

**ORAL SESSION:
CHEMICAL SENSORS**

GAS MICROSENSORS WITH METALLOPORPHYRIN-FUNCTIONALIZED CARBON NANOTUBE NETWORKED LAYERS

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Abstract

Gas sensors based on carbon nanotubes (CNTs) have been largely studied in the form of networked films for highly-sensitive gas detection applications [1-3]. Due to very high surface-to-volume ratio, hollow nanostructure, high electron mobility, great surface reactivities and high capability of gas adsorption, CNTs have been investigated as building blocks for fabricating novel devices at nanoscale such as high-performance gas sensors and nano-platforms for biosensing.

Networked films of carbon nanotubes (CNTs) have been grown by CVD technology onto low-cost miniaturized alumina substrates. The sidewalls of the CNTs films have been modified by spray-coating with two different metalloporphyrins (MPPs) consisting of a TetraPhenylPorphyrin coordinated by a central metal of zinc (Zn-TPP) and manganese (Mn-TPP) for enhanced sensitivity and tailored specificity. Hazardous gases such as NO₂, NH₃, H₂S, SO₂, N₂O and CO have been detected with various responsiveness in the range of concentration from 0.1 to 1000 ppm. The response of the chemiresistors in terms of p-type electrical conductance has been investigated as a function of the thickness of the functionalizing MPPs; and the effect of the temperature ranging from 20 to 150°C on the sensor response has been addressed as well. A response of the CNT-sensor functionalized by 2 layers of Mn-TPP has been measured as 0.43% to 0.5 ppm NO₂, at 150°C.

Carbon nanotubes (CNTs) are 1D-nanometre hollow structures rolled as single-walled or concentric multi-walled cylinders with high capability of gas molecules adsorption for enhanced gas sensitivity even at low sensor temperature. Various gas sensor nanomaterials include semiconducting metal oxides, conducting polymers, metal nanostructures and nanocomposites with nanofillers. However, it has been demonstrated that single-walled CNTs are functional nanostructures for detecting very low gas concentrations of NO₂ and NH₃ under ambient conditions [1]. Various principles of transduction using CNTs have been implemented for chemical sensing including Field Effect Transistors (FET), Surface Acoustic Waves (SAW), Quartz crystal Microbalance (QCM), optical fibers, electrochemical devices, chemiresistors. Here a two-pole chemiresistor has been integrated.

Surface modifications of the CNTs with different functionalizing materials have been employed to improve gas sensitivity and to tailor specificity. In fact, nanoclusters of noble metals (Au, Pt, Pd, Ag) have been used to enhance gas sensitivity of CNTs networked films, operating at a sensor temperature of 100-200°C [4-5]. Additionally, metalloporphyrins (MPPs), consisting of TetraPhenylPorphyrins (TPP) coordinated by a central metal of zinc and manganese, are functional materials that have been prepared as highly-sensitive receptors for artificial olfaction [6] and volatile organic compounds (VOCs) detection at room temperature [7]. In this study, MPP-modified CNTs networked films have been investigated for sub-ppm gas sensing of NO₂, NH₃, H₂S, SO₂, N₂O and CO in a working temperature range of 20-150°C.

The scheme of the fabricated two-pole chemiresistor is shown in Fig. 1a. CNTs films were grown by CVD technology onto cost-effective alumina substrates, equipped by Cr-Au contacts. MPPs

functionalizing CNTs films were spray-coated with tuned thickness (Fig. 1b). The morphology and structure of the CNTs networks has been characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). A dense network of bundles of multiple tubes consisting of multi-walled carbon nanostructures appears with a maximum length of 5-10 μm and single-tube diameter varying in the range of 5-35 nm.

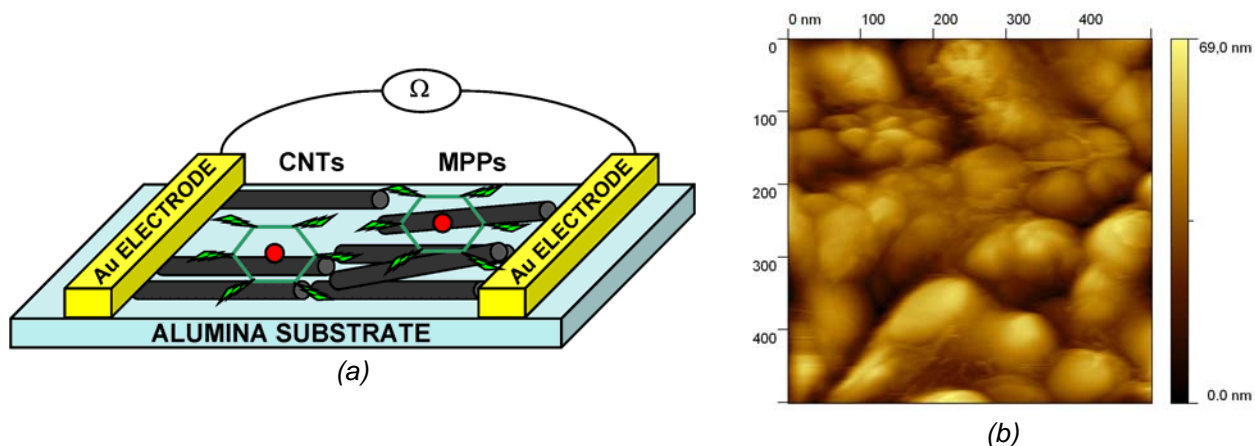


Fig. 1. (a) Scheme of integrated two-pole chemiresistor. (b) AFM image of Metalloporphyrin-modified CNTs layers.

The measured electrical conductance of the functionalized CNTs upon exposure of a given oxidizing (NO_2) or reducing (NH_3) gas is modulated by a charge transfer model with *p-type* semiconducting characteristics. Fig. 2 shows the typical time response in terms of electrical resistance change for four chemiresistors based on unmodified CNTs, MnTPP-modified CNTs (CNT+1MnTPP, CNT+2MnTPP), and ZnTPP-modified CNTs (CNT+2ZnTPP), exposed to NO_2 and NH_3 gas, at 150°C . The electrical resistance of all CNTs-sensors decreases (increases) upon a single gas exposure of the NO_2 oxidizing (NH_3 reducing) gas due to molecules adsorption.

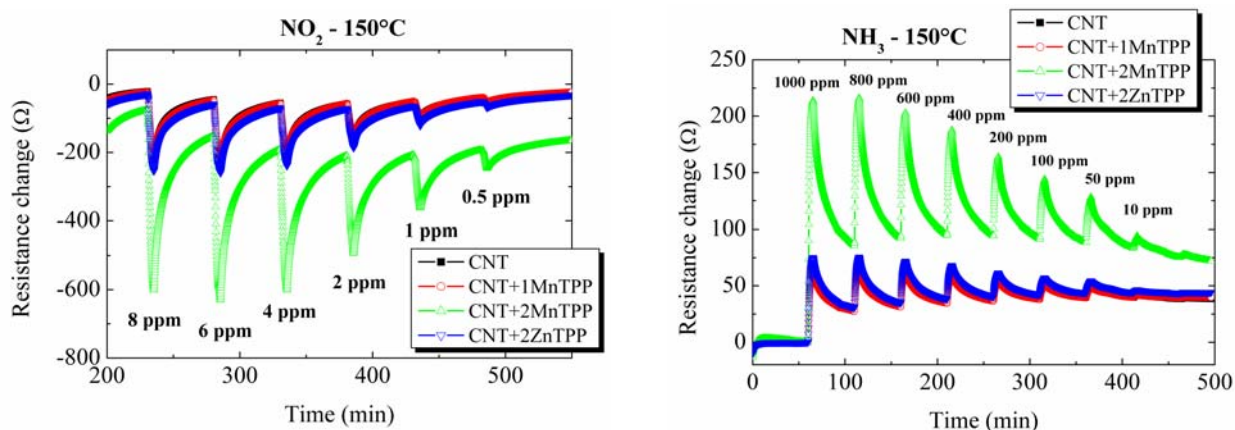


Fig. 2. Time responses towards 5-minute pulses of (a) NO_2 and (b) NH_3 of the four chemiresistors based on CNTs, unfunctionalized and functionalized with 1 and 2 sprayed-layers of Mn-TPP and 2 sprayed-layers of Zn-TPP, at 150°C .

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INKJET PRINTED CHEMICAL SENSORS

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Abstract

Polymer nanocomposites (PNCs), consisting of inorganic nanoparticles embedded in a polymer matrix, are currently being developed for potential applications in several fields, such as optics, electronics, mechanics, chemical sensing and biology. The structural flexibility and the solution processability properties of the polymers coupled with the thermal and mechanical stability, and the conductive properties of the inorganic component leads to a resultant hybrid system whose physico-chemical properties fit well the needs in different research sectors.

Chemiresistors based on polymer nanocomposite are particularly attractive as these compounds exhibit a high stability to different gases and vapours, and have the potential for room temperature operation. The operating mechanism of these chemical sensors is based on the disrupting of the conductive paths upon exposure to the analytes that results in a change of the electrical properties [1-5].

PNCs can be easily processed by techniques such as spin-coating or drop-casting and, recently, also by inkjet printing (IJP) technology, rapidly emerged as an innovative technique for the deposition of a wide variety of materials [6-11]. The advantages of IJP over the aforementioned techniques lie in its patterning capability, the efficient use of material, the reduced waste products and low cost of the process, and its potential for printing on both nonflexible and flexible substrates. As concerning this last item, the IJP technology has assumed a main role in the field of electronics wherever it is required to replace conventional nonflexible substrates with flexible ones.

In the present work, VOCs (volatile organic compounds) chemical sensors have been fabricated by printing a nanocomposite on different substrates, such as polyethylene terephthalate (PET), glass, etc. The effect of the substrate morphology (surface energy, roughness) on the printed product quality, in terms of wettability and adhesion, and, hence, on the device performances was also investigated.

The sensing material was a polystyrene (PS)/carbon black (CB) composite. The PS polymer matrix (80 mg) was dissolved in 1-Methyl-2-pyrrolidinone (NMP) and the CB conductive filler (20 mg) was dispersed in the polymeric solution (0.5 wt%) by means of ultrasonic bath. Lines, created by overlapped droplet sequences, have been printed on the interdigitated electrodes/substrate system.

The sensor response was measured upon exposure to organic vapours and quantitatively analyzed. Preliminary results indicate that the IJP technology allows to fabricate nanocomposite based chemical sensors onto different substrates, flexible and not, with performances better than those exhibited by PNC based chemical sensors fabricated with different techniques[11]. As an example, the photo of chemical sensor ink-jet printed on a PET substrate and its electrical response in acetone are shown in figure 1.

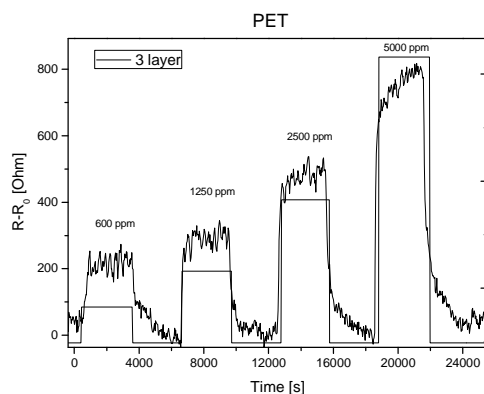
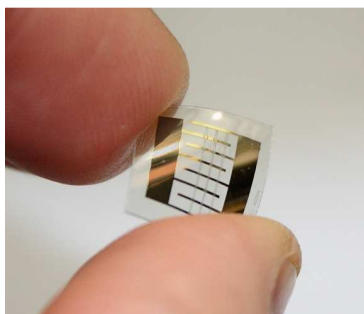


Figure 1: Photo of PS/CB device printed onto PET substrate and its electrical response.

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Oxygen Distribution Monitoring in Gas and Liquid

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Abstract

The measure of oxygen concentration is required in many different applications, such as environmental monitoring of atmosphere and water, and in the medical diagnosis. Here it is important to measure the oxygen content in breath and in blood. In industrial processes that utilize metabolizing organisms such as yeast for fermentation or microbes for producing drugs this kind of measurement is proven to be of a certain relevance [1]. The control of oxygen concentration also allows for monitoring of processes such as enzymatic glucose oxidation [2]. The luminescence quenching of metal complexes is a widespread diffuse technique for the measurement of oxygen concentration. Phosphorescence quenching can be quantified by either lifetime or intensity measurements [3].

In this work, a simple arrangement made by a UV fluorescent lamp used to excite the sensing layer and a digital camera as a detector is proposed to detect the phosphorescence quenching of metal complexes of porphyrins. Computer camera was already demonstrated to probe both absorption [4] and fluorescence [5] features of several chromophores. In this study palladium and platinum porphyrin complexes were used. They were dispersed in an oxygen permeable and transparent matrix made of plasticized PVC. Sensing layers were spotted onto a plastic UV transparent substrate and placed in a gas and liquid tight measurement cell. Both responses to gaseous oxygen and to dissolved oxygen were estimated. A sketch of the experimental set-up is displayed in figure 1.

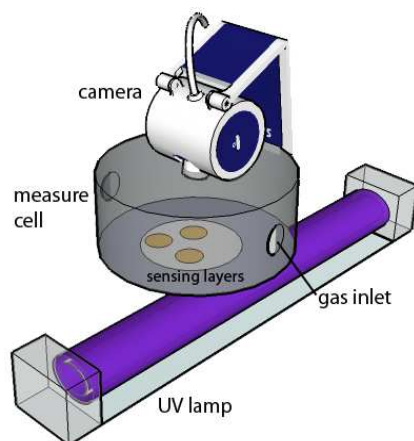


Figure 1. Sketch of the experimental arrangement composed of a UV fluorescent lamp, a measurement cell and a digital camera.

UV lamp light is peaked at 365 nm with a spread between 300 and 400 nm. Such a wavelength range is sufficiently separated from porphyrin excitation bands, so that additional filters are not necessary. In nitrogen atmosphere, all the porphyrin layers exhibit a strong luminescence in the red region (650–670 nm depending on the species) when illuminated with the UV lamp. A prompt quenching is recorded when layers are exposed to oxygen in air and to oxygen dissolved in water (Figures 2a-b).

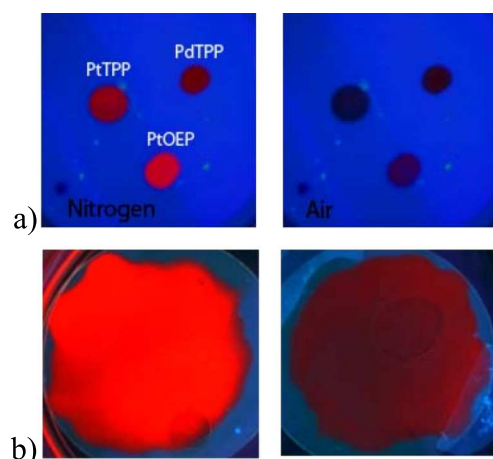


Figure 2. Images acquired by the webcam in absence and in presence of oxygen in air for the three porphyrins (a) and in water solution (b) for a uniform layer of PtOEP.

The phosphorescence intensity changes under increasing oxygen concentrations in the range 0-20% are shown in figure 3. Stern-Volmer plots for the three porphyrins give a regression curve that is linear, as shown in figure 3, and the best sensitivity is achieved in both cases with PtTPP. Only in the case of water solution a saturation for larger concentration of oxygen can be observed.

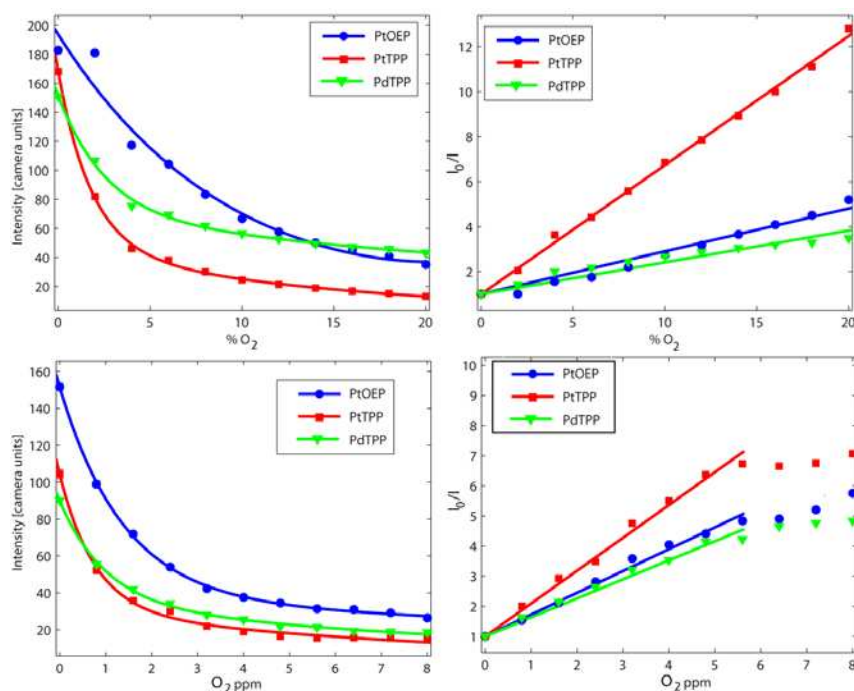


Figure 3. Phosphorescence changes and Stern Volmer plots for increasing concentration of oxygen in gaseous samples (a) and in water solution (b).

These results look promising and, thanks to the optical imaging, they open a wide range of possible applications for monitoring oxygen concentration and processes that involve oxygen consumption. Further data will take part of the full paper.

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CHEMICAL SENSORS INTEGRATED IN FURNITURE FOR INDOOR ATMOSPHERE MONITORING

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Abstract

In the last few years the need of environmental control of indoor ambient has been more and more stringent, for both safety and security reasons. Chemical sensors are the devices most promising for the satisfaction of such a requirement, but for residential ambient they should be integrated in the design architecture. In this work we present the attempt to integrate a sensing platform into furniture ideated for interior design, as a suitable approach for indoor atmosphere monitoring.

In this system we have exploited a modified Computer Screen Photoassisted Technique (CSPT) [1] approach, using a decor light emitting diode (LED) as light source, while the other components are the same of the usual CSPT apparatus, i.e. a webcam as the detector, and a computer to acquire and process the data. These decor LEDs can be used usually inside a cabinet or behind a wall-mounted TV (fig. 1).

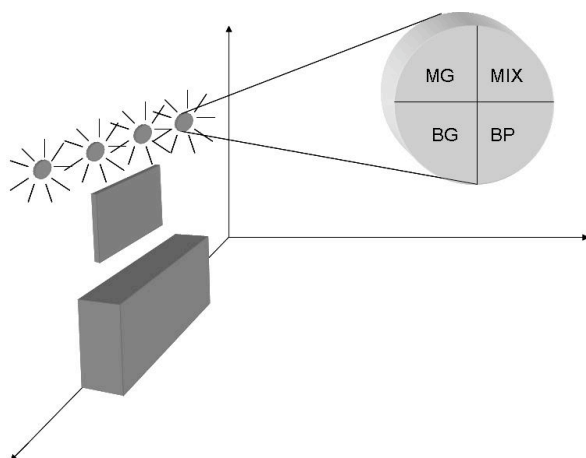


Fig.1 pH indicators membranes composition casted on décor LEDs. Leucomalachite green (MG), Bromocresol purple (BP), Leucomalachite green/Bromocresol purple (1:1) (MIX), background (BG).

In particular, the measuring setup involved a LED for multipurpose lighting, which provides a sequence of seven colours (red, green, blue, magenta, pale blue, yellow, white). To develop the sensing platform, the LED surface has been coated by a polymeric membrane (based on polyVinylChloride, PVC), where the chromophoric sensing materials have been dispersed. The LED circular shape has been divided in four quadrants (fig. 1), and in two of them pH sensitive dyes (Leucomalachite green and Bromocresol purple) have been dispersed, in the third a mixing of the dyes and in the last quadrant a background reference has been deposited. The working pH range is 11.6 – 14 for Leucomalachite green and 3.8-5.4 for Bromocresol purple.

The sensors were placed in a 25 Liters cell measurement, made in PLEXIGLASS®; the detector was represented by a Logitech Quickcam pro 4000 operating at resolution of 320 x 240 pixels. The software to acquire the video and to extract the information (fingerprints) from manually selected ROIs (region of interest), written in Matlab.

We decided to test the performances of the developed sensing system by using trimethylamine (TMA) as a case study. We used Leucomalachite green and Bromocresol purple as indicators, because they have been used in the past for TMA detection [2]. The system was exposed to TMA (22.98 ppm) for 1 hour. The gases were flowed inside the measurement chamber at different concentrations by a computer-assisted 4- channel mass-flow controller (MKS), diluting a certified TMA/nitrogen tank (500 ppm) with nitrogen, used as gas carrier. All the measurements were performed at constant temperature (298 K) and flow rate (200 mL/min).

The sensor array responses have been interrogated before, during and after the analyte fluxing by the webcam, providing a typical adsorption spectrum for each pH indicator at starting and ending pH point (fig. 2) and a RGB dynamic digital image, useful tool to monitor the changing during the exposure to amine (fig. 3).

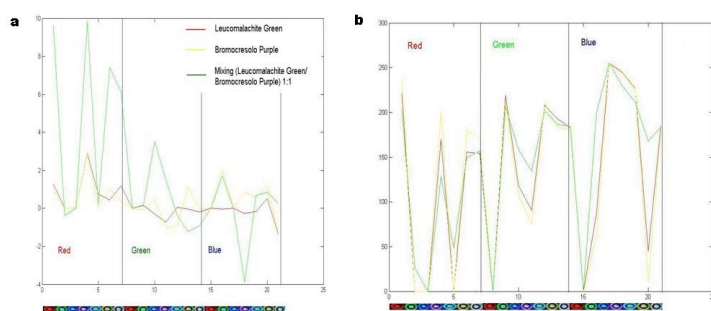


Fig.2: pH indicators fingerprint after exposure to TMA (a) and difference between the fingerprint before and after exposure to TMA (b).

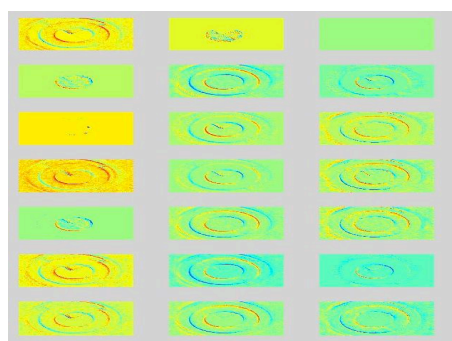


Fig. 3: RGB dynamic digital image during exposure to TMA.

The system is able to detect variation of amine concentration in the ppm range and it demonstrates the possible simple integration of a sensing platform inside a furniture element. The pH indicators can be useful to monitor some important indoor parameters, such as for example CO₂ concentrations. It is also worth mentioning that, by optimization of the chromophores dispersed in the polymeric membranes, it is possible to create a sensor array able to monitor a wide range of analytes. Further work is in progress in such a direction and the results will be reported in due course.

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