Sensors and Actuators B 134 (2008) 521–531

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Detection of organic vapors and NH_3(g) using thin-film carbon black–metallophthalocyanine composite chemiresistors

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ARTICLE INFO

Article history:
Received 18 March 2008
Received in revised form 23 May 2008
Accepted 26 May 2008
Available online 12 June 2008

Keywords:
Chemiresistor gas sensors
NH_3
Metallophthalocyanine
Electronic nose

ABSTRACT

Thin-film chemiresistive vapor sensors have been fabricated using composites of carbon black (CB) and metallophthalocyanines. The resulting sensors exhibited large, rapid, and reversible relative differential resistance changes upon exposure to a series of test organic vapors. The individual sensor responses, and collective sensor array properties for classification of a series of test organic vapors, were comparable to those of chemiresistor arrays made from composites of conductors and insulating organic polymers. In addition to displaying resistance responses to volatile organic compounds, the CB/metallophthalocyanine composite sensors exhibited a high sensitivity towards trace levels of NH_3(g) under ambient temperature and pressure conditions. No degradation in sensor response was observed after nearly 12 h of repeated exposure to 30 parts per million of NH_3(g) in air. Chemiresistors formed from composites of CB and zinc phthalocyanines demonstrated responses that were comparable to those of commercial NH_3(g) sensors. The CB/metallophthalocyanine composites thus broaden the types of materials that can be used for this type of low-power chemiresistive gas sensing, and broaden the types of analytes that can be sensitively detected to include inorganic gases as well as organic vapors.

1. Introduction

Chemiresistive materials have been used as detectors for gaseous analytes for several decades [1]. A principal advantage that chemiresistors have is their comparatively simple and compact design. In their simplest form, chemiresistive sensing systems are naturally low power (0.1–1 mW) [2] devices aptly suited for miniaturization and portability [3,4]. Our laboratory has focused on the development and implementation of low power, inexpensive chemiresistive materials. We have previously reported on composite chemiresistive thin films comprised of insulating organic material and electronically conductive carbon black that function as vapor detectors under ambient conditions [5–8]. Chemiresistive films composed of carbon black and insulating polymers (CB/IP) operate via a volumetric sensing modality, i.e. concomitant analyte(s) absorption and volumetric-expansion render a reversible change in total DC film resistance [6]. For carbon black loadings above the percolation threshold [9], the observed resistance changes are proportional to the volume of absorbed analyte [10]. Accordingly, these composite materials generally exhibit excellent sensor response characteristics towards organic vapors at low absolute concentrations, readily allowing the detection, identification, and discrimination of chemical warfare agent simulants and trace vapor signatures of explosives [7,11].

A constraint of volumetric signal transduction is the inverse dependence of the detector sensitivity on the vapor pressure, P^0, of the gaseous analyte of interest [12,13]

$$K = \frac{1000\rho RT}{\gamma M P^0} \tag{1}$$

where K is the partition coefficient of the gaseous analyte into the sensor material, T is the system temperature, ρ is the sensor material density (g cm^{-3}), R is the ideal gas constant (atm mol^{-1} dm^3 K^{-1}), γ is the activity coefficient of the analyte within the sensor material, and M is the molar mass of the analyte (mol dm^{-3}). For analytes with high-vapor pressures ($P^0 > 1$ atm), low absolute vapor concentrations will consequently generate small signals, because the equilibrium driving force favors keeping the analyte largely in the gas phase rather than in the solid phase. Hence, these sorption-based chemiresistors are relatively

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doi:10.1016/j.snb.2008.05.047

insensitive to extremely low absolute concentrations of inorganic gases. Many toxic inorganic gases, e.g. Cl_2, HCN, SO_2, NO_2, and NH_3, are hazardous even at trace (parts per million, ppm) concentrations [14,15], so an ongoing effort in our group is to increase the sensitivity of composite chemiresistors films without sacrificing their inherent low-power consumption, thereby increasing the sensing capacity without compromising the utility of these chemiresistor arrays.

We have previously demonstrated that specific chemical interactions between the analyte and insulating organic material can improve certain responses the sensors. For example, the sensitivity of carbon black-polyethyleneimine sensors towards carboxylic acid vapors is 10^3 times larger than that of other carbon black-polymer composite chemiresistive thin films [16,17]. We have recently described functional composite chemiresistors that consist of carbon black and non-polymeric organic (CB/NPOM) materials [18,19]. Non-polymeric organic materials allow a greater density of chemical functional groups relative to that in a comparable functionalized polymer. Further, CB/NPOM sensors are not limited in composition by materials that are solely available as polymers [18]. Hence, one potential approach for increasing the sensitivity of composite chemiresistive thin films towards inorganic gases is to choose a non-polymeric insulating material that has strong interaction with the gaseous analyte.

Organometallic compounds have often been used as sensor materials for the detection of gaseous analytes [20–24] and are thus an interesting class of materials for the sorptive fraction of CB/NPOM sensors. In particular, the conductance of crystalline metallophthalocyanine films can be particularly sensitive to reducing and oxidizing gases [23,25–29]. The modulation of the electrical properties of these materials by exposure to oxidizing or reducing gases is known to arise from their semiconductor behavior [30–32]. While neat metallophthalocyanine thin films can, under controlled conditions, function as responsive chemiresistors, they have important operational drawbacks as standalone sensors. Metallophthalocyanines generally require both a high temperature (80–170 °C) [33] as well as a large applied electric field to function as chemiresistors [22]. Further, metallophthalocyanine sensors are generally insensitive towards common organic vapors [22].

In this work, we describe the use of metallophthalocyanine-based CB/NPOM sensors for the analysis of gaseous analytes under ambient operating conditions. With this sensor design, we demonstrate that metallophthalocyanine-based CB/NPOM sensors can function as conventional sorption chemiresistors for the detection and discrimination of various organic vapors. Importantly, this same array of sensors, under the same operating conditions (i.e. no field effect conductivity or elevated temperature), can also identify and detect low levels of an inorganic gas. We demonstrate that metallophthalocyanine CB/NPOM sensors can respond to trace levels of $NH_3(g)$ ($P^0 = 8.69$ atm at $T = 25\,^\circ C$), i.e. levels below the 8 h recommended permissible exposure level, PEL, of $NH_3(g)$ [34]. The more sensitive metallophthalocyanine CB/NPOM sensors showed no reduction in response after nearly 12 h of periodic exposure to 30 ppm of $NH_3(g)$ in air, with a signal-to-noise ratio of ~300:1. We highlight the pertinent features of the metallophthalocyanine CB/NPOM signal transduction modes, demonstrating that these sensors are capable of both volumetric expansion and adsorptive conductance changes because the carbon black fraction, rather than the metallophthalocyanine fraction, supports the film conductance. The findings reported here expand the potential applications for inexpensive composite thin-film chemiresistor arrays.

2. Experimental

2.1. Sensor preparation

Sensor films were spray cast from suspensions that contained Black Pearls 2000 carbon black (Cabot Co.), and the desired nonconductive component of the composite (Table 1). The solvent was 50 ml of tetrahydrofuran (THF, reagent grade, EM Science). After preparation, the suspensions were sonicated for 2 h and then immediately used for fabrication of sensor films. The weight fractions of CB used for the CB/metallophthalocyanine sensors were chosen based upon prior optimization of signal-to-noise and response linearity of related CB/NPOM chemiresistive films [18].

Substrates for the sensors were prepared by sequentially evaporating 20 nm of Cr, followed by 70 nm of Au, onto masked glass slides. The Cr underlayer was necessary to improve the adhesion of the Au film to the glass substrate. This process produced two metallic electrodes, separated by a 0.2 cm gap, on each slide. The sensor films were spray cast onto the substrates using an airbrush (CM-C Plus, Iwata Inc.) that was connected to filtered laboratory air, pressurized at 1 atm [35]. The composite suspension was sprayed through a 0.3 cm long × 0.45 cm wide mask until a nominal resistance of 5 kΩ was measured between the electrodes. Following preparation, the sensors were dried under vacuum (~10^{-1} Torr) for at least 30 min and/or presented with 200 exposures (60 s background; 80 s hexane; 70 s background purge) of hexane at $P/P^0 = 0.0050$. This preconditioning was not necessary for sensor activity but did eliminate spurious initial sensor variability.

Table 1
Sorption materials used in CB/NPOM and CB/polymer composite sensors[a,b]

Sensor material	Abbreviation	Source	Amount (mg)[c]	
			Sorbent	CB
Phthalocyanine	H_2Pc	Fluka	30	90
Co(II) phthalocyanine	CoPc	Fluka	30	90
Cu(II) phthalocyanine	CuPc	Aldrich	30	90
Fe(II) phthalocyanine	FePc	Strem	30	90
Sn(II) phthalocyanine	SnPc	Aldrich	30	90
Zn(II) phthalocyanine	ZnPc	Aldrich	30	90
Zn(II) tetranitrophthalocyanine	ZnPc-*t*-NO_2	Aldrich	30	90
Zn(II) 2,9,16,23-tetra-tert-butyl-29H,31 H-phthalocyanine	ZnPc-*t*-tb	Aldrich	30	90
Zn(II) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine	ZnPc-*op*-OC_8	Aldrich	30	90
Cu(II) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine	CuPc-*op*-OC_8	Aldrich	30	90
Tetracosane	Tetracosane	Aldrich	30	90
Poly(ethylene-co-vinyl acetate)[d]	PEVA	Polymer science	72	48

[a] As-received Black Pearls 2000 carbon black (CB).
[b] In 50 ml of tetrahydrofuran (THF).
[c] The values denote the composition of each suspension used for sensor preparation.
[d] 18 wt.% acetate.