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NOVEL RESISTIVE OZONE SENSOR

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Introduction

This paper reports the design and manufacturing processes for a resistive ozone sensor employing halogenated perovskite/fluorinated nanocarbonic materials as a sensing layer. The halogenated perovskites used are $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_3-xClx$, the nanocarbonic structures being of the fluorinated carbon nanohorns type (CNHs-F-Fig.1a) and onion-type fluorinated nanocarbon materials (CNOs-F Fig.1b).

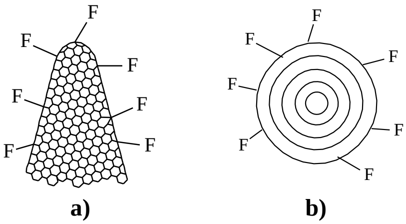

Figure 1.
a) structure of CNHs-F
b) structure of CNOs-F

Sensor architecture

The generation of the sensitive layer goes through the following stages:

1) The glass substrate is cleaned for 10 minutes in the ultrasonic bath using sequentially equal volumes of acetone, ethanol, and finally deionized water.

2) The synthesis of fluorinated carbon nanomaterials is carried out by plasma treatment of F_2 and N_2 (volumetric mixture 1:1) at a pressure of 0.6 bar, in a nickel reactor, at room temperature. The injection time is 5 minutes, the exposure time varies between 2 and 10 minutes.

3) The dispersion of fluorinated carbon nanomaterials is prepared by dissolving 1 mg of CNHs-F or CNOs-F in 3 mL of isopropyl alcohol, under magnetic stirring for three hours, at room temperature.

4) The obtained solution is deposited by the "drop casting" method using the glass substrate with linear electrodes or interdigitated electrodes (after masking the contact area beforehand).

5) 5 µL of 0.55M solution of PbI_2 in dimethylformamide (DMF) is mixed with 15 µL of 0.55M solution of CH_3NH_3I in dimethylformamide and subjected to magnetic stirring for 6 hours, at a temperature of 60 °C.

6) The obtained solution is deposited by the "spin coating" method (1500 rpm for 20 sec; 3000 rpm for 40 sec) on the glass substrate over which the fluorinated carbon nanohorns were initially deposited.

7) The obtained layer is subjected to a heat treatment at 100 °C, 30 minutes.

8) The halogenated perovskite penetrates the layer of fluorinated carbon nanohorns forming a hybrid structure of $CH_3NH_3PbI_3$ / fluorinated carbon nanohorns.

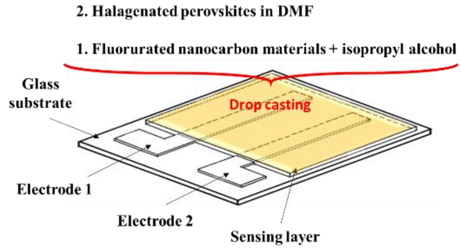

Figure 2. Sensing device architecture with linear electrodes

Advantages of the proposed sensing layer

Through the ad/absorption of ozone molecules, electrons are transferred from the nanocarbon structure to the gas (ozone is a molecule with electron-attracting properties). Both CNHs-F and CNOs-F are p-type semiconductors. Thus, by reducing the number of electrons, the concentration of holes increases, leading to a proportional decrease in resistance.

The use of halogenated perovskite nanocomposite / fluorinated nanocarbon materials gives the sensor several significant advantages:

- both CNHs-F and CNOs-F give a high specific surface/volume ratio, as well as a variation in the resistance of the sensitive layer upon contact with ozone molecules;
- the halogenated perovskite shows an increased affinity for ozone molecules as well as a variation in the resistance of the sensitive layer upon contact with them;
- due to the increased electronegativity, the fluorine atoms increase the polarity of the surface of the nanocarbon material, creating temporary dipoles that facilitate the interaction with ozone molecules;
- detection over a wide temperature range;
- fas response of the sensor to variations in the ozone concentration value;
- reversibility;
- chemical and thermal stability.

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