



A miniature chemiresistor sensor for carbon dioxide



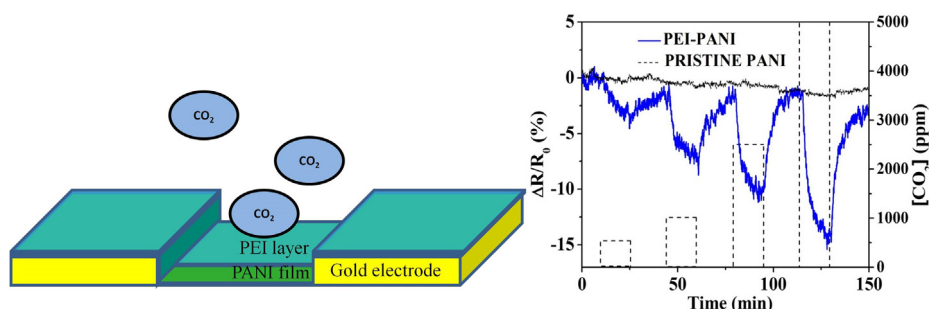
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HIGHLIGHTS

- Poly(ethyleneimine) functionalized polyaniline nanothin film miniature chemiresistor CO₂ sensor.
- Detection by CO₂-amines reactions of acid–base, dissolution and base-catalyzed hydration.
- pH change from acids and carbamates produced and detected by polyaniline nanothin film.
- Sensor was accurate, precise, highly sensitive and selective.
- Suitable for portable multi-analyte breath analysis and environmental monitoring detector.

GRAPHICAL ABSTRACT



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ABSTRACT

A carpet-like nanostructure of polyaniline (PANI) nanothin film functionalized with poly(ethyleneimine), PEI, was used as a miniature chemiresistor sensor for detection of CO₂ at room temperature. Good sensing performance was observed upon exposing the PEI–PANI device to 50–5000 ppm CO₂ in presence of humidity with negligible interference from ammonia, carbon monoxide, methane and nitrogen dioxide. The sensing mechanism relied on acid–base reaction, CO₂ dissolution and amine-catalyzed hydration that yielded carbamates and carbonic acid for a subsequent pH detection. The sensing device showed reliable results in detecting an unknown concentration of CO₂ in air.

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1. Introduction

Growing concerns on environmental conditions have motivated researcher worldwide to focus attention in developing effective methods for environmental monitoring and efficient devices that

run on low-power and are portable for on-site measurement. In particular, CO₂ detection in ambient air has continued to be a challenge due to stability of the compound and interferences from several species, such as nitrogen dioxide (NO₂) and carbon monoxide (CO). Further, a CO₂ sensor can be greatly beneficial to a wide range of applications, including breath and blood analysis for medical diagnosis [1–3], portable gas detector for personal protection and gas monitoring for climate control [4].

Current approaches for CO₂ detection, including spectrophotometry [4,5], solid electrolyte electrochemical sensors [6] and semiconductive metal oxide based sensors [7], are limited by their cost, bulky size or high energy consumption, leaving the

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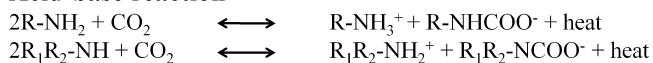
Severinghaus electrode [4,6] as the most prominent option for a miniature sensor. The Severinghaus principle relies on CO₂ dissolution in aqueous electrolyte, generating carbonic acid that can be monitored via a potentiometric pH electrode. The issue regarding the Severinghaus principle concerns base line shift in the Ag/AgCl reference of the pH sensing unit, necessitating a regular maintenance to keep the device well calibrated. Hence, a selective, highly sensitive and low-powered CO₂ sensor with an ability to be installed in a compact area or implemented in a sensor array is still needed.

Following the Severinghaus' approach, certain kind of alkyl amines, such as poly(ethyleneimine) [1,8] and 3-aminopropyltrimethoxysilane [9,10], have been employed as CO₂ recognition layers, producing carbamates [11] and carbonic acid that contribute to the pH change in the amine phase. Depending on types of the amine sorbents (primary, secondary or tertiary) temperature and relative humidity, CO₂ reaction/interaction occurs through three possible paths (Fig. 1): acid–base reaction, dissolution, and base-catalyzed hydration of CO₂ [12].

The primary and secondary amines are favored for the acid–base reaction generating carbamates while the tertiary amine is a preferred catalyst in CO₂ dissolution accelerating carbonic acid formation via the base-catalyzed hydration. When considering reaction rate, the base-catalyzed hydration is slower than the acid–base reaction; however, it captures more CO₂ (1 mol CO₂ per 1 mol amine) and regenerates faster (lower heat of regeneration) in comparison [12]. Thus, a practical/preferred approach is to employ the PEI, containing primary, secondary and tertiary amines, as the CO₂ recognition layer combining advantages and balancing disadvantages from all different amine types. In addition, a branched-structure of the PEI offers steric effect that inhibits acid–base reaction channeling the amines for the base-catalyzed hydration and resulting in a high CO₂ loading capacity and a good amine recovery [12].

Polyaniline (PANI) is an attractive material for sensor applications owing to its excellences in mechanical flexibility, reductant/oxidant reactivity, acid/base sensitivity, and huge range of tunable conductivity (>10 orders of magnitude). When applied for a pH sensing, PANI is induced by acid/base conditions that cause protonation/deprotonation in the polymer chains leading to a reversible transformation between the conductive state emeraldine salt (PANI-ES) and the insulating state emeraldine base (PANI-EB) [13,14]. Our group has previously demonstrated a highly-sensitive chemiresistive gas sensor based on 2-D nanostructure PANI nanothin film [15]. The pristine PANI film device exhibited an excellent sensing performance to NH₃ and NO₂ gases, which was comparable to that of the 1-D nanostructures, as a result of nanometer-thin film and carpet-like surface morphology that helped enhancing the surface reaction. The objective of this work was to fabricate a CO₂ chemiresistor sensor utilizing CO₂ recognition ability of the PEI and pH sensitivity of the PANI

I. Acid-base reaction



II. CO₂ dissolution



III. Base-catalyzed hydration

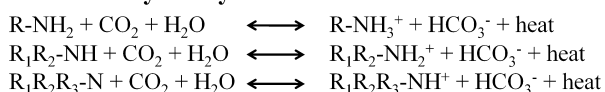


Fig. 1. Paths for amines–CO₂ reactions [12].

nanothin film. The film was electropolymerized on a prefabricated microelectrodes and further functionalized with the PEI via a dip coating technique. The sensing device was employed for CO₂ detection in the operation range of 50–5000 ppm, and also tested against other selected analytes including ammonia (NH₃), methane (CH₄), carbon monoxide (CO), and nitrogen dioxide (NO₂) to investigate cross reactivity, i.e. sensor selectivity. Reliability of the sensor device was validated by comparing a CO₂ in compressor air sensing readout to that of the nondispersive infrared spectrometry (NDIR). The effects of humidity and temperature on CO₂ sensing ability were also studied.

2. Experimental

2.1. Device fabrication

Unless stated otherwise, all compounds were reagent grade and used with no further treatment. All solutions were prepared using deionized water (Milli-Q water), and, if required, were deoxygenated by purging with nitrogen stream. The details regarding PANI nanothin film fabrication and characterization can be referred to our previous work [15]. In brief, the film device was prepared on a pair of gold microelectrodes (100 μm wide × 200 μm long) that was separated by a 3-μm gap. The microelectrodes were defined on heavily doped p-type silicon substrate coated with silicon oxide dielectric layer using standard photolithography. The chip with microelectrodes was cleaned in piranha solution (1.5 mL H₂O₂ + 3.5 mL H₂SO₄), rinsed with deionized water and dried under nitrogen stream. Next, the dried substrate was silanized by incubating in 2% (v/v) octadecyltrichlorosilane (OTS) in toluene, followed by rinsing with fresh toluene and ethanol, sequentially. The purpose of silanization was to functionalize the SiO₂ surface with long hydrocarbon chains making the SiO₂ portion of the substrate highly hydrophobic.

Hydrophobicity of the OTS-silanized substrate helped attracting aniline monomer and enhancing electropolymerization rate of PANI film in lateral direction [16]. Monomer accumulation as a result of hydrophobicity of the substrate was the key to a realization of the nanothin film nanostructure. Next, the chip was placed in a standard electrochemical cell along with Ag/AgCl reference and platinum strip counter electrodes and submerged in the aniline monomer solution (0.5 M aniline + 1 M perchloric acid). The electropolymerization was performed by applying constant potentials of 0.6 V and 0.8 V versus the Ag/AgCl of the two gold electrodes while electrochemical currents were plotted versus operating time creating chronoamperometric curves of the two electrodes. During electropolymerization, chronoamperometric curves bifurcated at a certain point indicating a film bridging across the 3-μm gap channel. The result was a uniform and nanometer-thick PANI film (9–20 nm [15]) with a carpet-like structure (Fig. 2). Functionalization of the PANI with PEI was achieved by dip coating the device in a pH controlled 0.5% (w/v) PEI solution (PEI: *M_w* ~750,000; P3143 FLUKA; pH ~7), followed by low-vacuum drying in a desiccant chamber. After functionalization, a thin layer of PEI was observed under optical microscope as transparent gel on top of the PANI nanothin film.

2.2. Gas detection/sensing

In order to investigate the CO₂ sensing performance of the device, the PEI–PANI nanothin film was mounted into a custom-made gas sensing system that provided a temperature controlled chamber with mass flow controlled gas streams (mass flow controllers, MFCs: Alicat Scientific Inc., AZ, USA). Electrical resistance of each device was acquired via a FieldPoint module (National Instrument, TX, USA) by continually measuring current

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