

A Drift-Resistant Amine-based Chemiresistive Printed Sensor for Carbon Dioxide Monitoring

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Summary:

Flexible CO₂ sensors based on carbon nanotubes (CNTs) modified with a Polyethyleneimine (PEI)-1,5-Diaminonaphthalene (DAN) composite are presented. DAN is introduced for the first time in CO₂ sensing, stabilizing the amine environment and reducing baseline drift. The device shows a 6.04% response at 2500 ppm (50% RH) with a sensitivity of $1.68 \times 10^{-3} \text{ ppm}^{-1}$. Screen-printed CNT sensors, functionalized with the same layer, achieve a 27.36% response at 2000 ppm and a sensitivity of $0.92 \times 10^{-2} \text{ ppm}^{-1}$, demonstrating scalable, drift-resistant CO₂ sensing.

Keywords: CO₂ Sensor, Drift, Carbon nanotubes, DAN, Screen printing

Introduction

Accurate CO₂ sensing under varying environmental conditions remains challenging for low-power gas sensors. Signal drift, humidity sensitivity, and limited stability often hinder practical deployment. Although sensitivity is widely reported, drift remains a critical yet insufficiently addressed issue.

Nanomaterials such as CNTs offer advantages over traditional metal oxide sensors due to their large surface area, high conductivity, and room-temperature operation [1]. Functionalization with PEI enhances CO₂ sensitivity, but PEI-CNT systems often suffer from signal drift. In this work, DAN, an NH₂-rich aromatic molecule, is introduced. π - π interactions between DAN and CNTs enhance interfacial coupling and charge transfer, effectively reducing drift during response-recovery cycles.

Materials, Fabrication and Functionalization

Sensors were fabricated on Kapton flexible substrates with screen-printed silver interdigitated electrodes and drop-casted CNT sensing layers functionalized with a PEI-DAN composite [2]. In addition, CNT deposition was investigated via screen-printing of a single-walled CNT (SWCNT) ink. CNTs (42 mg in 5 mL ethanol) were sonicated with sodium dodecylsulfate (SDS, 5 mg) as dispersant and mixed with ethyl cellulose and an ethanol-terpineol solvent sy-

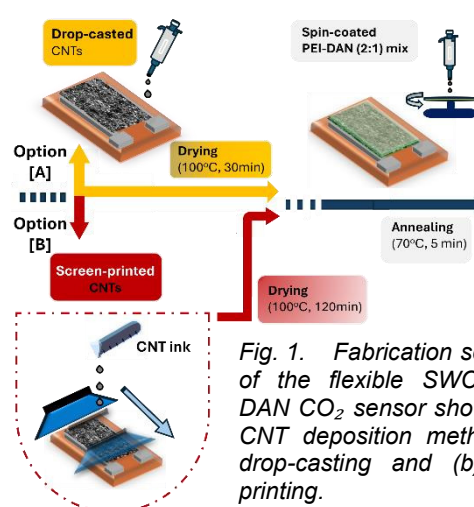


Fig. 1. Fabrication schematic of the flexible SWCNT/PEI-DAN CO₂ sensor showing two CNT deposition methods: (a) drop-casting and (b) screen-printing.

stem [3]. After ethanol evaporation, the semi-dried CNT material was diluted 40× in ethyl cellulose/terpineol binder, screen-printed, and cured at 100 °C for 120 min (Fig. 1).

Mechanism, Characterization and Results

The fabricated sensors were evaluated by testing under varying CO₂ concentrations ranging from 500 to 2500 ppm (RT, RH 50%) and the response was calculated using Equation 1:

$$\Delta R(\%) = \frac{R_f - R_0}{R_0} \times 100\% \quad (1)$$

where R_f denotes sensor resistance in the pre-

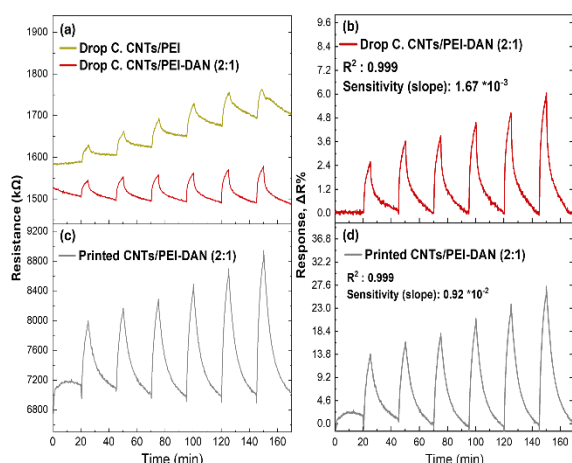


Fig. 2. (a, c) Baseline drift comparison of drop-casted CNT/PEI, CNT/PEI-DAN, and screen-printed CNT/PEI-DAN sensors under six different CO₂ concentrations; (b, d) corresponding response changes of the CNT-based PEI-DAN sensors.

sence and R_0 in the absence of target gas, respectively.

The sensing mechanism of amine-based chemiresistive CO₂ sensors arises from interactions between CO₂ (Lewis acid) and amine groups (Lewis bases) in the PEI-DAN layer [1]. CO₂ diffusion into the polymer leads to amine protonation and formation of bicarbonate species under humid conditions (Eq. 2), decreasing SWCNT conductivity (sensing signal). The reversible reaction enables room-temperature operation and recovery upon CO₂ desorption:



As shown in Fig. 2a,c, baseline drift is significantly reduced after DAN addition. In contrast, the CNT/PEI sensor exhibits drift due to partial poisoning and humidity-induced swelling of PEI during adsorption-desorption cycles. The improvement is attributed to π - π interactions between DAN and CNTs, which stabilize the sensing layer, reduce moisture sensitivity [2], and limit bicarbonate trapping, leading to near-complete recovery after CO₂ removal.

Consequently, the sensor shows a 6.04% response at 2500 ppm (50% RH) with a sensitivity of $1.68 \times 10^{-3} \text{ ppm}^{-1}$. Screen-printed CNT sensors yield a higher response of 27.36% at 2000 ppm and a sensitivity of $0.92 \times 10^{-2} \text{ ppm}^{-1}$ (Fig. 2b,d). This enhancement is attributed to a more uniform and interconnected CNT network, enabling more homogeneous functionalization, more efficient CO₂ diffusion, and improved charge transport.

SEM images (Fig. 3) reveal clear morphological differences between drop-cast and screen-printed CNT networks, with the latter forming a denser and more interconnected structure. In both cases, PEI deposition leads to inhomogeneous coverage/pore formation.

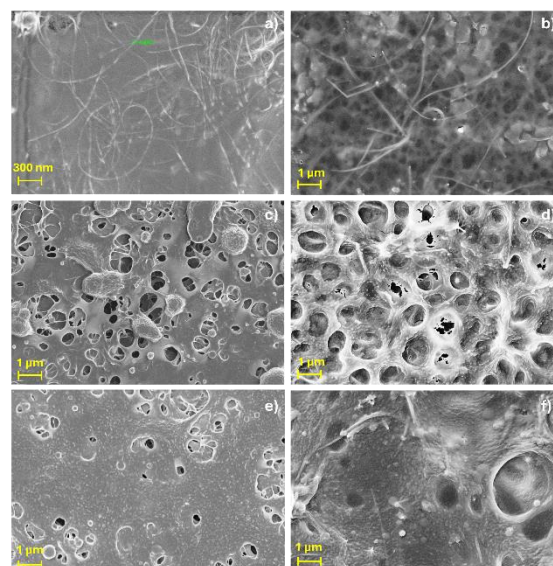


Fig. 3. SEM images of SWCNT-based sensing layers. (a,c,e) Drop-cast CNT networks: (a) pristine CNTs, (c) CNTs functionalized with PEI, and (e) CNTs functionalized with PEI-DAN. (b,d,f) Screen-printed CNT networks: (d) pristine CNTs, (d) CNTs functionalized with PEI, and (f) CNTs functionalized with PEI-DAN.

The addition of DAN results in a more uniform and smoother morphology. This improved organization facilitates more efficient CO₂ adsorption-desorption cycles by limiting trapping and PEI chain swelling, leading to enhanced reversibility and minimal drift.

Conclusion

CNT-based CO₂ sensing is often limited by drift and humidity effects, which also impact highly sensitive PEI-based sensors. Introducing DAN stabilizes the sensing layer through interactions with CNTs, reducing CO₂ trapping and improving reversibility. In addition, screen-printed sensors form a more uniform and interconnected network, leading to enhanced overall performance.

References

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