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POLYANILINE DOPED WITH SULFONIC GROUP-FUNCTIONALIZED OXIDIZED ONION-TYPE CARBON NANOMATERIALS FOR RESISTIVE HUMIDITY SENSOR LAYERS

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Introduction

Monitoring relative humidity is a crucial process across various domestic and industrial sectors, including indoor air quality control, the textile and paper industries, the medical field, the pharmaceutical industry, the woodworking and automotive industries, paint booth monitoring, agriculture, and meteorology.

Regardless of the type of humidity sensor employed—whether optical, gravimetric, electrochemical, capacitive, piezoresistive, or resistive—the material used as the sensitive film plays a critical role in achieving superior sensor performance. Commonly used sensing materials include nanocarbon materials, polyelectrolytes, and metal oxide semiconductors. Conductive polymers, such as polyaniline, offer an alternative option as a sensitive layer in the development of humidity sensors.

Materials and methods

The preparation of ox-CNOs-SO₃H involved several steps:

Onion-type nanocarbon materials (CNOs) were synthesized from nanodiamonds through heat treatment at 1650 °C in a helium atmosphere. CNOs were oxidized using Ar-O₂ plasma (4:1 volumetric ratio) at room temperature and 5 torr pressure, with an injection time of 2 minutes and exposure time varying between 2–8 minutes. This process optimizes the C:O atomic ratio, enhancing hydrophilicity. Functionalized Ox-CNOs-SO₃H was made by dispersing 50 mg of oxidized CNOs in 10 mL of 95% sulphuric acid, heating the mixture in a Teflon autoclave at 200 °C

for 20 hours, washing with deionized water, and drying under vacuum at 150 °C for six hours.

Polyaniline (emeraldine base) was synthesized by oxidizing aniline with ammonium peroxodisulfate in an acidic solution, followed by precipitation, filtration, washing, and drying at 80 °C. Doping involves mixing 10 mg of ox-CNOs-SO₃H with 10 mg of emeraldine in dimethylformamide, stirring for 20 hours, and washing (Figure 1).

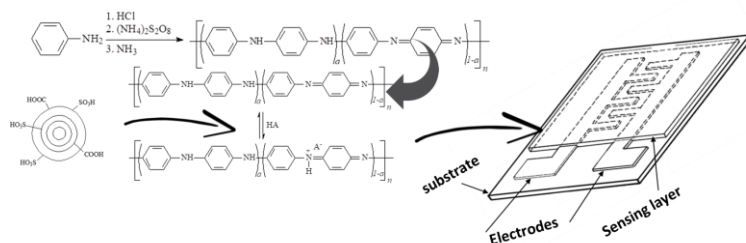


Figure 1 - Sensitive layer preparation

The sensitive layer was created by electrospinning the doped polyaniline onto a PET substrate with linear or interdigitated electrodes. A protective photoresist layer was applied and later removed to enable electrical contact. The final layer was dried at 90 °C for 40 minutes (Figure 1).

Results and conclusions

Humidity sensors utilizing conductive polyanilines as sensitive layers face several challenges: polyanilines are prone to dedoping, a process that becomes more significant with smaller dopant sizes. This dedoping converts polyanilines into insulators (emeraldines), compromising the sensor's long-term stability. The high hydrophobicity of the sensitive film and the absence of a porous structure reduce sensitivity by limiting the material's affinity for water molecules. Furthermore, polyanilines exhibit modest mechanical properties, limiting their performance.

The study addresses these issues by synthesizing new conductive polyanilines in the form of nanofibers, which are sensitive to changes in relative humidity. This was achieved by doping emeraldine with oxysulfonated onion-type nanocarbon materials. The conductive polyaniline sensitive layer demonstrates the ability to reliably monitor relative humidity changes under these conditions.

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