CuBr@SiO_2 Mesoporous Composite for ppb Level Ammonia Detection in Humid Environment at Room Temperature

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***Abstract*— The need for non-invasive methods to improve medical monitoring is growing and transdermal gas monitoring seems relevant. We aim to fabricate a gas sensor for ammonia transdermal detection as ammonia is a biomarker of chronic kidney disease. We previously showed that the synthesis of mesoporous SiO_2 thin film followed by CuBr impregnation led to a room-temperature selective ammonia sensor with very high sensitivity. Here, we show that the device detection limit and resolution are suitable for the detection of the very small quantities emitted from the skin. To evaluate the possibility of implementing this sensor in a skin-like environment, we also studied the effect of temperature and humidity on the sensing performances. Temperature has a small impact on the sensor baseline but a bigger impact on the sensor response. The humidity effect on the sensor response to ammonia is low below 30%. The effect is higher at 50% relative humidity and may be attributed to the film mesoporous structure. This paper shows that the sensing properties of the sensor make it a good candidate for transdermal ammonia detection.**

Keywords- mesoporous sensor; CuBr; ammonia.

I. INTRODUCTION

New devices for medical monitoring are being developed to improve both the medical monitoring of patients and our understanding of diseases. The detection of skin-emitted gas would allow both, by offering a non-invasive monitoring for the patient and access to new biomarkers for the medical practitioners. In this contribution we aim at developing an ammonia sensor to detect skin-emitted ammonia on patients suffering from chronic kidney disease as it is a potential biomarker of an acid load increase caused by this disease. Its use would complement the analyses carried out today, such as urine and blood tests that are invasive, costly, and are carried out too infrequently to provide proper monitoring of patients. To be used in this purpose, the developed sensor has to be extremely sensitive as the transdermal ammonia concentrations are estimated around 100 ppb [1], and selective to ammonia. In addition, the development of a room-temperature device would allow fabrication cost and energy consumption reduction.

Current technologies for ammonia detection include resistive gas sensors generally based on metal oxide sensitive layer [2]–[4]. Although the latter provide good sensitivity to ammonia, their lack of selectivity and their high working temperature make them unsuitable for our application. Room-temperature ammonia sensors exist in the literature and are generally made of composite materials using conductive polymers or graphene-based materials. However, very few studies report on the ammonia detection associating great selectivity, sensitivity and stability in a single sensor.

In a previous study, we showed that the fabrication of resistive sensor based on the impregnation of the ionic conductor CuBr in a mesoporous thin film led to a selective and very sensitive room-temperature ammonia sensor. The sensor has a basic structure composed of two layers on Si/SiO_2 substrate. The platinum interdigitated electrodes are deposited by rf sputtering. The sensitive layer is deposited by the simple and inexpensive dip-coating method, which is a significant advantage for the accessibility of the sensor. Here, we study the sensor performances in conditions closer to skin environment namely humidity and temperature variation. We evaluate the sensor detection limit and resolution as well as the effect of the temperature and humidity on the baseline and on the ammonia response. The paper is organized as follows. Section II describes the materials and methods used to fabricate and characterize the sensor. Section III presents the results obtained for the detection limit and the resolution in III. A, the effect of temperature in III. B and the effect of humidity in III. C. The acknowledgement and conclusion close the article.

II. MATERIALS AND METHODS

A. Sensitive layer

The sensor structure is made of a Si/SiO_2 substrate with 100 nm-thick interdigitated platinum electrodes. The mesoporous layer is deposited by dip-coating from a sol-gel solution with the following ratio: TEOS:F127:HCl:EtOH:H_2O 1:0.006:0.38:70:6. The ratio 0.06 between the silica precursor TEOS and the porous agent F127 is chosen to obtain a hexagonal porous network.

The SiO_2 layer is cured at 450°C and impregnated in a 1wt% CuBr solution in acetonitrile and removed with the dip-coater at 1 mm/s. The thickness, porosity and homogeneity are evaluated with ellipsometry-porosimetry. The SiO_2 layer is 90nm thick and the whole mesoporous layer is impregnated homogeneously by CuBr.

To evaluate the contribution of SiO_2 and CuBr in the CuBr@SiO_2 sensitive layer, a mesoporous SiO_2 layer without CuBr impregnation is also used as a sensitive layer as well as a CuBr layer without SiO_2.

B. Sensing performance evaluation

The sensor performances are evaluated under ammonia in a microchamber connected to a gas generation system. The dilution system enables the generation of concentration down to 60 ppb of ammonia and humidity levels from 0% to 80%. The chamber outlet is connected to a Proceas-Indus analyzer to measure real-time ammonia concentration in the chamber. The test chamber is located in a thermoregulated chamber at 34°C (skin temperature). Sensor response R_g/R_a is calculated as the ratio between R_g the sensor resistance in ammonia and the R_a sensor resistance in air.

III. RESULTS AND DISCUSSION

A. Limit of detection and resolution

To evaluate the sensor limit of detection, we exposed two sensors fabricated in the same conditions to small NH_3 concentrations from 0 to 52 ppb. The ammonia concentration in the chamber is monitored by the gas analyzer and compared to the sensor resistances. The results related to the analyzer and to one of the sensors are reported in Figure 1.

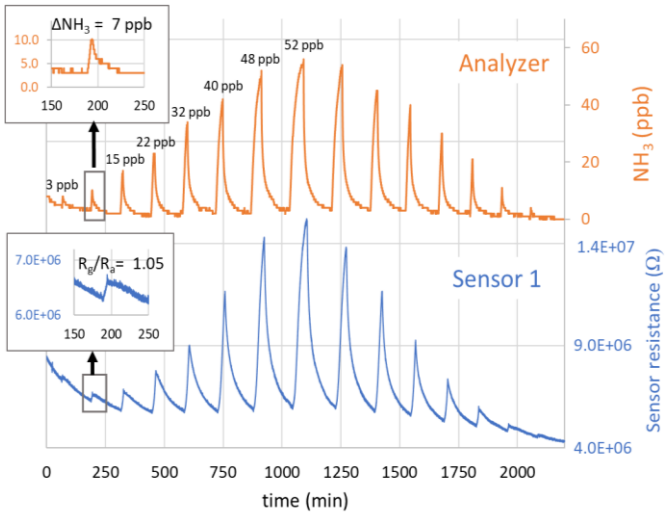

Figure 1. NH_3 concentration detected by the gas anayzer (orange) at 34°C with a flow rate of 500 sccm and the corresponding sensor resistance (blue). The inserts are magnification of the analyzer and sensor signals during the 7 ppb exposure.

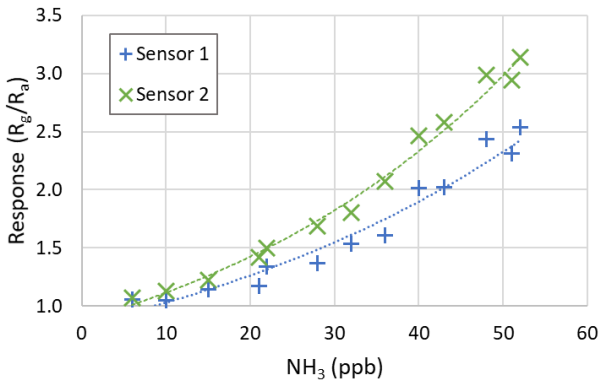

Figure 2. Calibration curves of CuBr@SiO_2 sensor exposed to NH_3 from 7 ppb to 53 ppb at 34°C.

The limit of detection is considered to be the smallest concentration to induce a sensor resistance variation superior to 3 times the background noise. In this case, such a variation is obtained for an ammonia variation of 7 ppb. The corresponding response is 1.05. As illustrated in Figure 2, where the sensor responses are reported, the two sensors show very similar behavior, proving the reliability of our results as well as the reproducibility of our process fabrication.

Resolution is assessed by exposing the sensor to 60 ppm NH_3 followed by 10 ppb steps up to 130 ppb. The analyzer and the sensor signal are overlaid in Figure 3. The resistance variation between two NH_3 concentration is calculated as the ratio between the maximum and the minimum resistances. The insets in Figure 3 show that a variation of 10 ppb NH_3 from 76 ppb to 86 ppb is detected by the sensor with a response of 1.1. This is in good accordance with the calibration curves presented above. The second sensor showed the same response to a variation of 10 ppb. Thus, we can affirm that CuBr@SiO_2 mesoporous sensors can detect small NH_3 concentrations as low as 7 ppb with a resolution of at least 10 ppb.

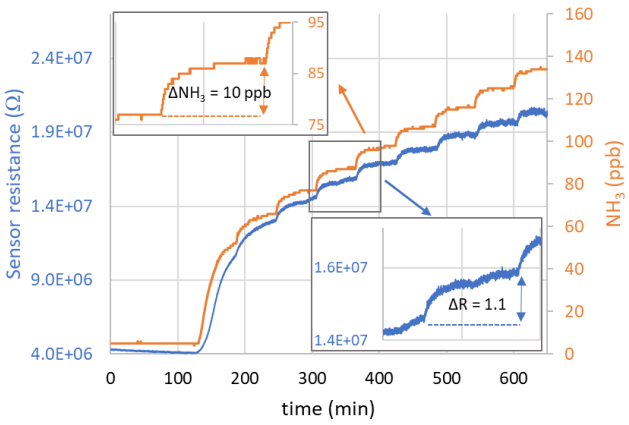

Figure 3. Gas analyzer signal (orange) and sensor resistance (blue) during CuBr@SiO_2 sensor exposure to increasing NH_3 concentration in 10 ppb steps for resolution evaluation.

B. *Effect of temperature*

As the sensor operates without a heating system, the effect of environmental temperature on the sensing performances has to be studied. Here, we measured the baseline and the sensor response to short NH_3 exposures of 2 minutes at 20°C, 30°C and 40°C. The temperature, the ammonia concentration detected by the analyzer and the sensor resistance are reported in Figure 4. From these results, one can see that the baseline resistance decreases with temperature as well as the sensor response. For example, at 20°C the sensor response to the highest concentration tested is more than 10 times superior to the sensor response at 40°C.

The decrease of resistance under dry air with temperature is attributed to the mobility of charge increase favored by heat and it is in accordance with results reported in literature regarding the temperature dependence of CuBr conductivity from 30°C to 490°C [5]. The decrease of response with temperature is imputed to a temperature-induced shift in the adsorption/desorption equilibrium in favor of desorption. Although this temperature dependence could make it difficult to interpret the data in real-life conditions, it is necessary to assess its magnitude in order to take corrective action later on by adding a temperature sensor and artificial intelligence in the system.

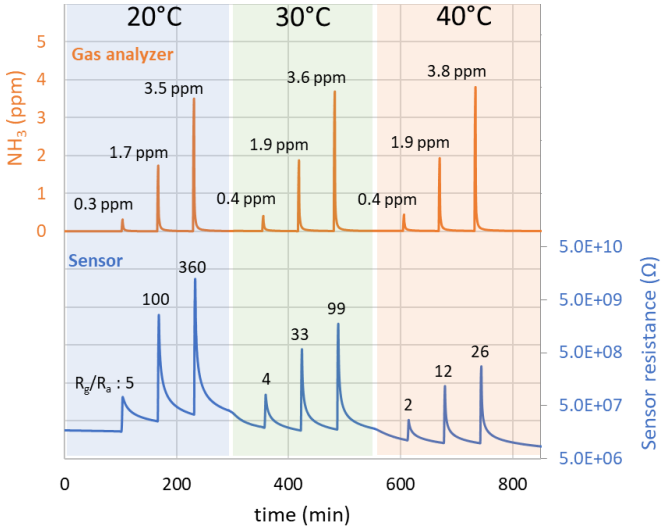

Figure 4. NH_3 concentration detected by the analyzer (orange) and corresponding CuBr@SiO_2 sensor resistance (blue) at 20°C, 30°C and 40°C.

C. *Effect of humidity*

The humidity effect on the sensing performances of CuBr@SiO_2 sensor is evaluated at 0%, 10%, 30% and 50% relative humidity. After baseline stabilization at each humidity, the sensor is exposed to 1 ppm ammonia. To evaluate the contribution of SiO_2 and CuBr, the sensors SiO_2 and CuBr are subjected to the same test conditions. The results are reported in Figure 5. Even though SiO_2 sensor presented an n-type response to NH_3, it is calculated as R_g/R_a to be consistent with the other sensors and to illustrate the SiO_2 contribution in a more visual way in Figure 5.

SiO_2 sensor is too resistive under dry air thus no baseline could be measured. The exposure to 1 ppm and 5 ppm NH_3 did not lead to a signal. Under humid condition SiO_2 resistance is measurable. The baseline decreases with humidity from 5.3 x 10^8 Ω at 10% to 1.5 x 10^8 Ω at 50%RH. The response of SiO_2 to ammonia is a characteristic to an n-type sensor as the resistance under ammonia decreases. This behavior is consistent with literature [6,7] and is attributed to the reaction between NH_3 and OH groups on the SiO_2 surface as SiO_2 is highly hydrophilic. However, SiO_2 sensor response to 1 ppm ammonia is low and constant for each humidity level.

CuBr sensor baseline increases with humidity. This increase is attributed to the adsorption of H_2O on CuBr as a reductive species, thus inducing a response similar to NH_3. The response of CuBr sensor to 1 ppm NH_3 increases with humidity. One could expect a decrease of the response due to a competition between H_2O and NH_3 acting both as reductive species. Here, the observed phenomenon is the opposite. Thus, we believe that the presence of H_2O on CuBr increases the NH_3 interactions on the layer.

CuBr@SiO_2 sensor behavior under humidity appears more complex. The baseline increases with humidity which is consistent with the affinity between H_2O and CuBr reported above.

The response is almost unaffected from 0 to 30%RH but undergoes a big drop at 50%RH. This sudden decrease might be related to the porous structure of the layer. While the pores are covered but not filled with water below 30%RH, the water pressure at 50%RH is high enough to fill completely the pores with water, thus preventing ammonia to interact with CuBr. This hypothesis is consistent with ellipsometry-porosimetry measurement where we observe a sudden increase of the adsorbed water at a certain water partial pressure, due to capillary condensation and in direct relation with pore size and geometry [8].

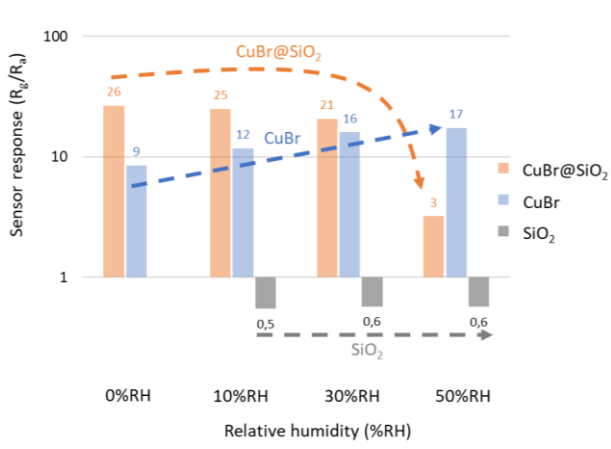

Figure 5. $CuBr@SiO_2$, CuBr and SiO_2 response to 1 ppm NH_3 under humid condition from 0 to 50% relative humidity.

The effect of humidity on SiO_2, CuBr and $CuBr@SiO_2$ showed that the SiO_2 contribution in ammonia detection is nil in dry conditions. Under humidity, its response to NH_3 is low and constant so its participation in NH_3 sensing is negligible. However, the mesoporous structure of SiO_2 can be responsible for a decrease of the sensor response at 50%RH. This effect of humidity could be addressed by adding a humidity filter when integrating the sensor into a device.

IV. CONCLUSION

Mesoporous $CuBr@SiO_2$ sensor exhibits sensing properties compatible with a potential use as transdermal ammonia sensor. The detection limit is experimentally determined at 7 ppb which is below the estimated ammonia concentration emitted from the skin. The sensor can detect minor fluctuations of NH_3 with a resolution of 10 ppb or less. The temperature increase leads to a sensitivity decrease attributed to the desorption of NH_3 favored by temperature. Humidity affects the baseline but the response to 1 ppm is only slightly affected up to 30%RH. The response decreases more significantly at 50%RH. This behavior might be the consequence of the mesoporous structure of SiO_2. The simple structure and ease of fabrication combined with good selectivity and very high sensitivity, make this sensor a good candidate for integration in a device for skin-emitted ammonia detection.

ACKNOWLEDGMENT

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