

Colorimetry-based System for Gaseous Carbon Dioxide Detection: Membrane Optimization

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Abstract

The study of sensing materials to the detection of carbon dioxide (CO₂) was achieved using p-nitrophenol (pNPh) as a colorimetric indicator. The sensing material was polymerized (NPLn), functionalized with 3-triethoxysilyl propyl isocyanate (IPTES) which sensitivity was tested in the form of a membrane as is and encapsulated in hollow silica nanoparticles. The sensing membranes were tested in a closed gas system comprising very precise flow controllers to deliver different concentrations of CO₂ (vs. N₂). The combination of the sensing membranes with multimode optical fibers and a dual-wavelength diode (LED) allows the measurement of the CO₂ through the analysis of the induced absorbance changes with a self-referenced ratiometric scheme. The analysis of the sensing materials have shown significant changes in their chemical and physical properties and the results attest these materials with a strong potential for assessing CO₂ dynamics in environmental, medical, and industrial applications.

Author Keywords. Carbon Dioxide Detection, Colorimetric Membrane, Polymerization, Optical Fiber.

Type: Research Article

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1. Introduction

In the last years, materials with different chemical and physical properties have been used to develop sensors for a large diversity of applications. Currently, polymerized materials have the domain in the sensors field ([Cichosz, Masek, and Zaborski 2018](#)). They can assume a wide range of forms, such as solutions, gels, self-assembled nanoparticles, or solids. The working principle of these materials consists in change its own chemical and/or physical properties when influenced by an external stimulus. This can be transduced in qualitative and/or quantitative signal by different techniques such as optical or electrochemical, among others. Sensors using materials responding to pH, temperature, ions presence, light radiation, magnetic and electric fields, and bioactive molecules have been widely used in diversified fields ([Hu and Liu 2010](#)). Around the world, there are a large number of policies that have

intensified the need for the development of sensing equipment to monitor air quality, toxic gases and vapors, and water quality (Adhikari and Majumdar 2004). If the sensors developed for liquid applications are important, gas sensors also sensing a large variety of pollutants all over the world. Gas sensors can be developed using materials, such as polymers functionalized carbon nanotubes (Chiou and Wu 2017), conducting polymers (Crowley et al. 2008), metal oxide thin layers (Mohammad et al. 2016; Rieu et al. 2016), or graphene on a metal foil, which can be further transferred for a flexible substrate (Lee et al. 2012; Yang et al. 2013), and metal coating on a PDMS membrane (Lee et al. 2011). The fabrication technique should be chosen according to the material features and properties. Furthermore, procedures such as spin-coating, chemical vapor deposition, physical vapor deposition, printing, self-assembling, *in-situ* polymerization, and *in-situ* growth are usually reported in the literature as the most used techniques to perform sensing devices for gaseous applications (Alrammouz et al. 2018). Gas sensors are widely used to detect diverse pollutants in fields such as medicine (Ryabtsev et al. 1999), food industry (Vargas-Sansalvador et al. 2019), and environmental monitoring (Pathakoti, Manubolu, and Hwang 2018). Asad and Sheikhi (2016) reported a sensing material composed by CuO-SWCNT (copper oxide-single walled carbon nanotubes) to detect low concentrations of hazardous hydrogen sulfide (H₂S). Chaudhary and Kaur (2016) reported that polyaniline nanostructures-based sensors can be successfully used for sulfur dioxide detection, and Chakravarty, Datta, and Sen Sarma (2017) reported a polyvinyl alcohol formaldehyde-based composite for the detection of the same analyte. Due to its reputation in the environment and in the food industry, carbon dioxide (CO₂) is a gas of interest, so its detection and evaluation are of special interest (Anwar et al. 2019). During food spoilage, it is imperative to monitor the amount of this gas, which is a qualitative indicator of the food status (Puligundla, Jung, and Ko 2012) and also assess the tightness of the package (Neethirajan, Jayas, and Sadistap 2008). In this paper is present the development of a solid-state membrane composed by a sensitive material with chemical and physical properties for gaseous CO₂ recognition, highlighting different methods to enhance the sensitivity of the p-nitrophenol for the detection of low concentrations of CO₂.

2. Materials and Methods

2.1. Chemical reagents

The sensing membranes were manufactured using the following chemical reagents: p-nitrophenol (Sigma-Aldrich ReagentPlus[®], ≥99%); tetraoctylammonium hydroxide solution (TOA-OH, Sigma-Aldrich, 20% in methanol); Hydrogel D4 solution (AdvanceSource Biochemicals) and poly(2-hydroxyethyl methacrylate) (pHEMA, Sigma Aldrich). For the functionalization, was used the 3-triethoxysilyl propyl isocyanate (IPTES; Sigma Aldrich, 95%). For the silica nanoparticle synthesis was used deionized water (Wasserlab, Micromatic – Type II Analytical Grade Water), tetraethyl orthosilicate (TEOS; Sigma Aldrich) and ammonia hydroxide (Supelco, EMSURE[®] ISO). As primary solvents were used ethanol (EtOH; AGA, 96% and Absolut), methanol (MeOH; Sigma Aldrich, ≥ 99.9%), and dimethyl sulfoxide solution (DMSO; Sigma Aldrich, ReagentPlus[®], ≥99.5%). Dry Nitrogen (N₂) was supplied from a 50 L bottle (Linde, ≥99.99%) and CO₂ from 30 L bottle (Linde, ≥99.99%).

2.2. Sensing membranes synthesis and sensing methodology

The chemistry behind the sensitivity of this material to CO₂ involves an ion-pair formation between the quaternary ammonium (QA⁺) and the colorimetric indicator (QA⁺pNPh⁻) that results from the interaction of pNPh with the TOA-OH converting the sensitive dye in its deprotonated anionic form. The interaction with the gas seems to be linked to the association

of this ion-pair with a few molecules of water ($QA^+pNPh^- \cdot xH_2O$) absorbed from the air humidity (Equation 1) (Mills 2009). The CO_2 interaction with the membrane matrix induce internal pH changes turning it more colorless. When the gas leaves the system, the internal pH increases and the membrane recovers its original color (deep yellow). Figure 1 shows the process of sensing layer fabrication.

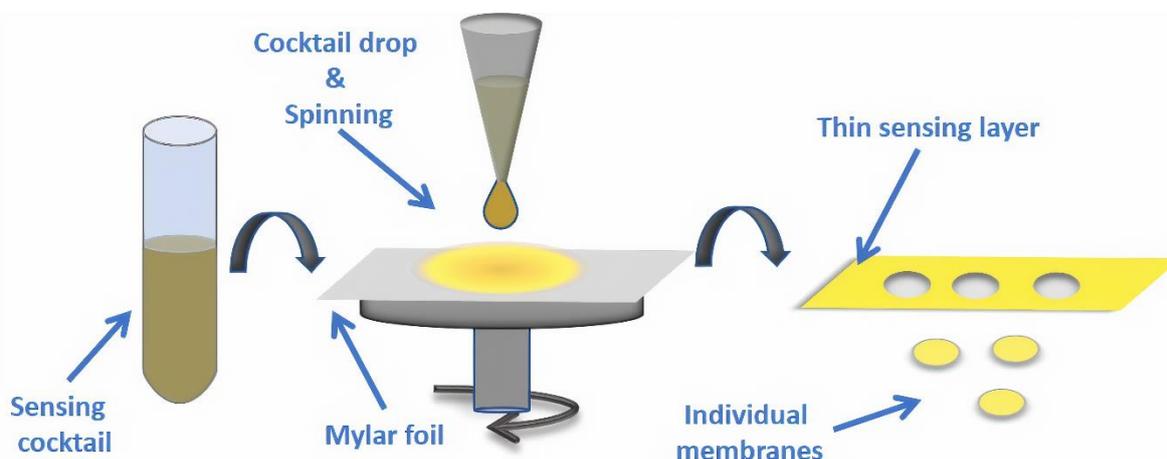
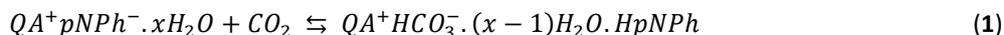


Figure 1: Schematic representation of the sensing membrane fabrication process

In the following sub-sections, the procedures for the preparation of the cocktails used to perform the different sensing layers, linked to the respective sensitive study, will be described. The cocktails were named as following: pNPh (indicator); NPL n (polymerized indicator; n = number of chains); NPL n _IPTES (polymerized indicator functionalized) and NPL n _Np (polymerized colorimetric indicator in silica nanoparticles). All the membranes were attained by spreading the respective cocktail on a Mylar foil (spin-coating (homemade equipment) at 600 rpm for 60 s) and letting dry at room temperature and high relative humidity for 2h.

2.2.1. Effect of the polymerization

For this study two different cocktails were used: pNPh and NPL11. Obtaining the polymeric chains from the monomer is a patent-pending process (WO2016051217A1) (Figure 2). The sensing cocktails were prepared dissolving 5.0 mg and 1.5 mg of pNPh and NPL11, respectively, in a 0.05 ml MeOH:H₂O solution (1.5:1) and 0.5 ml of 0.5 M of TOA-OH solution. After complete dissolution, 0.1 mL of a 10 % hydrogel solution in EtOH (96%) was added to the previous mixtures.

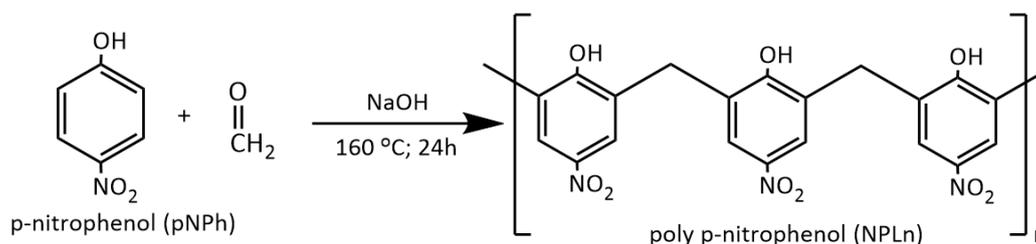


Figure 2: Chemical equation for poly p-nitrophenol production from the p-nitrophenol monomer

2.2.2. Effect of material functionalization

For this study two different cocktails were used and compared, the same NPL11 cocktail described in the sub-section 2.2.1., and the NPL11 cocktail functionalized with IPTES

(NPL11_IPTES). The NPL11_IPTES was attained by dissolving of 1.5 mg of NPL11 in 0.05 ml DMSO. After total dissolution (~ 24h) 0.5 ml of TOA-OH solution and 0.1 ml of pHEMA solution (20% in DMSO) were added to the NPL11_IPTES cocktail. The mixture was stirred during 24h.

2.2.3. Effect of silica nanoparticles

The layers containing silica nanoparticles were produced in the same way of the NPL11_IPTES layers. After the cocktail is ready, it is mixed in a ratio 1:1 (v/v) with the silica nanoparticles solution and stirred for, at least, 24h. During this process, the silica nanoparticles cavities are filled with the sensing cocktail. The nanobeads were prepared as described in the literature (Rao et al. 2005).

2.3. Measurement setup

A set of experiments were executed in order to evaluate the sensitivity of the different sensing layers. For the purpose, a plastic structure was designed and 3D printed (Zortax M2000; material: Z-Ultra T) assembled with an RGB LED (additive color model in which Red, Green and Blue light are added together; Kingbright Europe) and powered through an electric wire (Figure 3). The system works in two specific wavelengths (460 nm using the blue light as a detection band and 645 nm using the red light as a reference signal) and was attached to a CCD spectrometer (ScanSpec UV-Vis; 250-800 nm) using a multimode optical fiber cable. The structure was also endowed with two plastic lenses (Roithner LaserTechnik GmbH) to collimate the light (optical collimator) increasing the active area of detection while improves the light signal.

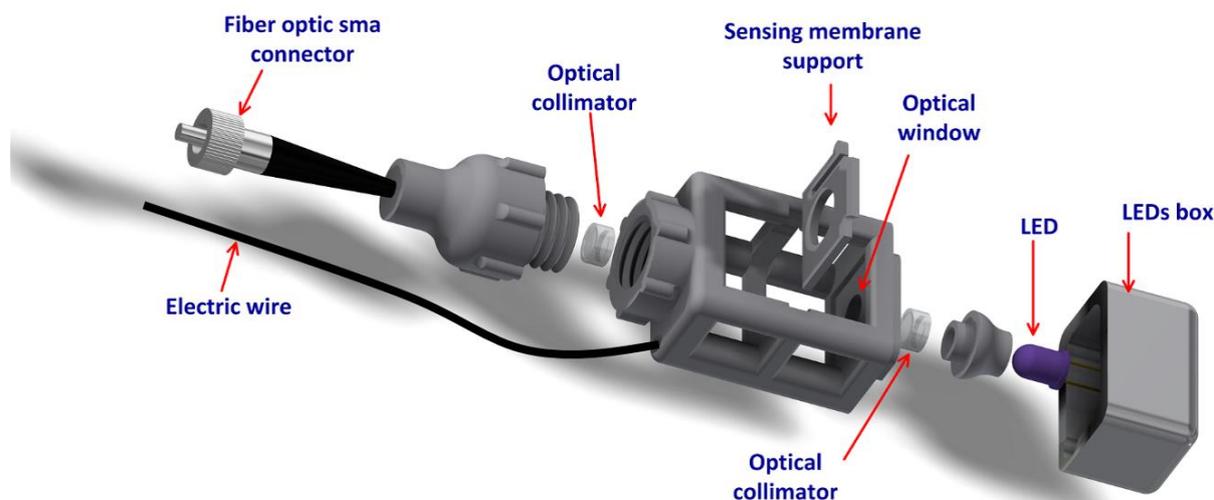


Figure 3: Sensing structure used to evaluate the sensitivity of the different sensing layers

The sensitivity of the sensing membranes was attested using the gas system outlined in Figure 4, comprising a humidified gas mixture composed by CO₂ and N₂ sourced from gas bottles. The amount of each gas was varied and controlled by high-resolution mass-flow controllers (Brooks, SLA5800 Series). All the membranes were tested for 35 min inside of the gas chamber, varying the CO₂ concentration at every 5 min.

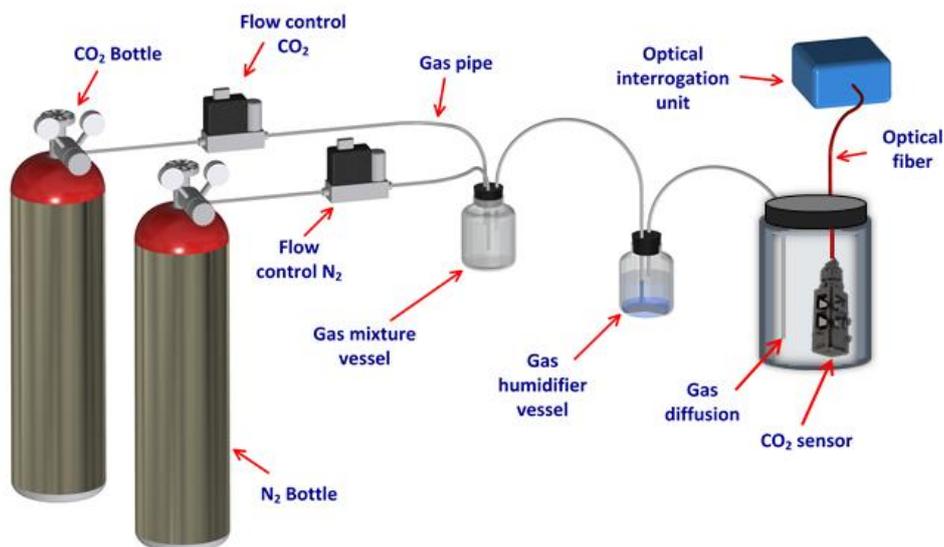


Figure 4: Schematic assemblage of humidified CO₂-N₂ gas system (adapted with permission from Mendes et al. (2019) - Open Access CC BY license)

3. Results and Discussion

As was explained before, the working principle of this system comprises a direct interaction of the gas with the sensing surface of the membranes, which enables a chemical reaction that acidifies the sensing layer reducing its color intensity. When the system releases the CO₂ (naturally or forced by other gases such as N₂ or O₂), the membrane becomes less acidic and the color is restored. Figure 5 shows an example of how the membrane responds to the increasing amounts of CO₂. Fluctuations in the chemical properties of the sensing membrane affects its own color causing variations in the range of absorbance. The blue color ($\lambda = 460 \text{ nm}$), from the blue LED, is absorbed by the yellow color of the sensing membrane when it is intense, but more blue light will pass through the membrane when the yellow color loses its intensity due to the action of the CO₂. The red light ($\lambda = 645 \text{ nm}$) remains stable and is used to correct small interferences (such as pressure variations) in the gas chamber. In the next subsections, the showed data is already the corrected value (reference signal – detection signal) for each concentration (in %) of CO₂ (vs. N₂).

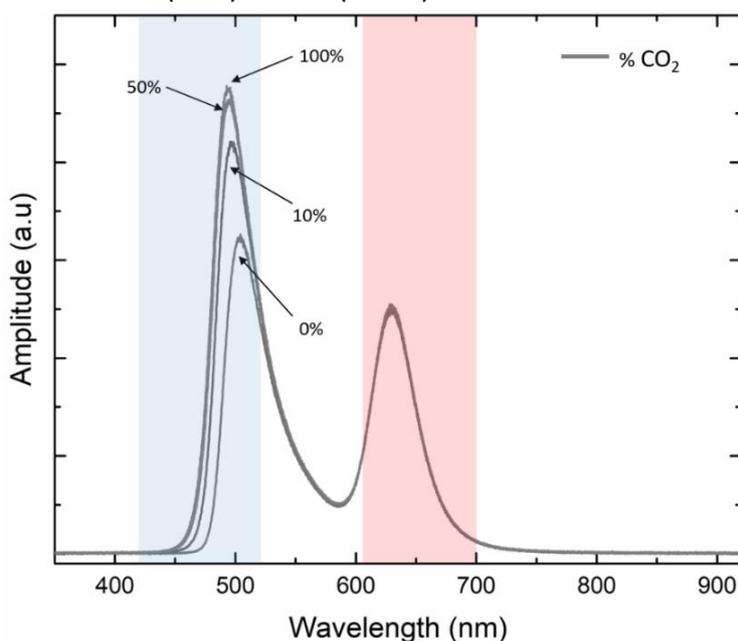


Figure 5: Sensing membrane optical transmission to gaseous CO₂ variations

3.1. Effect of the polymerization

The effect of the polymerization in the material sensitivity was studied, increasing the CO₂ concentration from 0 to 0.7 % (vs. N₂) (Figure 6). The response of each material is quite different. While the pNPh responds linearly, the NPL11 responds logarithmically. That difference can be explained by the higher sensitivity of the NPL11 material in the lowest range of gas concentration (steeper slope from 0 to 0.3 %). This abrupt change in sensitivity results from the modification of the chemical properties given by the polymerization process (Jasso-Gastinel, Soltero-Martínez, and Mendizábal 2017). As this system is based on internal pH changes, the acid-base equilibrium between the membrane and the external media is very important (Xie et al. 2016). Recently, Heffernan and O'Reilly (2019) reported a new type of polymeric synthesis and realized that the pK_a seems to be linked to the sensory capabilities of the material. Polymerization induced new chemical properties in the sensing material related to the acid-base equilibrium. The introduction of polymeric chains induces strongest hydrogen bonds enhancing the sensory features and the stability between pH changes caused by the membrane-gas interaction.

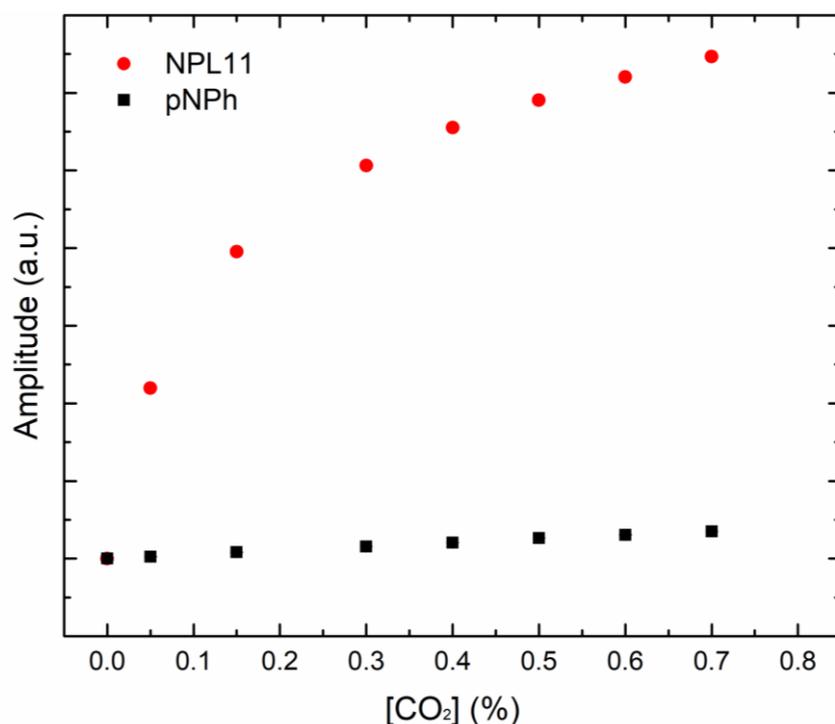


Figure 6: Comparison of pNPh and NPL11 based sensors response to different amounts of CO₂

3.2. Effect of material functionalization

In this study, was compared the sensitivity of the polymerized material with the functionalized polymer (Figure 7). The sensitivity of both materials was tested in the same range (0 to 0.7 %), and the resultant data show that the materials respond differently to the same concentrations. The functionalized membrane with IPTES is more sensitive, and that fact is more notorious at higher concentrations of gas. This increase in sensitivity can be explained by the covalent modification of the sensing material (Lian and Yan 2015). IPTES functionalization allows strong interactions between its alkoxy functional groups and the hydroxyl groups of the poly p-nitrophenol chains (Yan 2017). This type of functionalization was also used by Haghdadeh et al. (2019) to improve the mechanical properties of graphene oxide nanosheets with good results. Moreover, Wang and Yan (2006) used IPTES to functionalize

hybrid materials, improving their luminescent capabilities. The presence of the IPTES allows a more efficient hydrogen transfer and reinforces the hydrogen bonds' existents in the system.

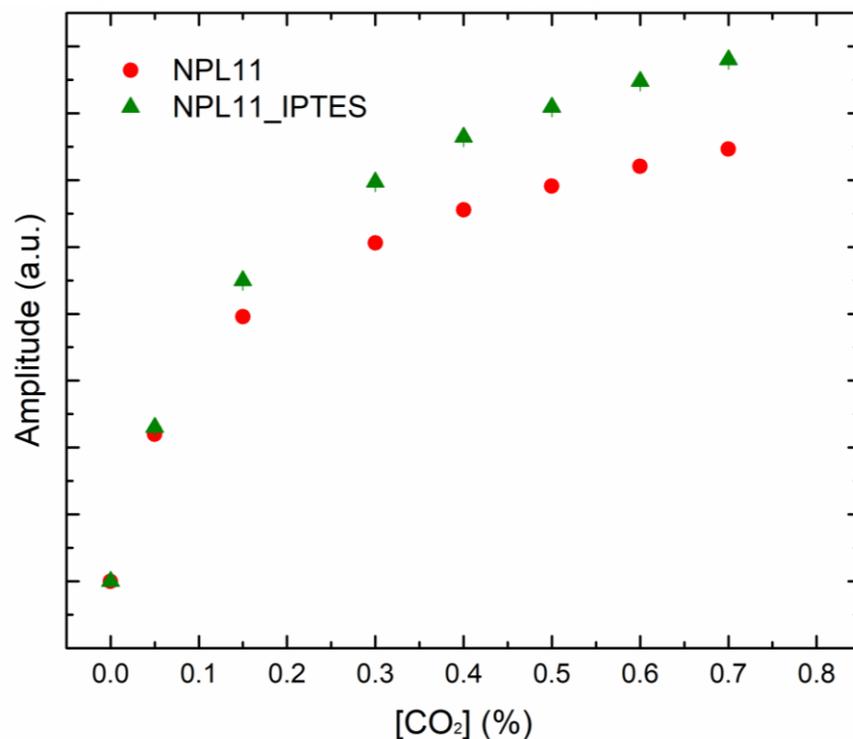


Figure 7: Comparison of NPL11 and NPL11_IPTES based sensors response to different amounts of CO₂

3.3. Effect of silica nanoparticles

In order to study the effect in the sensitivity of the membrane, the nanoparticles were filled with NPL11_IPTES cocktail and dropped on a Mylar foil, resulting in the NPL11_Np membrane. The obtained results (Figure 8) showed a decrease in the sensitivity of the material encapsulated in silica nanoparticles, even when compared with the non-functionalized material (NPL11). This fact can be explained by the “difficulty” of the gas particles to penetrate the silica cavities. So, perhaps, to achieve the same amplitude for the same gas concentration, the system containing the nanobeads needs more time to meet the equilibrium due to the gas diffusion into the nanobeads and more studies are need to understand this phenomena. However, the presence of silica nanoparticles can increase the time-life of the sensing layer, as was reported by [Chiu et al. \(2010\)](#) that used silica nanoparticles together with gold nanoparticles to enhance the characteristics of a polymer light-emitting devices. In other researches, [Gao et al. \(2011\)](#) showed a pH-responsive core-shell fluorescent silica nanoparticles based sensor; [Abnous et al. \(2018\)](#) reported the development of a fluorescent aptasensor for cocaine detection in human serum, based on silica nanoparticles coated with streptavidin; and [Gao et al. \(2020\)](#) demonstrated polymer-encapsulated hollow mesoporous silica nanoparticles to be applied in agriculture as insecticide deliverers.

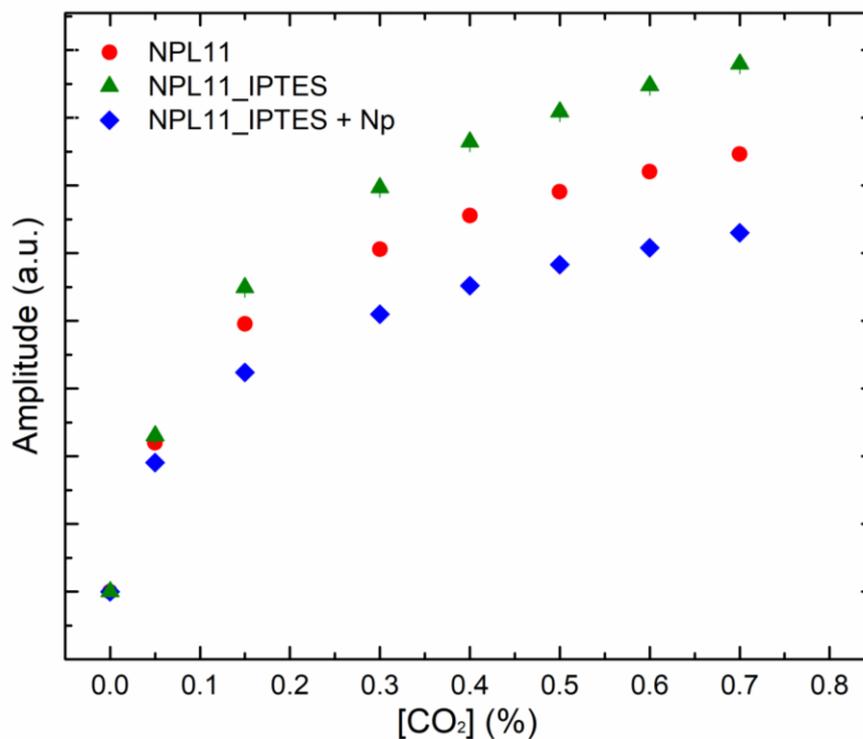


Figure 8: Comparison of NPL11, NPL11_IPTES and NPL11_Np based sensors response, response to different amounts of CO₂

4. Conclusions

The CO₂-induced absorbance variation on a material with colorimetric properties was studied. The sensitive dye was mixed with different materials to produce solid-state membranes, offering a range of possibilities to enhance its sensitivity. The presented data show that polymerization is a significant step to achieve the proposed objective. The functionalization process enables stronger chemical interactions between the compounds that make up the membrane. Consequently, the strengthening of the interactions significantly improves the sensitivity. However, due to the use of organic reagents and the time spent to produce the membranes, its usage is unjustified since the standard polymerized material has a similar response. The same conclusion is valid for the encapsulation in silica nanoparticles. The sensitive capabilities of these materials, together with adequate transduction and interrogation methods, are promising not just for gas sensing, but also for be applied in the monitoring of dissolved CO₂ in water systems.

References

- Abnous, K., N. M. Danesh, M. Ramezani, S. M. Taghdisi, and A. S. Emrani. 2018. "A novel amplified double-quenching aptasensor for cocaine detection based on split aptamer and silica nanoparticles". *Analytical Methods* 10, no. 26 (july): 3232-36. <https://doi.org/10.1039/c8ay00755a>.
- Adhikari, B., and S. Majumdar. 2004. "Polymers in sensor applications". *Progress in Polymer Science* 29, no. 7 (july): 699-766. <https://doi.org/10.1016/j.progpolymsci.2004.03.002>.
- Alrammouz, R., J. Podlecki, P. Abboud, B. Sorli, and R. Habchi. 2018. "A review on flexible gas sensors: From materials to devices". *Sensors and Actuators A: Physical* 284 (december): 209-31. <https://doi.org/10.1016/j.sna.2018.10.036>.
- Anwar, M. N., M. Iftikhar, B. Khush Bakhat, N. F. Sohail, Mujtaba Baqar, A. Yasir, and A. S. Nizami. 2019. "Sources of carbon dioxide and environmental Issues". In *Sustainable*

- Agriculture Reviews* 37, 13-36. Cham: Springer. https://doi.org/10.1007/978-3-030-29298-0_2.
- Asad, M., and M. H. Sheikhi. 2016. "Highly sensitive wireless H₂S gas sensors at room temperature based on CuO-SWCNT hybrid nanomaterials". *Sensors and Actuators B: Chemical* 231 (august): 474-83. <https://doi.org/10.1016/j.snb.2016.03.021>.
- Chakravarty, S., A. Datta, and N. Sen Sarma. 2017. "An electrical solid-state sulphur dioxide vapour sensor based on a polyvinyl alcohol formaldehyde composite". *Journal of Materials Chemistry C* 5, no. 11: 2871-82. <https://doi.org/10.1039/c7tc00442g>.
- Chaudhary, V., and A. Kaur. 2016. "Surfactant directed polyaniline nanostructures for high performance sulphur dioxide chemiresistors: Effect of morphologies, chemical structure and porosity". *RSC Advances* 6, no. 98: 95349-57. <https://doi.org/10.1039/c6ra14113g>.
- Chiou, J. C., and C. C. Wu. 2017. "A wearable and wireless gas-sensing system using flexible polymer/multi-walled carbon nanotube composite films". *Polymers (Basel)* 9, no. 9 (september): Article number 457. <https://doi.org/10.3390/polym9090457>.
- Chiu, P.-H., C.-J. Huang, C.-F. Yang, T.-H. Meen, and Y.-H. Wang. 2010. "Enhanced lifetime characteristics in flexible polymer light-emitting devices by encapsulation of epoxy/silica-coated gold nanoparticles resin (ESGR)". *Materials Science and Engineering: B* 172, no. 3 (september): 317-20. <https://doi.org/10.1016/j.mseb.2010.05.031>.
- Cichosz, S., A. Masek, and M. Zaborski. 2018. "Polymer-based sensors: A review". *Polymer Testing* 67 (may): 342-48. <https://doi.org/10.1016/j.polymertesting.2018.03.024>.
- Crowley, K., A. Morrin, A. Hernandez, E. O'Malley, P. Whitten, G. Wallace, M. Smyth, and A. Killard. 2008. "Fabrication of an ammonia gas sensor using inkjet-printed polyaniline nanoparticles". *Talanta* 77, no. 2 (december): 710-17. <https://doi.org/10.1016/j.talanta.2008.07.022>.
- Gao, F., X. Chen, Q. Ye, Z. Yao, X. Guo, and L. Wang. 2011. "Core-shell fluorescent silica nanoparticles for sensing near-neutral pH values". *Microchimica Acta* 172, no. 3-4 (march): 327-33. <https://doi.org/10.1007/s00604-010-0494-y>.
- Gao, Y., Y. Xiao, K. Mao, X. Qin, Y. Zhang, D. Li, Y. Zhang, et al. 2020. "Thermoresponsive polymer-encapsulated hollow mesoporous silica nanoparticles and their application in insecticide delivery". *Chemical Engineering Journal* 383 (march): Article number 123169. <https://doi.org/10.1016/j.cej.2019.123169>.
- Haghdadeh, P., M. Ghaffari, B. Ramezanzadeh, G. Bahlakeh, and M. R. Saeb. 2019. "Polyurethane coatings reinforced with 3-(triethoxysilyl)propyl isocyanate functionalized graphene oxide nanosheets: Mechanical and anti-corrosion properties". *Progress in Organic Coatings* 136 (november): Article number 105243. <https://doi.org/10.1016/j.porgcoat.2019.105243>.
- Heffernan, M. A., and E. J. O'Reilly. 2019. "Rapid microwave assisted synthesis and characterisation of a semiconducting polymer with pKa tuneable degradation properties". *European Polymer Journal* 114 (may): 206-12. <https://doi.org/10.1016/j.eurpolymj.2019.02.005>.
- Hu, J., and S. Liu. 2010. "Responsive polymers for detection and sensing applications: Current status and future developments". *Macromolecules* 43, no. 20 (october): 8315-30. <https://doi.org/10.1021/ma1005815>.
- Jasso-Gastinel, C. F., J. F. A. Soltero-Martínez, and E. Mendizábal. 2017. "Introduction: Modifiable characteristics and applications". In *Modification of polymer properties*, edited

- by C. F. Jasso-Gastinel and J. M. Kenny, 1-21. William Andrew Publishing. <https://doi.org/10.1016/B978-0-323-44353-1.00001-4>.
- Lee, C., J. Ahn, K. B. Lee, D. Kim, and J. Kim. 2012. "Graphene-based flexible NO₂ chemical sensors". *Thin Solid Films* 520, no. 16 (june): 5459-62. <https://doi.org/10.1016/j.tsf.2012.03.095>.
- Lee, J., W. Shim, E. Lee, J. S. Noh, and W. Lee. 2011. "Highly mobile palladium thin films on an elastomeric substrate: Nanogap-based hydrogen gas sensors". *Angewandte Chemie - International Edition* 50, no. 23 (may): 5301-05. <https://doi.org/10.1002/anie.201100054>.
- Lian, X., and B. Yan. 2015. "Multi-component luminescent lanthanide hybrids of both functionalized IRMOF-3 and SBA-15". *New Journal of Chemistry* 39, no. 8 (august): 5898-901. <https://doi.org/10.1039/c5nj00862j>.
- Mendes, J. P., L. Coelho, B. Kovacs, J. Almeida, C. M. Pereira, P. A. S. Jorge, and M. T. Borges. 2019. "Dissolved carbon dioxide sensing platform for freshwater and saline water applications: Characterization and validation in aquaculture environments". *Sensors* 19, no. 24 (december). <https://doi.org/10.3390/s19245513>.
- Mills, A. 2009. "Optical sensors for carbon dioxide and their applications". In *Proceedings of the NATO Advanced Study Institute on Sensors for Environment, Health and Security: Advanced materials and technologies*, edited by M.-I. Baraton. Dordrecht: Springer Netherlands. https://doi.org/10.1007/978-1-4020-9009-7_23.
- Mohammad, S. M., Z. Hassan, R. A. Talib, N. M. Ahmed, M. A. Al-Azawi, N. M. Abd-Alghafour, C. W. Chin, and N. H. Al-Hardan. 2016. "Fabrication of a highly flexible low-cost H₂ gas sensor using ZnO nanorods grown on an ultra-thin nylon substrate". *Journal of Materials Science: Materials in Electronics* 27, no. 9 (september): 9461-69. <https://doi.org/10.1007/s10854-016-4993-4>.
- Neethirajan, S., D. S. Jayas, and S. Sadistap. 2009. "Carbon dioxide (CO₂) sensors for the agri-food industry: A review". *Food and Bioprocess Technology* 2, no. 2: 115-21. <https://doi.org/10.1007/s11947-008-0154-y>.
- Pathakoti, K., M. Manubolu, and H.-M. Hwang. 2018. "Nanotechnology applications for environmental industry". In *Handbook of nanomaterials for industrial applications*, edited by C. M. Hussain, 894-907. Elsevier. <https://doi.org/10.1016/B978-0-12-813351-4.00050-X>.
- Puligundla, P., J. Jung, and S. Ko. 2012. "Carbon dioxide sensors for intelligent food packaging applications". *Food Control* 25, no. 1 (may): 328-33. <https://doi.org/10.1016/j.foodcont.2011.10.043>.
- Rao, K. S., K. El-Hami, T. Kodaki, K. Matsushige, and K. Makino. 2005. "A novel method for synthesis of silica nanoparticles". *Journal of Colloid and Interface Science* 289, no. 1 (september): 125-31. <https://doi.org/10.1016/j.jcis.2005.02.019>.
- Rieu, M., M. Camara, G. Tournier, J.-P. Viricelle, C. Pijolat, N. F. de Rooij, and D. Briand. 2016. "Fully inkjet printed SnO₂ gas sensor on plastic substrate". *Sensors and Actuators B: Chemical* 236 (november): 1091-97. <https://doi.org/10.1016/j.snb.2016.06.042>.
- Ryabtsev, S. V., A. V. Shaposhnick, A. N. Lukin, and E. P. Domashevskaya. 1999. "Application of semiconductor gas sensors for medical diagnostics". *Sensors and Actuators B: Chemical* 59, no. 1 (october): 26-29. [https://doi.org/10.1016/S0925-4005\(99\)00162-8](https://doi.org/10.1016/S0925-4005(99)00162-8).
- Vargas-Sansalvador, I. M., M. M. Erenas, A. Martínez-Olmos, M. D. Fernández-Ramos, and L. F. Capitán-Vallvey. 2019. "Carbon dioxide sensors for food packaging". In *Reference module in food science*. Elsevier. <https://doi.org/10.1016/B978-0-08-100596-5.22632-2>.

- Wang, Q.-M., and B. Yan. 2006. "Designing a family of luminescent hybrid materials by 3-(triethoxysilyl)-propyl isocyanate grafted 2-hydroxynicotinic acid bridge molecules". *Journal of Organometallic Chemistry* 691, no. 17 (august): 3567-73. <https://doi.org/10.1016/j.jorgchem.2005.12.061>.
- Xie, X., J. Zhai, Z. Jarolimova, and E. Bakker. 2016. "Determination of pK_a values of hydrophobic colorimetric pH sensitive probes in nanospheres". *Analytical Chemistry* 88, no. 6 (march): 3015-18. <https://doi.org/10.1021/acs.analchem.5b04671>.
- Yan, B. 2017. *Photofunctional rare earth hybrid materials*. Springer Series in Materials Science, vol 251. Singapore: Springer. <https://doi.org/10.1007/978-981-10-2957-8>.
- Yang, G., C. Lee, J. Kim, F. Ren, and S. J. Pearton. 2013. "Flexible graphene-based chemical sensors on paper substrates". *Physical Chemistry Chemical Physics* 15, no. 6 (february): 1798-801. <https://doi.org/10.1039/c2cp43717a>.

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