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Room temperature measurements of aromatic hydrocarbons by QCM-based gas sensors: intercomparison between phthalocyanines and phthalocyanine/CNTs hybrid material

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Abstract

This paper deals with metallo-phthalocyanines and functionalized nanocarbons as sensitive materials for microsensors development dedicated to BTX monitoring at room temperature. Because of the nature of gas/materials interactions involved, QCM has been chosen as transducer. Sensors were tested in different concentration ranges. Out of different phthalocyanines materials studied, tert-butyl substituted metallo-phthalocyanines showed highest sensitivity. Aiming to further improve the sensitivity, ttb-CuPc/CNT hybrid nanomaterials were synthesized. The sensitivity measured for this hybrid nanomaterial was found to be greater as compared to individual sensitivity of ttb-CuPc and CNT.

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1. Introduction

Air pollution is a global problem nowadays affecting every components of environment either directly or indirectly. With the rapid increase in urban traffic and change in life-style, a new type of pollutants, Volatile...
Organic Compounds (VOCs) is posing a great threat to this environment. Among these hydrocarbon pollutants, Benzene, toluene and xylenes (BTX) are particularly a grave concern in urban indoor environments [1]. Their continuous monitoring becomes necessary taking into account the serious health consequences they pose through direct or indirect exposure. The conventional methods of BTX detections are mainly based on gas chromatography[2], which is although highly sensitive technique but have certain limitations which restrict wide-scale and real-time monitoring. A gas microsensor can be a promising alternative which can be employed for continuous and sensitive detection of BTX gases at competitive cost. Organic molecular semi-conductors are a class of materials with high potentialities for the development of innovative electronic components including gas sensors. Among these molecular materials, phthalocyanines are especially well-known for their high reactivity with oxidizing gases leading to very sensitive chemosensors [3]. Because of their aromatic nature and their resulting non-covalent interactions [4], phthalocyanines are also relevant sensing materials for aromatic hydrocarbons measurements. Moreover, inexpensive availability, rich solution chemistry, flexibility in molecular engineering and high thermal stability position these materials as a preferred choice. Continuous π-conjugation in these molecules opens a lot of possibility to develop hybrid material with a similar macromolecular system like nano-carbon through non-covalent interaction which can enhance sensing performances. The concentration of aromatic hydrocarbons adsorbed on phthalocyanines or hybrid sensitive layer can be determined from mass variations by means of Quartz Crystal Microbalance (QCM). Indeed, QCM is an appropriate transducer which can measure qualitatively and quantitatively the interactions involved in a real-time situation for long hours of continuous operation in accordance with the Sauerbrey’s equation [5]:

$$\Delta f = -\frac{Cf_0^2 \Delta m}{A}$$  \hspace{1cm} (1)

A is the area of sensitive layer and C the mass sensitivity constant (4.816×10^-10 m²sg⁻¹) of quartz crystal.

In this work, phthalocyanines and phthalocyanine/nanocarbons based QCM microsensors were developed for the measurement at room temperature of BTX gases in the ppm range. Sensing layers were deposited on quartz crystals either by thermal evaporation or drop casting. Sensors were tested at different concentrations of BTX gases and their metrological characteristics were investigated. Most sensitive metallo-phthalocyanine material was then used to functionalize SWNT and QCMs based on this hybrid layer were investigated. Role of nanocarbon in improving BTX sensitivity was demonstrated.

2. Materials and methods

![Fig. 1: Schematic representation of experimental gas testing facility.](image-url)
Commercially available Phthalocyanines materials and single walled nanotubes were layered on 5 MHz AT-cut QCM of diameter 25.4 mm with Au/Cr electrodes by thermal evaporation or drop casting. Deposited films were characterized by SEM, FTIR and XRD techniques to confirm their thermal stability and correlate structural and morphological properties to sensor responses. Sensors were tested on a laboratory developed gas testing facility schematically shown in Fig. 1. It consists of a fluidic circuit connected to sensor chamber and a computer, which synchronously controls experimental parameters like gas dilution, valve switching and acquisition of sensor responses. The setup has been explained in detail in reference [6].

3. Results and discussion

Out of different phthalocyanines materials studied, tert-butyl substituted metallo-phthalocyanines showed highest sensitivity to BTX gases. We selected copper-tetra-tert-butyl copper phthalocyanine (ttb-CuPc) based QCM for detailed investigation of different metrological characteristics. The sensor was tested in a range of 30–200 ppm of BTX gases at room temperature. The variation of frequency shifts of QCM with test gas concentration was established as calibration curve and has been shown in Fig. 2.

![Figure 2: Sensitivity of ttb-CuPc based QCM sensor to BTX gases at room temperature.](image)

A linear variation in QCM response with gas concentrations was measured. Sensitivity, which can be represented by the slope of linear fit of these curves, is highest for xylesnes at 0.243 Hz/ppm and lowest for benzene at 0.083 Hz/ppm. As measured sensor signal was very stable manifested by noise level of 0.06 Hz, which leads to a sub-ppm BTX detection limit of the sensor. The limit of detection (LOD), which is generally defined as three times the ratio of frequency noise level to the sensitivity, and quantifies the lowest concentration of analyte that can be reliably detected was assessed for benzene, toluene and xylesnes as 2.15 ppm, 1.8 ppm and 0.75 ppm respectively. These values of LOD of the sensors for BTX gases are much below the guidelines set by different health and environment protection agencies especially for toluene and xylesnes.

Sensing characteristics including reversibility, repeatability, baseline stability, gas-exposure history, resolution and selectivity are explained in detail in reference [6]. Sensor exhibited stable, reversible and repeatable response in the studied concentration range. Study of kinetics of sensor signal evolution revealed response time less than 3 minutes and 10 minutes for toluene and xylene respectively. A resolution of 10 ppm in sensor response was determined for toluene and xylesnes in the current experimental test facility. Cross-sensitivity studies to common atmospheric pollutants showed no sensitivity to NO₂, CO and H₂S. High QCM sensor response of ttb-CuPc from other studied phthalocyanines can be attributed to presence of tert-butyl groups which increases the non-covalent interactions with BTX gases. If the presence of -CH₃ units enhances the CH–π interactions, its extended spatial volume provides a large surface area for dispersion interactions.

Further enhancements in sensing characteristics were obtained with ttb-CuPc functionalized nanocarbons. As
expected, an increase in toluene sensitivity was observed as shown in Fig. 3. The toluene sensitivity of ttb-CuPc/CNT hybrid was found to be higher as compared to individual sensitivity of ttb-CuPc or CNT.

Fig. 3: inter-comparison of ttb-CuPc/CNT hybrid, ttb-CuPc and CNTs sensitivity towards toluene.

Highest sensitivity for ttb-CuPc/nanocarbon hybrid was a result of enhanced gas adsorption within the sensing layer facilitated by high specific surface area of nano-carbon. In terms of molecular scale interaction, the presence of extended conjugation in nanotubes provides addition interaction sites to BTX gases within the hybrid layer.

4. Conclusion

We have demonstrated the BTX sensing characteristics of QCM sensors having a coating of tert-butyl substituted metallo-phthalocyanines and their related hybrid with nanocarbons at room temperature. High sensitivity of the sensor was manifested by the sub-ppm detection limit, linear response and high resolution in response. Further improvement in sensitivity was achieved by using a ttb-CuPc/nanocarbon hybrid as sensing layer.

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