Chapter 8
A Novel Organic/MWCNTs Semiconductor Composite for Resistive Gas Sensors

F. Fontana, T. Caronna, N. Donato, M. Latino, A. Bonavita, G. Rizzo and G. Neri

Abstract The synthesis, electrical and sensing properties of 7,8-diazabenzo [*ghi*]perylene (DABP) mixed with multi-walled carbon nanotubes (MWCNTs) have been reported. DABP was synthesized through a photochemical reaction approach and resulted suitable for solution processing, allowing the easy deposition of films on the sensor substrate. Thin films of DABP/MWCNTs composites have shown an electrical behavior depending on the carbon nanotubes loading. Sensing properties of resistive devices fabricated using DABP/MWCNTs semiconducting composites have revealed a high and fast response to relative humidity and vapor of protonated organic solvents.

8.1 Introduction

The preparation of organic materials stable in air, solution-processable and with suitable electrical conductivity, is a fundamental step in organic electronics. Organic materials based on π-conjugated molecules are intensively studied

F. Fontana (✉) · T. Caronna
Department of Industrial Engineering, University of Bergamo, Bergamo, Italy
e-mail: fontana@unibg.it

N. Donato
Department of Matter Physics and Electronics Engineering, University of Messina, Messina, Italy

M. Latino
Department of Chemical Science and Technologies, University of Rome Tor Vergata, Rome, Italy

A. Bonavita · G. Rizzo · G. Neri
Department of Industrial Chemistry and Materials Engineering, University of Messina, Messina, Italy

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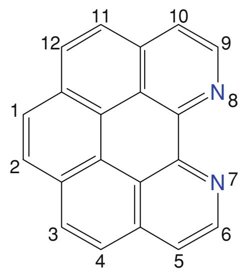

Fig. 8.1 Molecular structure of 7,8-diazabenzo[*ghi*]perylene (DABP)

nowadays in the field of organic semiconductors as a complement to the shortcomings of inorganic semiconductors [1, 2]. Organic semiconductors offer, with respect to current inorganic-based technology, greater substrate compatibility, device processability, flexibility, large area coverage, and reduced cost.

In the framework of our recent interest towards new π-electron organic systems for sensing applications, we have focused the attention on the synthesis of aza-helicenes (with 5 or 6 or even more orthocondensed benzenic or pyridinic rings) and aza-perylenes (with 5 benzenic or pyridinic peripheric rings). These organic molecules appear very promising for gas sensing, due to the presence of a reactive nitrogen functionality on the pyridinic ring, which could be able to interact reversibly with specific gases. Most important, the possible existence of a charge transfer might considerably alter the electronic structure of the conduction channels in the highly conjugated molecule system, modifying as a consequence the transport properties making them very attractive for fabricating resistive chemosensors. In particular, in this study we report data obtained in the investigation of the electrical and sensing properties of 7,8-diazabenzo[*ghi*]perylene (DABP).

8.2 Experimental

The molecular structure of DABP is shown in Fig. 8.1. DABP was synthesized through a photochemical reaction carried out in two steps, as reported elsewhere [3].

DABP is a dark orange solid material with high melting point (226–234°C), and results stable in air. It shows moreover a good solubility in many organic solvents, allowing to prepare processable solutions for thin films deposition. However, notwithstanding the large conjugation, the conductivity of DABP is low, and not suitable for the application in chemoresistive sensors. Therefore the organic material was mixed with a suitable amount of multi-walled carbon nanotubes (MWCNTs), in order to enhance the conductivity of the sensing film.

The composite sensor was fabricated depositing by drop-coating from dichloroethane solution thin films of DABP/MWCNTs on an alumina substrate provided with interdigited electrodes. The sensor was preliminarly conditioned in air for 2 h at room temperature. Electrical tests were carried out at room temperature (25°C). *I*/*V* curves were acquired by means of a Keithley 2400 source meter. The sensing tests were carried out in a home-made apparatus. The relative humidity (RH) and

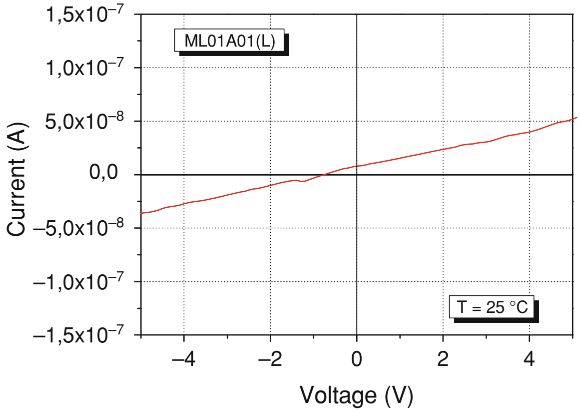

Fig. 8.2 *I*/*V* characteristics of a DABP/MWCNTs composite film

organic vapours were generated by using a bubbler connected to a mass flow control system, in order to vary their concentration.

8.3 Results and Discussion

8.3.1 Electrical Properties

Electrical properties of the pure DABP film and DABP/MWCNTs composite films with different carbon nanotubes loading, were studied in order to evaluate the effect of the amount of CNTs on the films conductivity.

Figure 8.2 shows the output currents of a DABP/MWCNTs composite film at room temperature as a function of input bias. While the output signal of the pure DABP film is not readable due to its very low conductivity, we noted that the output signal is remarkably amplified with the addition of carbon nanotubes, thus indicating the improvement in conductivity of the active layer. Specifically, current level increases with increasing CNTs loading, likely due to electron transfer from carbon nanotubes to DABP, thus increasing the electron density in the conduction band of the organic molecule. The dependence of conductivity on the CNT content in the composites is in agreement with previously reported results of polymer/CNT composites in which the conductivity exhibits a percolation behavior [4].

8.3.2 Sensing Tests

First, the effect of humidity on the electrical characteristics of the DABP/MWCNTs composite was investigated. A strong variation of current with humidity change was observed, suggesting that the sensor can be used as resistive sensor for

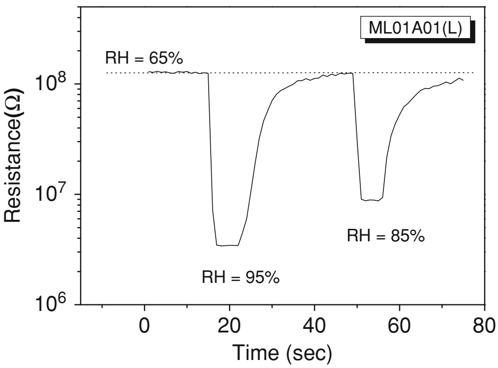

Fig. 8.3 Transient response of the composite sensor to different relative humidity variations

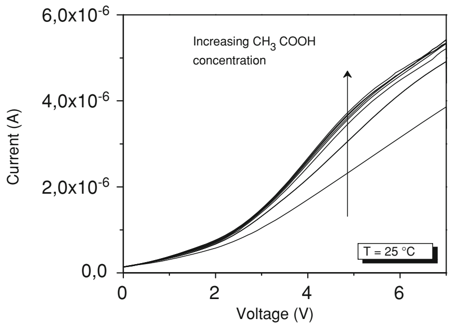

Fig. 8.4 *I*/*V* characteristics of DABP/MWCNTs composite film-based sensor at different acetic acid concentrations

monitoring relative humidity. Experiments have also shown that no significant variations of currents occurs on devices based only on DABP or MWCNTs, confirming that changes observed on the composite sensor are due to the synergic action between carbon nanotubes and the organic material.

The transient response of the composite sensor to different RH variations is reported in Fig. 8.3. It can be noted a strong decreases of resistance as the relative humidity value increase. Moreover, the response is well reversible, exhibiting a fast response/recovery time.

According to other authors [5], we explained this behaviour assuming that DABP manifests a strong affinity for protons. The electron transferring (hopping) assisted by the presence of a proton trap such as the heterocyclic nitrogen may be considered responsible of the resistance variations observed in humid ambient.

To support the above hypothesis, experiments aimed to investigate the effect of gases of different chemical nature (e.g. cyclohexane and acetic acid) have been carried out. The results of the tests have shown that the DABP/MWCNTs composite film-based sensor displays large variations of the electrical resistance with varying the concentration of acetic acid (Fig. 8.4).

No significant variations were instead observed when cyclohexane vapours contacted the sensor, confirming the formulated hypothesis.

8.4 Conclusion

A novel composite based on a diaza-perylene organic material mixed with MWCNTs has been developed, having the potentiality for selective gas sensing. The sensing mechanism has been investigated and electrical and sensing data acquired have indicated that the proton affinity of the nitrogen functionality of the organic material is the main factor influencing the sensor response. In a more general perspective, the interesting electrical characteristics here reported, in conjunction with the peculiar chemical properties, suggest them as attractive candidates for their investigation in chemo-selective gas sensors.

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