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TRIFLUOROMETHYL-ONION-LIKE CARBON-BASED NANOCOMPOSITE AS SENSING FILM FOR RESISTIVE TRIMETHYLAMINE SENSOR

Bogdan Catalin Serban[1], Octavian Buiu[1], Marius Bumbac[2], Cristina Mihaela Nicolescu[3], Maria Ruxandra Salagean[4], Vlad Diaconescu[5], Matei -Gabriel Ursachescu[6]

[1]National Institute for Research and Development in Microtechnologies, IMT-Bucharest, 126A, Str. Erou Iancu Nicolae, 077190, Voluntari, Ilfov, Romania
[2]Valahia University of Târgoviște, Faculty of Sciences and Arts, Sciences and Advanced Technologies Department, 13 Aleea Sinaia, 130004, Târgoviște, marius.bumbac@valahia.ro, Romania
[3]Valahia University of Târgoviște, Institute of Multidisciplinary Research for Science Technology, 13 Aleea Sinaia, 130004, Târgoviște, Romania
[4]National College "Saint Sava", 23 General H.M. Berthelot, 010168, Bucharest, Romania
[5]University of Medicine and Pharmacy "Carol Davila", Dionisie Lupu Street, 37, Bucharest, 020021, Romania
[6]National College "B. P. Hasdeu", Gării Bld., 1, 120218, Buzău, Romania

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Introduction

Trimethylamine (TMA) is a colorless, hygroscopic organic compound that plays a key role in industrial organic synthesis. It is a gaseous amine at room temperature and poses hazards to human skin, eyes, and the respiratory tract. The National Institute for Occupational Safety and Health (NIOSH) recommends a maximum exposure limit of 10 ppm for 10 hours and 15 ppm for 15 minutes. During the spoilage of fish and marine organisms, microbial degradation of trimethylamine N-oxide results in the accumulation of TMA. As a result, TMA concentration is widely used as an indicator of fish and seafood freshness for human consumption. This has driven interest in developing trimethylamine sensors with low detection limits. This paper explores the use of sensitive layers in resistive TMA sensors, employing a sensitive film made from an equimass binary nanohybrid of onion-type oxidized nanocarbon materials functionalized with trifluoromethyl and CuO groups.

Materials and methods

The process for obtaining ox-CNOs-CF3 involved the following steps:
Synthesis of onion-type nanocarbon materials (CNOs) - CNOs were synthesized from nanodiamonds through heat treatment at 1650 °C in a helium atmosphere.
Functionalization with trifluoromethyl groups (CNO-CF_3) - CNOs were treated in CF_4 plasma at 1 bar pressure in a nickel reactor at room temperature. The injection time was 5 minutes, with an exposure time ranging from 2 to 20 minutes.
Oxidation to obtain ox-CNOs-CF_3 - CNO-CF_3 was oxidized in an Ar-O_2 plasma (3:1 volumetric mixture) inside a quartz tube at 4 torr pressure and room temperature. The injection time was 10 minutes, with exposure times between 2 and 10 minutes.

Preparation of the ox-CNO-CF_3/CuO Sensitive Film - The raw materials include $Cu(CH_3COO)_2{\cdot}2H_2O$ (precursor), a solvent mixture of ethanol and ethanolamine, polyethylene glycol (stabilizer, molecular weight 5,000), and ox-CNO-CF_3. The molar ratio of $Cu(CH_3COO)_2{\cdot}2H_2O$ to ethanol is 1:4.

Magnetic Stirring – was conducted in two stages: at 50 °C for 2 hours, and at 70 °C for 2 more hours, during which ox-CNO-CF_3 was added.

The solution was stabilized at room temperature for 12 hours and was deposited via the drop-casting method after masking the contact area.

The sensor substrate was made of Si/SiO_2, measuring 5 mm, with gold electrodes. The electrodes were approximately 200 microns wide and separated by 6 mm, arranged either linearly or in an interdigitated configuration. The sensitive layer underwent thermal treatment in two stages: in air at 300 °C for 10 minutes followed by 1 hour at 400 °C.

Results and conclusions

The sensitive film used for resistive trimethylamine sensors was an equimass binary nanohybrid composed of oxidized onion-type nanocarbon materials functionalized with trifluoromethyl groups. The detection principle is based on the increase in the film's resistance as the trimethylamine concentration rises. The use of this nanohybrid material, combined with CuO, as the sensitive layer offers several advantages: high specific surface area, electron-attracting effect (trifluoromethyl groups enhance the number of carriers in the nanocarbon materials due to their strong electron-withdrawing properties), hydrophobicity (fluorine atoms reduce water molecule affinity, improving sensor performance in humid environments), and synergistic effect of CuO (CuO, a p-type semiconductor, interacts synergistically with the p-type nanocarbon materials upon exposure to trimethylamine). CuO also modifies the pore distribution at the interface, increasing the specific surface area.

The detection mechanism involves the adsorption of residual O_2 molecules on the CuO surface, leading to the formation of anionic species and hole-type charge carriers via the following reactions:

$$O_2\ (gas) \rightarrow O_2\ (ads)$$

$$O_2\ (ads) \rightarrow O_2^-\ (ads) + h^+$$

$$O_2^-\ (ads) \rightarrow 2O^{2-} + 3h^+$$

Upon exposure to trimethylamine, the holes are consumed in the reaction:

$$N(C_2H_5)3 + O^{2-} + 2h^+ \rightarrow N_2 + H_2O + CO_2$$

This reduces the hole concentration, thereby increasing the resistance of the semiconductor metal oxide. The interaction between trimethylamine molecules and the ox-CNO-CF_3 layer can be explained using HSAB (Hard-Soft Acid-Base) theory. Trimethylamine molecules, as strong bases, interact with the strong acid-like holes in ox-CNO-CF_3, resulting in a proportional increase in resistance with trimethylamine concentration.

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