

Activated Carbon in Focus: Is It the Key to Better NO₂ Gas Sensors?

Proscovia Kyokunzire¹, Jean Zaraket¹, Vanessa Fierro¹, Alain Celzard^{1,2}

¹Université de Lorraine, Centre National de la Recherche Scientifique (CNRS), Institut Jean Lamour (IJL), F-88000, Épinal, France

²Institut Universitaire de France (IUF), 75231 Paris, France

Corresponding Author's e-mail address: proscovia.kyokunzire@univ-lorraine.fr

Summary:

Gas sensors play a crucial role in detecting harmful environmental gases. This work therefore gives an insight into the sensing performance of a commercial Activated Carbon (AC) for NO₂ detection at room temperature. NO₂ sensing was assessed over a dynamic concentration range from 1 to 20 ppm and 20 to 1 ppm. The impact of increasing and decreasing NO₂ concentration, and saturation on sensor response was examined. NO₂ sensing proceeded by adsorption, facilitated by the porosity and high surface area of AC, and a response limit close to 65% was observed at sensor saturation.

Keywords: Resistive gas sensor, Activated carbon, Adsorption, Saturation, Response

Background, Motivation and Objective

Air pollutants cause significant adverse effects on the natural environment and human health, and are presently considered to be one of the main drivers of climate change [1]. Among these pollutants, NO₂ plays an important role in the deterioration of air quality [2]. Current health regulations set by the US Environmental Protection Agency (EPA) define an annual standard level of 53 parts per billion (ppb) NO₂, with a one-hour daily maximum concentration of 100 ppb [3]. It is therefore necessary to develop new, more efficient, real-time sensors to monitor NO₂ accurately.

The potential of ACs as sensitive layers for gas sensors has been explored due to their well-developed internal porous structure, high specific surface area, rich surface chemistry, ability to tailor their structure to specific applications, chemical stability and ease of preparation [4]. These features greatly enhance the adsorption and retention of gas molecules in the carbon matrix, thus improving sensor response. Our previous meticulous review of the literature revealed that only one article had explored the use of AC for the detection of NO₂ gas [5]. This limited research represents a significant gap in understanding the overall operation and sensing performance of AC in the detection of NO₂, which is considered a major environmental pollutant.

Therefore, the objective of this work is to examine the NO₂ gas sensing capability of unmodified AC used as a sensitive layer at 25 °C, with

particular emphasis on the influence of various parameters on sensor response and to optimize the operation of NO₂ gas sensors based on AC.

Experimental details

Commercial AC (Norit® A Supra) and Nafion® used as the binder were supplied by Norit, Netherlands and Sigma Aldrich, respectively. Interdigitated electrodes (IDEs) were purchased from Nano SPR, USA.

AC was dispersed in an isopropanol/water solution (20/80, v/v) containing 0.2 wt.% Nafion® binder. The mixture was sonicated for 1 hour to obtain a uniform dispersion. Four 2-μL drops of the resulting ink were drop-cast onto pre-cleaned gold-plated IDEs, followed by drying under an infrared lamp, and then placed in a vacuum oven at 80 °C for 12 hours for complete drying.

The obtained sensing layers were tested at various NO₂ concentrations (1-20 ppm) at 25 °C. Relative responses were calculated as a function of resistance in NO₂ gas (R_{GAS}) and dry synthetic air (R_{AIR}) in two distinct ways: (i) fixing the initial or baseline resistance (R_{AIR_i}) of the sensors; (ii) using each new cycle's resistance ($R_{AIR_{ci}}$) as the initial resistance to calculate the responses.

$$\text{Response, } R_i (\%) = \frac{R_{AIR_i} - R_{GAS}}{R_{GAS}} \times 100\% \quad (i)$$

$$\text{Response, } R_{ci} (\%) = \frac{R_{AIR_{ci}} - R_{GAS}}{R_{GAS}} \times 100\% \quad (ii)$$

Results

Fig. 1(a, b) shows real-time dynamic response curves of sensors exposed to 1-20 ppm and 20-1 ppm NO₂ gas concentrations. The responses R_i (%) increased with increasing and decreasing NO₂ concentration, whereas R_{ci} (%) decreased with decreasing concentration. Since this specific AC is characterized by a high degree of microporosity and a large surface area with a multitude of adsorption sites, a greater number of NO₂ molecules at high concentration interact with the available sites, resulting in a higher degree of adsorption. This increased adsorption is directly correlated with a higher sensor response, indicating that a greater number of molecules are detected. The increase in R_i (%) at decreasing concentration can be attributed to an enhanced response resulting from the formula $R = (R_{air}(\text{initial}) - R_{gas})/R_{gas}$.

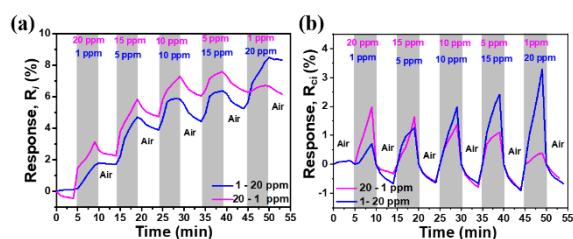


Fig. 1. Real-time dynamic responses of the AC-based sensor; (a) R_i and (b) R_{ci} exposed to 1-20 ppm (blue) and 20-1 ppm (pink) of NO₂ gas at 25 °C

As shown in Figs. 2(a, b) a limit in the response of our AC-based sensors was reached after 5.5 hours of exposure to 20 ppm NO₂ gas, with a constant response (R_i and R_{ci}) of 64.7%. The observed response limit is linked to the fact that a greater number of NO₂ gas molecules are

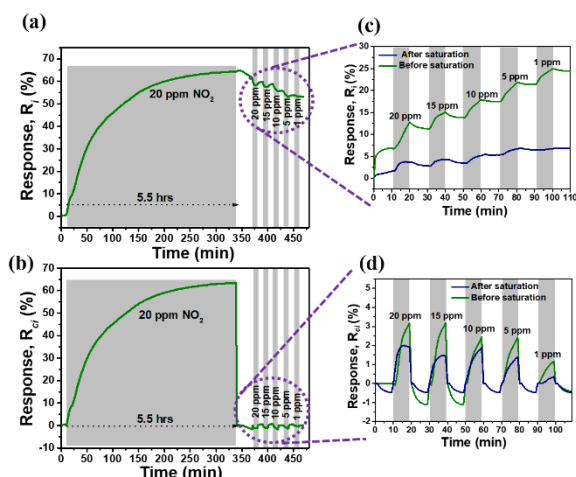


Fig.2 Response (a) R_i (%) and (b) R_{ci} (%) curves for saturation under 20 ppm NO₂ and dynamic response from 20 to 1 ppm. Responses (c) R_i (%) and (d) R_{ci} (%) curves showing the dynamic responses of the sensors for a new unsaturated sample (in green) and after saturation (blue, zoomed in from (a, b) when exposed to 20 ppm to 1 ppm of NO₂ gas after 5.5 hours at 25 °C.

physically adsorbed in the micropores via the pore-filling mechanism.

When the adsorption/desorption cycles were repeated for decreasing NO₂ gas concentrations after saturation, a change in resistance could be observed, as illustrated in Figs. 2(a, b). The magnitude of the post-saturation response was weaker compared with a fresh new sample shown in green in Figs. 2(c, d). This can be attributed to high-energy binding sites on the AC that were tightly occupied by NO₂ molecules during saturation, resulting in an unrecoverable response. The saturation response (64.7%) remained higher than that of the fresh AC-based sensor at 20 ppm NO₂ gas, indicating that the charge transfer of previously strongly adsorbed NO₂ molecules significantly improves the overall response.

Conclusion

This work reports the capability of ACs to detect NO₂ gas at 25 °C and contributes to a deeper understanding of the performance of AC-based NO₂ gas sensors that are currently less studied.

References

- [1] G. Jeong, H.J. Cheon, S.Y. Shin, E. Wi, P. Kyokunzire, H. Cheon, V. Van Tran, T.T. Vu, M. Chang, Improved NO₂ gas sensing performance of nanoporous conjugated polymer (CP) thin films by incorporating preformed CP nanowires, *Dye. Pigment.* 214 (2023)111235. <https://doi.org/10.1016/j.dyepig.2023.111235>.
- [2] J.Y. Kim, A. Mirzaei, J.H. Kim, SnO₂ Nanowire/MoS₂ Nanosheet Composite Gas Sensor in Self-Heating Mode for Selective and ppb-Level Detection of NO₂ Gas, *Chemosensors.* 12(2024)107. <https://doi.org/10.3390/chemosensors12060107>.
- [3] US EPA, Primary National Ambient Air Quality Standards (NAAQS) for Nitrogen Dioxide | US EPA, (n.d.). <https://www.epa.gov/NO2/pollution/primary-national-ambient-air-quality-standards-naaqs-nitrogen-dioxide> (accessed September 16, 2024).
- [4] R. Pietrzak, T.J. Bandosz, Activated carbons modified with sewage sludge derived phase and their application in the process of NO₂ removal, *Carbon N. Y.* 45 (2007) 2537–2546. <https://doi.org/10.1016/j.carbon.2007.08.030>.
- [5] P. Kyokunzire, J. Zaraket, V. Fierro, A. Celzard, Recent developments in the use of activated carbon-based materials for gas sensing applications, *J. Environ. Chem. Eng.* 12(2024)113702. <https://doi.org/10.1016/j.jec.2024.113702>.

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