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Novel Resistive Ozone Sensor

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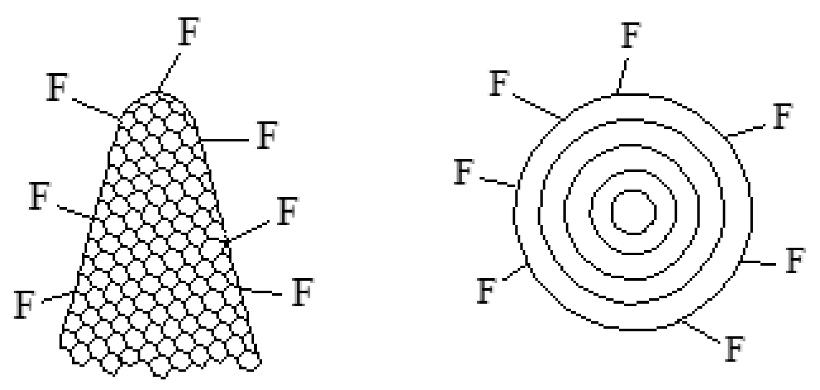
Scope:

Design and manufacturing processes for a resistive ozone sensor using as sensing layers new nanocomposites with halogenated perovskites ($CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-x}Cl_x$) and fluorinated nanomaterials of the type carbon nano-horns and carbon nano-onions.
Monitoring of the O_3 in closed spaces or in premises where ozone is used in technological purposes (*i.e.* disinfection of the atmosphere storage facilities in agri-food industry) is very important. Severe negative influence to humans' respiratory function and eyes may be caused by exposure to environments with ozone (i.e. concentrations of 0.1 ppm - 1 ppm) even for reduced time periods (2h - 6h).

Original approach:

- halogenated perovskites such as CH3NH3PbI3 and CH3NH3PbI3−xClx, provide affinity for ozone molecules
- the fluorinated nanocarbonic materials, due to their specific structures (nanohorns type CNHs-F / Fig.1a, and onions-type fluorinated nanocarbons CNOs-F / Fig.1b), and properties provide high specific surface / volume ratio, and electrical resistance variation upon contact to atmospheres of variable compositions



a) b)

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

- functionalization of nanocarbon materials is achieved through F2 – N2 plasma treatment at room temperature, 0.6 bar, at a volumetric ratio of the two gases of 1:1, with 5 minutes injection time, and exposure time in the range 2 – 10 minutes
- O_3 is a molecule with electron-attracting properties, and thus its ad/absorption processes are associated with electron-transfer processes from the nanocarbon structure, as both the CNHs-F and the CNOs-F are *p*-type semiconductors

Sensor architecture:

- glass substrate ultrasonically cleaned for 10 minutes using sequentially equal volumes of solvents (ethanol, acetone, deionized water)
- preparation of fluorinated nanocarbonic materials dispersion in isopropyl alcohol by 3h magnetic stirring, at room temperature
- deposition of nanocarbons dispersion on the substrate with either linear, or interdigitated electrodes (contact areas previously masked) by drop casting
- preparation (magnetic stirring 6h @ 60°C) and deposition (spin coating 20s @ 1500 rpm; 40s @ 4000 rpm) of the 1:3 (v/v) mixture: 0.55M PbI2 solution in dimethylformamide (DMF) and 0.55M CH3NH3I solution in DMF onto the glass substrate that already holds the nanocarbons layer, followed by thermal treatment for 30 min. @ 100°C; the halogenated perovskite penetrates the layer of fluorinated carbon nanomaterial to form a hybrid structure

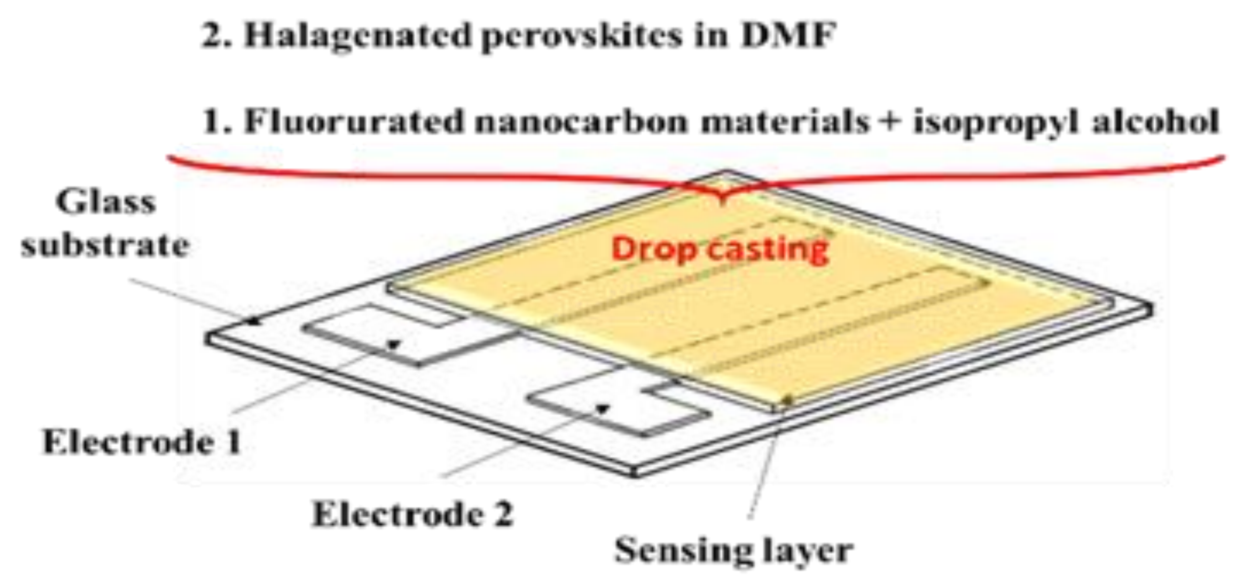


Fig. 2. Sensing device architecture with linear electrodes

Advantages of the novel resistive ozone sensor:

- both nanocarbon materials CNHs-F and CNOs-F offer a high specific surface / volume ratio, and variation of sensitive layer electrical resistance upon contact with ozone molecules;
- halogenated perovskite shows an increased affinity for ozone molecules, and variation of sensitive layer resistance upon contact with O_3;
- due to their increased electronegativity, the fluorine atoms increase the polarity of the nanocarbon material surface, and thus creating temporary dipoles that facilitate interaction with ozone molecules;
- fast response of the sensor to variations the ozone concentration values;
- chemical and thermal stability; reversibility; detection over a wide temperature range.

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