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# BINARY MIXTURE OF FLUOROGRAPHENE AND FLUORINATED CARBON NANO-ONIONS AS SENSING LAYER FOR CHEMIRESISTIVE $NO_2$ SENSORS

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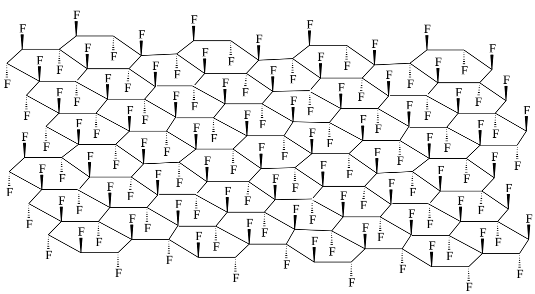
## *Introduction*

Nitrogen dioxide ($NO_2$) is a reddish-brown gas with a strong, suffocating odor that poses significant toxicity risks to both humans and animals, making it a critical air pollutant. The primary anthropogenic sources of $NO_2$ include fossil fuel combustion, internal combustion engines, vehicular traffic, and various industrial activities. Given the wide range of $NO_2$ sources and its high toxicity, there has been substantial growth in the development of nitrogen dioxide sensors over the past few decades.

A variety of materials have been employed as sensitive layers in the fabrication of $NO_2$ sensors, including metal oxides, polymers, metal sulfides, and nanocomposite matrix polymers-specifically, semiconductor metal oxides. Moreover, graphene-based nanocarbon materials, carbon nanotubes, semiconductor metal oxide nanocomposite matrices combined with nanocarbon materials, polymer nanocomposite matrices with nanocarbon materials, and metal nanocomposites integrated with nanocarbon materials have garnered significant attention as promising sensitive materials for $NO_2$ detection.



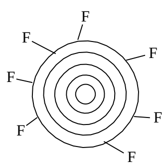


**Figure 1.** Structure of fluorographene (FG) and fluorinated nano-onions (CNOs-F).

The sensitive layers explored in this study, intended for the development of resistive $NO_2$ sensors, consist of fluorographene (FG) nanocomposite matrices combined with fluorinated onion-type nanocarbon materials (CNOs). The structures of FG and CNOs are presented in Figure 1. The tested detection mechanism is based on the variation in the resistance of the sensitive layer in response to different concentrations of $NO_2$. The results are explained by considering the interaction between $NO_2$ molecules and the fluorographene and fluorinated onion-type nanocarbon materials using the HSAB (Hard and Soft Acids and Bases) theory.

***Materials and methods***

The designed process to obtain the sensitive layer of FG: CNOs-F is the following:
FG is synthesized from graphene (powder) by plasma treatment of $F_2$ and Ar (volume mixture 1:8) at a pressure of 0.6 bar, in a nickel reactor, at room temperature. The injection time was set to 5 minutes, the exposure time varying between 2 and 10 minutes.
Onion-type nanocarbon materials (CNOs) are synthesized from nanodiamond, by thermal treatment at 1650°C, in a helium atmosphere. The synthesis of CNOs-F is carried out by plasma treatment of $F_2$ and $N_2$ (volume mixture 1:10) at a pressure of 0.5 bar, in a nickel reactor, at room temperature. The injection time is 4 minutes, the exposure time varies between 1 and 10 minutes.
The FG dispersion is prepared by dissolving 1 mg of FG in 5 mL of ethanol, under magnetic stirring for three hours, at room temperature.1 mg of CNOs-F is added to the FG dispersion obtained, under magnetic stirring for three hours, at room temperature.
The obtained dispersion is deposited by the "drop casting" method using a Si/$SiO_2$ substrate with linear electrodes or with interdigitated electrodes (after masking the contact area beforehand).
The sensitive layer obtained is subjected to a two-hour heat treatment at 120°C in a vacuum.
The $NO_2$ monitoring capability is investigated by applying a constant current between the two electrodes and measuring the voltage at different values of the $NO_2$ concentration.

***Results and conclusions***

Fluorine functionalization of a sensing substrate is an effective technique for enhancing the performance of $NO_2$ (nitrogen dioxide) gas sensors. The incorporation of fluorine can increase the sensitivity of the substrate to $NO_2$ molecules, improve the sensor's selectivity, stabilize its performance over time, reduce drift to ensure consistent and reliable measurements and accelerate the sensor's response time. The interaction between $NO_2$ molecules and FG and CNOs-F can be explained using the Hard and Soft Acids and Bases (HSAB) theory. Furthermore, fluorinated carbon nano-onions and FG offer a high specific surface area-to-volume ratio, which contributes to the significant variation in the resistance of the sensitive layer upon contact with $NO_2$ molecules. The newly synthesized sensing layer provides several notable advantages, including detection at room temperature, chemical and thermal stability, and superior mechanical properties.