computer aided data book of vapor-liquid equilibria*, Elsevier Science & Technology, Amsterdam, 1975.
- [3] J. Roales, J. M. Pedrosa, M.G. Guillén, T. Lopes-Costa, S. M. Pinto, M. J. Calvete and M. M. Pereira. Optical detection of amine vapors using ZnTriad porphyrin thin films. *Sens. Actuators B Chem.* **2015**, *210*, 28-35.