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RESISTIVE ETHANOL SENSORS BASED ON BINARY NANOHYBRIDS OF ONION-TYPE NANOCARBON MATERIALS FUNCTIONALIZED WITH TRIFLUOROMETHYL GROUPS AND NICKEL OXIDE

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Introduction

Monitoring ethanol concentration is crucial in various industries, including the wine industry (e.g., fermentation monitoring), biofuel production, traffic safety (alcohol sensors in portable devices or car dashboards), food production, industrial environments (ensuring worker safety by monitoring alcohol levels), and the medical field (breath analysis). Ethanol, especially in high concentrations, is highly flammable and toxic, posing risks to human health. The performance of ethanol sensors, whether resistive, electrochemical, capacitive, optical, or electromagnetic, depends significantly on the material used for the sensitive film. Semiconducting metal oxides, either simple, doped, or nanocomposites, are widely employed as sensing elements. Examples include SnO_2, SnO_2 doped with Ni, SnO_2-ZnO, SnO_2-CuO, ZnO, ZnO doped with Al, TiO_2 (doped with Pt or Nb), In_2O_3, In_2O_3-$ZnSnO_3$, ZnO-In_2O_3, Fe_2O_3 (doped with Pd), Cu_2O, CuO-Cu_2O, V_2O_5, and V_2O_5-TiO_2.
This work describes sensitive films for resistive ethanol sensors, comprising equimass binary nanohybrids of onion-type nanocarbon materials functionalized with trifluoromethyl groups and nickel oxide.

Materials and methods

The process for obtaining the sensitive film is as follows:
Synthesis of functionalized CNOs: Onion-type nanocarbon materials (CNOs) are synthesized from nanodiamond through thermal treatment at 1650°C in a helium atmosphere. CNOs are functionalized with trifluoromethyl groups (CNO-CF_3) by CF_4 plasma treatment at 1 bar pressure in a nickel reactor at room temperature. The injection time is 3 minutes, with exposure times ranging from 2 to 20 minutes. A dispersion of CNO-CF_3 was prepared by dissolving 1 mg of the material in 5 mL of isopropyl alcohol and stirring magnetically for 5 hours at room temperature.

Synthesis of NiO nanopowder: A mixture of 0.237 g (1.0 mmol) of $NiCl_2·6H_2O$ and 0.06 g of $Na_2C_2O_4$ was dissolved in 15 mL of water and 2 mL of ethylene glycol under magnetic stirring. The solution was transferred to a stainless steel autoclave and heat at 200°C for 12 hours. After cooling, the solid product was separated by centrifugation, wash with deionized water and ethanol, and dried in air. The product was heated gradually to 300°C at a rate of 3°C/min, maintained for 1 hour.

Preparation of composite dispersion and film deposition - 1 mg of NiO nanopowder to the CNO-CF_3 dispersion. The Kapton substrate was cleaned in an ultrasonic bath for 10 minutes using equal volumes of ethanol, acetone, and deionized water sequentially. The dispersion was deposited onto the Kapton substrate with linear or interdigitated electrodes using the "drop casting" method (with the contact area masked). The sensitive layer was heated in a nitrogen atmosphere at 100°C for 120 minutes for densification.

Results and conclusions

The increase in the resistance of the ethanol-sensitive film is attributed to the physicochemical properties of its components and their interactions. Residual O_2 molecules adsorb on the nickel oxide surface, attracting electrons to form anionic species (O_2^-).

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

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

Upon exposure to ethanol, electrons are released into the conduction band via the reaction:

$$C_2H_6O + 3O_2^-(ads) \rightarrow 3H_2O + 2CO_2 + 3e^-.$$

This reduces the hole concentration, increasing the nickel oxide's resistance.

The interaction of ethanol with CNO-CF_3 can be explained by the HSAB theory, where ethanol (a strong base) reacts with nanocarbon voids (strong acids), causing a proportional resistance increase. Additionally, hydrogen bonding via CF_3 groups enhances sensitivity. Finally, the Fermi levels of the metal oxide in the p-p junction with CNO-CF_3 modulate the accumulation and depletion layers, significantly affecting conductivity.

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