



L'Institut Pascal est membre d'IMobS³ et de FACTOLAB, laboratoire commun avec MICHELIN.

Title of the thesis: **Development of microsensors based on nanocarbons decorated by metallic nanodots for the measurement of sulfuric pollutants (SO₂, H₂S)** Supervisor : **Christelle Varenne** co-supervisor : **Amadou Ndiaye** Group: PHOTON; (Team: System for Chemical Sensor (SCS)) Email and Phone : <u>christelle.varenne@uca.fr</u> 0473407246 <u>Summary :</u>

In the recent years, there is an alarming situation caused by the number of death attributed to pollution worldwide [1]. In France, solutions to control and monitor the pollutants with air quality agencies became a crucial issue. In this context, the development of innovative, low power consuming, robust and reliable sensors is a new priority in the field of sensors research and development. For example, when accidentally inhalated, hydrogen sulfide (H₂S), which is identified as toxic gas, can cause unconsciousness (~500ppm) or even death at higher concentrations (> 1000 ppm, within a short period) [2]. The lower recommendation thresholds (TLV-TWA : Threshold Limit Value – Time Weight Average and TLV-STEL: Threshold Limit Value - Short Term Exposure Limit) for these two gases: TLV-TWA = 5ppm/8h and TLV-STEL = 10 ppm/15min for H₂S; and a TLV-TWA = 0.5 ppm/8h and TLV-STEL = 1 ppm/15min for SO₂, mean that a regular and specific control for security reasons is needed for domestic and industrial context, in both indoor and outdoor area [3]. In the research of reliable and miniaturisables sensors we focused on nanocarbonaceous materials such as graphene and carbon nanotubes (CNTs) which have demonstrated a huge potential as relevant materials in the future of gas sensors. However, they suffer from long term stability, lacks of selectivity and solubility that represent limiting factors for their implementation in sensors devices. The key elements for their sensing potentialities are mainly their higher specific surface area (theoretical value estimated to 2600 m^2/g for graphene [4]) and their conductivity for resistive sensors [5]. Recent reports have shown that functionalization can improve the sensing performances such as response time and limit of detection. In this sense the functionalization /decoration of carbon materials is an issue for carbon based sensors [6].

Here we proposed the elaboration of sensing materials for the sulfuric pollutants (H₂S and SO₂) by the functionalization and decoration of carbon materials (graphene and CNTs). For this proposal, the Chemical Sensor-System (CSS) team skills on sensor for air quality control [7-8], propose a novel approach based on the non-covalent functionalization of carbon materials by metals such as gold(Au), copper (Cu) or platinum (Pt). Both physical (thermal evaporation, sputtering) and chemical (reduction of metal ions through soft chemical route) functionalization methods will be investigated. The chosen metals possessing strong affinity with the target gases (H₂S or SO₂), they bring selectivity of detection by tuning functionalization rate and functionalization methodology.

Hybrids materials which are achieved through metal decoration will be characterized by SEM, MET, Raman spectroscopy, TGA and electrical characterizations. A specific test bench dedicated to sensing performances evaluation will be setup. In collaboration with ENVEA [9], sensing performances will be determined in real-conditions of pollution exposure. SILSEF, a society partner of the ANR project CAPTAIN, could proceed to the microstructuration of the metallic layers to improve their sensing performances (increase in hydrophobic property, enhancement of selectivity)

Références :

[1]: A. Prüss-Ustün, J. Wolf, C. Corvalán, R. Bos, M. Neira, Preventing disease through healthy environments, World Health Organization 2016.

[2] :https://travail-emploi.gouv.fr/sante-au-travail/prevention-des-risques-pour-la-sante-au-travail/autres-dangers-et-risques/article/hydrogene-sulfure

[3]: Sulfure d'hydrogène, Fiche toxicologique n° 32, INRS (<u>http://www.inrs.fr/publications/bdd/fichetox/fiche.html?refINRS=FICHETOX_32</u>)
[4]: F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A.C. Ferrari, et al., Science, 347(2015) 1246501.

[5] I.V. Zaporotskova, N.P. Boroznina, Y.N. Parkhomenko, L.V. Kozhitov, Modern Electronic Materials, 2(2016) 95-105.

[6] : M. Meyyappan, Small, (2016) 2118-29.

[7]: (a) A.L. Ndiaye, J. Brunet, C. Varenne, A. Pauly, The Journal of Physical Chemistry C 2018, 122, 21632-21643. (b) A.L. Ndiaye, C. Varenne, P. Bonnet, E. Petit, L. Spinelle, J. Brunet., Sensors and Actuators B: Chemical 2012, 162, 95-101. (c) J. Brunet, M. Dubois, A. Pauly, L. Spinelle, A. Ndiaye, K. Guérin, Sensors and Actuators B: Chemical 2012, 173, 659-667.
[8]: Membre du réseau européen sur les nanomatériaux et les microcapteurs destinés au contrôle de la qualité de l'air (Action COST TD 1105 - EuNetAir)

[9] : ANR PRCE « CAPTAIN » (2018-2022) , LabHC (Saint Etienne), IP (Clermont Ferrand), SILSEF (Grenoble), ENVEA (Paris).



Institut Pascal UMR 6602 - Université Clermont Auvergne - CNRS - SIGMA Campus Universitaire des Cézeaux 4 Avenue Blaise Pascal TSA 60026 - CS 60026 63178 AUBIERE Cedex - France Tél : +33 (0)4 73 40 72 50 - Télécopie : +33 (0)4 73 40 72 62