Interfacial Engineering Strategies for CO_2 Detection in Single-Walled Carbon Nanotubes

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Chemiresistive gas sensors based on adsorption-induced resistance changes are attractive for environmental and industrial monitoring due to their simple structure and low cost. Single-walled carbon nanotubes (SWCNTs) are promising sensing materials because of their high surface area and room-temperature operation[1]. However, detection of weakly redox-active gases such as CO_2 remains challenging, as adsorption induces only limited carrier density modulation.

In this study, we explored two approaches to enhance CO_2 sensing: (i) polymer functionalization with polybenzimidazole (PBI) and (ii) hybridization with Mg-MOF-74 (MOF-74)[2], a metal–organic framework (MOF) with high CO_2 adsorption capacity.

(i) PBI-coated SWCNT (PBI-SWCNT) films were fabricated by solution processing. CO_2 adsorption measurements showed enhanced uptake in the low-pressure region due to interactions between CO_2 and benzimidazole units. Under 100 ppm dry CO_2, pristine SWCNTs exhibited negligible response, whereas PBI-SWCNT showed a resistance increase ($\Delta R/R_0$ = 0.0422%) with a limit of detection of 52.1 ppm. Seebeck coefficient measurements confirmed enhanced hole depletion upon CO_2 adsorption, indicating that PBI introduces effective adsorption sites and improves carrier modulation.

(ii) SWCNT/MOF-74 composite films were synthesized via in situ growth of MOF-74 within the SWCNT network. The composite exhibited 5.2-fold higher CO_2 uptake than pristine SWCNTs and showed a resistance change of $\Delta R/R_0 \approx 0.255\%$ at 100 ppm CO_2. Although the response was slower due to strong CO_2 affinity in MOF-74, simultaneous breakthrough and resistance measurements revealed that resistance changes correlate with CO_2 adsorption dynamics. These results indicate that CO_2 adsorbed in MOF-74 diffuses to the SWCNT interface and modulates carrier density.

Overall, PBI functionalization improves CO_2 sensing under dry conditions, while MOF-74 hybridization dramatically enhances sensitivity. The findings provide mechanistic insight and design guidelines for developing high-sensitivity CNT-based CO_2 sensors.

Reference

(1) V. Schroeder, S. S., M. He, S. Lin, T. M. Swager. *Chem. Rev*. **2019**, *119*, 599.

(2) Z. Bao, L. Yu, Q. Ren, X. Lu, S. Deng. *J. Colloid Interface Sci.* **2011**, *353*, 549.