

Ammonia resistive sensor

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Field of invention

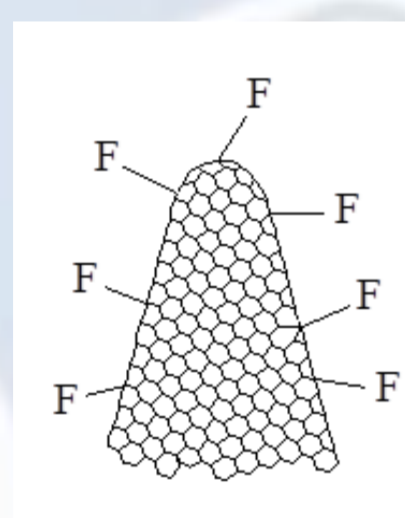
Ammonia is one of the most important raw materials on the chemical products market, being widely used in multiple areas of domestic and industrial activity. Ammonia is a key ingredient in the composition of many cleaning products, being also used in the chemical industry with global production that exceeds 100 million tons per year.

Considering these aspects, the monitoring of ammonia concentration, has cardinal importance.

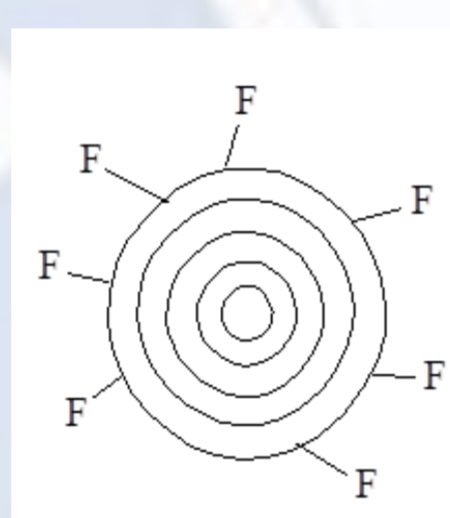
Original approach

Present invention claims a new resistive ammonia sensor using a fluorinated nanocarbon materials – based matrix nanocomposites.

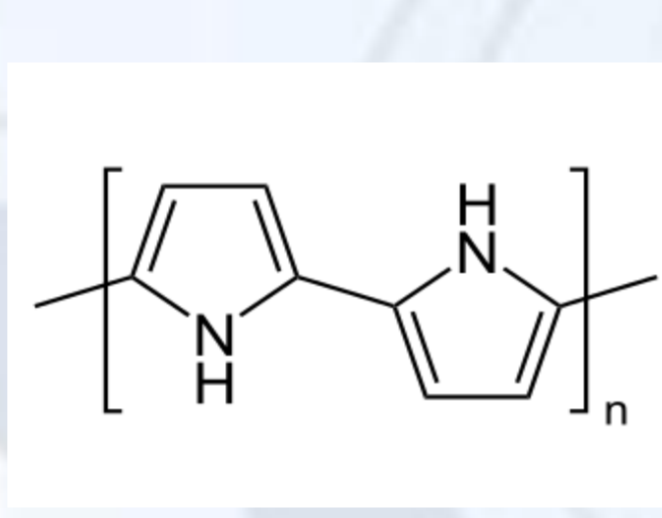
- The sensitive layers described in this invention are binary nanocomposites consisting of fluorinated nanohorns (CNHs-F) / polypyrrole (PPy), fluorinated onion-type nanocarbon materials (CNOs-F) / PPy as well as CNHs-F/ CNOs-F/PPy ternary nanocomposites.
- Functionalization of carbon nanohorns as well as onion-like carbon nanomaterials is achieved by F_2-N_2 plasma treatment.
- Polypyrrole can be used as a 5 % aqueous dispersion (commercial product) or it can be synthesized in situ by a chemical polymerization reaction using pyrrole (monomer), $FeCl_3$ (oxidizing agent) and sodium p-toluenesulfonate (doping agent).
- By ad/absorbing ammonia molecules, electrons are transferred to the nanocarbon structure. Both CNHs-F and CNOs-F are p-type semiconductors, the number of voids decreases, therefore the resistance of the nanocarbon material also increases proportionally.
- Polypyrrole is also a p-type semiconductor and by ad/absorption of ammonia molecules, the number of voids decreases, therefore the resistance of the polymer increases proportionally.
- Functional carbon nanohorn and onion-type nanocarbon materials in F_2-N_2 plasma has the advantage (through the variety of exposure time as well as its power) that it can ensure an optimal C : F ratio, for a better sensitivity a sensitivity as well as a reduction of hysteresis.



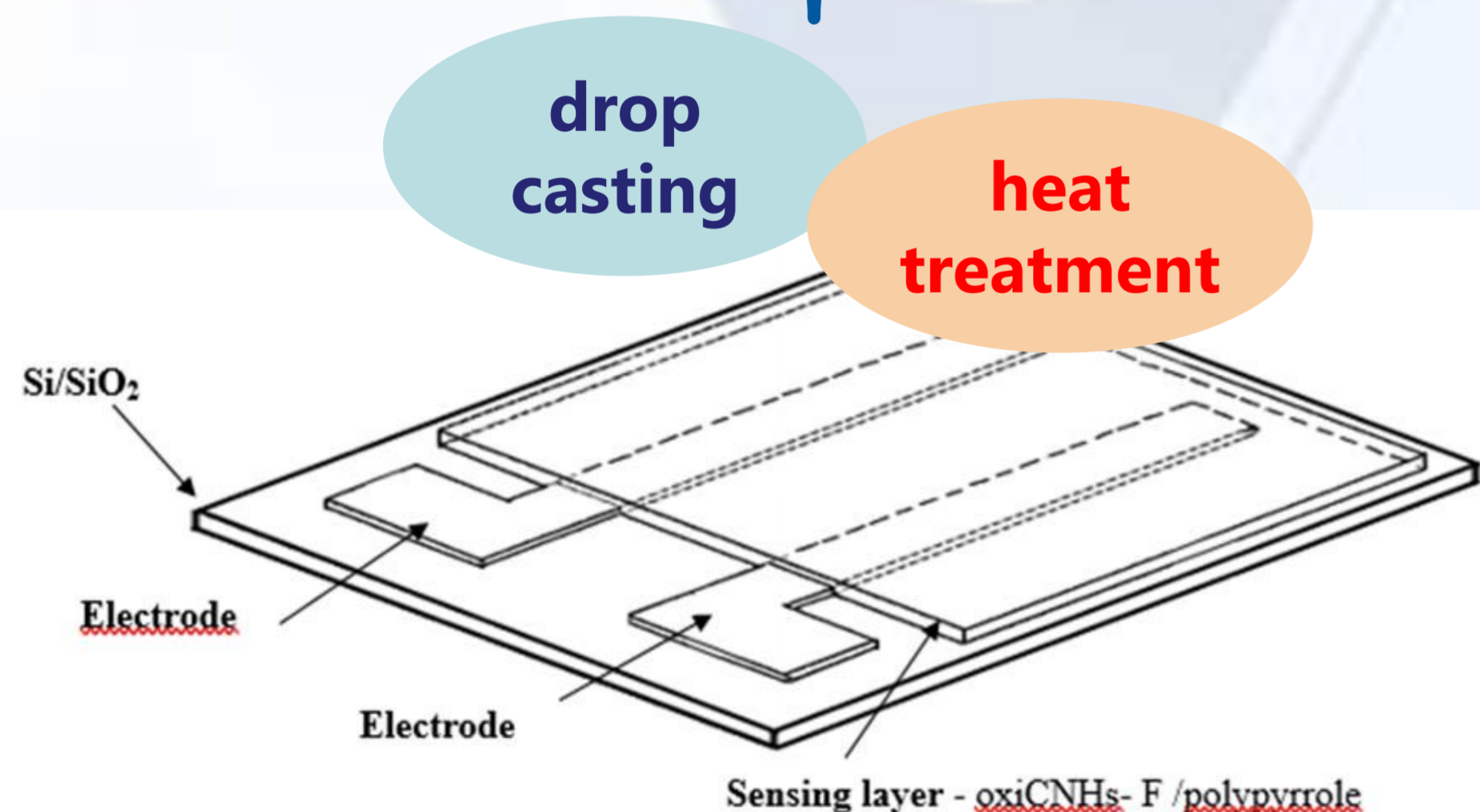
fluorinated
nanohorns
(CNHs-F)



fluorinated onion
type nanocarbon mat.
(CNOs-F)



polypyrrole
(PPy)



The structure of sensor with linear electrodes

Sensing structure

The dielectric substrate is glass, Si/SiO₂, PET, Kapton and can be between 50 microns and 5 millimeters thick. Electrodes can be deposited on the surface of the dielectric substrate by direct printing, sputtering or evaporation. The electrodes can be made of the same material (gold, platinum) or of different materials. They can be linear or have an interdigitated configuration.

Sensor manufacturing

Sensor preparation procedure comprise the following stages:

- 1) The glass substrate is cleaned for 10 minutes in the ultrasonic bath using sequentially equal volumes of acetone, ethanol and deionized water.
- 2) The synthesis of fluorinated carbon nanohorns is carried out by plasma treatment of F_2 and N_2 (volume mixture 1:5) at a pressure of 0.6 bar, in a nickel reactor, at room temperature. The injection time is 5 minutes, the exposure time varying between 2 and 10 minutes.
- 3) The dispersion of fluorinated carbon nanohorns is prepared by dissolving 10 mg of CNHs-F in 10 mL of ethanol, under magnetic stirring for six hours, at room temperature.
- 4) 0.1 mL of 5% polypyrrole aqueous dispersion is added to the obtained dispersion under magnetic stirring for 12 hours, at room temperature.
- 5) The obtained dispersion is deposited by the "drop casting" method using a glass substrate with linear electrodes or with interdigitated electrodes (after masking the contact area beforehand).
- 7) The obtained layer is subjected to a heat treatment at 200 °C, for one hour.

Advantages of the proposed sensing layer

- use of binary nanocomposites consisting of fluorinated nanocarbon materials (CNHs-F)/ polypyrrole (PPy), onion-type fluorinated nanocarbon materials (CNOs-F)/PPy, as well as ternary nanocomposites CNHs-F/ CNOs-F/PPy confers advantages notable in resistive ammonia detection;
- both CNHs-F and CNOs-F give a high specific surface / volume ratio, as well as a significant variation in the resistance of the sensitive layer when in contact with ammonia molecules; polypyrrole shows an increased affinity for ammonia molecules, as well as a variation in the resistance of the sensitive layer upon contact with them;
- detection over a wide temperature range; quick response of the sensor to variations in the ammonia concentration value; reversibility; chemical and thermal stability; superior mechanical properties.

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