

Chapter 12

Nanocomposites for Novel Sensing Systems

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Abstract The work performed under the National Research Program of Latvia and presented here is about advanced, chemical stimuli responsive materials. Sensor materials are produced on the basis of metallophthalocyanines or zirconia nanocrystals with the purpose of detecting small size molecular compounds like NH_3 , O_2 and O_3 . Polymer/nanostructured carbon composite is produced to detect large size molecular compounds like organic vapour. Basic gaseous compound sensing principles are discussed within this paper.

Keywords Organic semiconductors • Polymer/carbon nanocomposite • Zirconia nanocrystals • Gas sensors • Chemical vapor sensors

12.1 Introduction

The main goal of the National Research Program of Latvia “Development of novel multifunctional materials, signal processing and information technologies for competitive knowledge-based products” is the creation of the necessary pre-requisites for development of knowledge-based advanced products – nanomaterials, nanocomposites and a new generation of specific composites. The objectives for implementation of the program include the development of advanced functional materials for nanoelectronics, microelectronics, photonics and for various applications in biomedicine. Among these tasks the studies of novel sensing systems of gases and chemical

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vapors are of great importance. In this paper, three sensing systems based on polymer nanocomposites, zirconia oxide nanocrystals and thin metal phthalocyanine for oxygen and ammonia gasses and chemical vapors are presented.

12.2 A Phthalocyanine-Based Heterojunction for Ammonia Sensing

Nowadays, thin films of organic materials having semiconducting properties are being extensively studied due to the very promising applications in organic electronics [1, 2]. Among organic semiconductors (OS), the metallophthalocyanines (MPc), thanks to their processability, stability and rich substitution chemistry are one of the best candidates in designing novel molecular electronic devices.

Experimental data concerning the changes in the current-voltage (I-V) behavior of a molecular material-based heterojunction consisting of hexadecafluorinated nickel phthalocyanine ($\text{Ni}(\text{F}_{16}\text{Pc})$) and nickel phthalocyanine (NiPc), ($\text{Au}|\text{Ni}(\text{F}_{16}\text{Pc})|\text{NiPc}|\text{Al}$) in the presence of ammonia (NH_3) vapors have been presented as an unprecedented principle of transduction for gas sensing performances. This work introduces a structure made from both p- and n-type semiconducting materials in a heterojunction diode configuration, namely unsubstituted NiPc and $\text{Ni}(\text{F}_{16}\text{Pc})$ ($\text{Au}|\text{Ni}(\text{F}_{16}\text{Pc})|\text{NiPc}|\text{Al}$) as a device based on organic materials able to be used in ammonia sensing applications [3]. In agreement with its p-type semiconductivity, NiPc undergoes a decrease in current transport after being subjected to electron donor atmospheres as NH_3 , the contrary effect that electron acceptor agents as O_3 provoke [4, 5].

For the construction of the heterojunction sandwich devices, high purity NiPc , purchased from Fluka, and $\text{Ni}(\text{F}_{16}\text{Pc})$ powders, synthesized following the reported processes [6], have been vacuum sublimed at 10^{-6} Torr and 400°C and 450°C over a polycrystalline gold electrode covering a glass substrate. The average thickness of the each organic layer is in range of 400–700 nm. Al as the top electrode in the device has been applied. The device has been prepared so that the $\text{Ni}(\text{F}_{16}\text{Pc})$ layer is fully covered by PcNi layer (see Fig. 12.1a).

The experiments with partly covered $\text{Ni}(\text{F}_{16}\text{Pc})$ layer have shown remarkable changes in the morphology of the layers and non-reversible changes in electrical properties of the device.

The changes in current as a function of voltage $I(U)$ of thin films under streams of N_2 and NH_3 (from 0.015% NH_3 till 0.3% aqueous solution, using N_2 as gas carrier), using N_2 as purging gas between cycles have been measured by Keithley 617 electrometer. The scheme of the experiment is shown in Fig. 12.1b. In order to prevent the presence of water in the experiment, the stream of N_2 and NH_3 was transmitted through container with dry NaOH . The registration of each $I(U)$ characteristic lasted about 20 min.

$I(U)$ curves in N_2 stream of the $\text{Au}|\text{NiPc}|\text{Ni}(\text{F}_{16}\text{Pc})|\text{Al}$ sandwich device are of diode like character with slight rectification effect between the forward and reverse

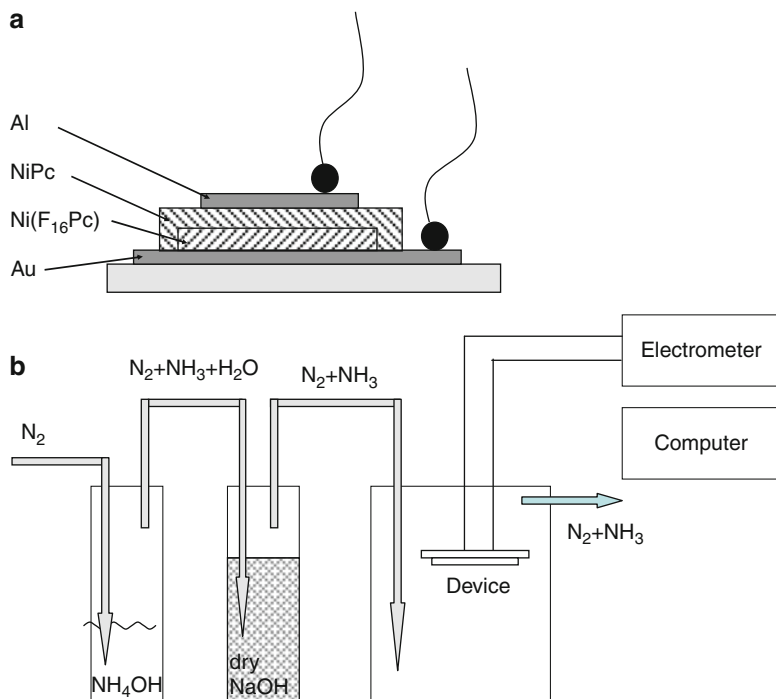


Fig. 12.1 (a) The scheme of the device and (b) scheme of experimental set-up

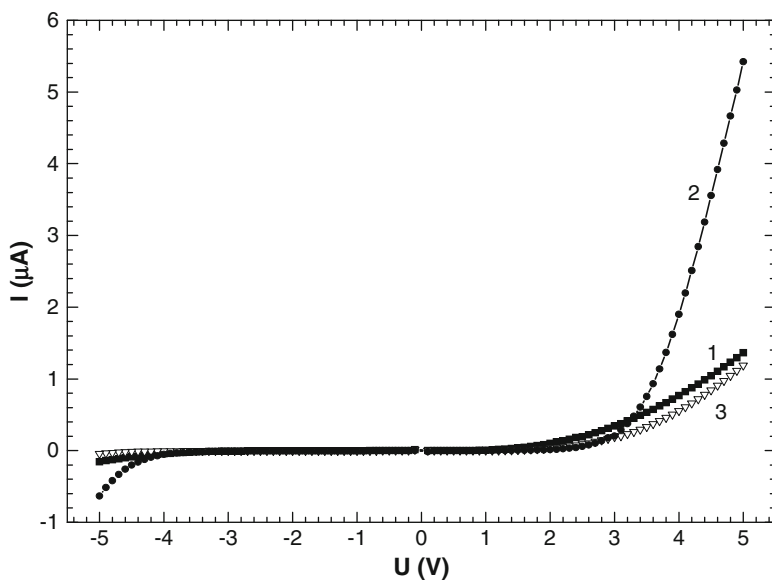


Fig. 12.2 The current-voltage characteristics $I(U)$ of the device in N₂ stream (1), in N₂ stream through 0.3% NH₃ solution (2), in N₂ stream after 24 h of exposition to ammonia (3). Polarity of the voltage corresponds to Au electrode

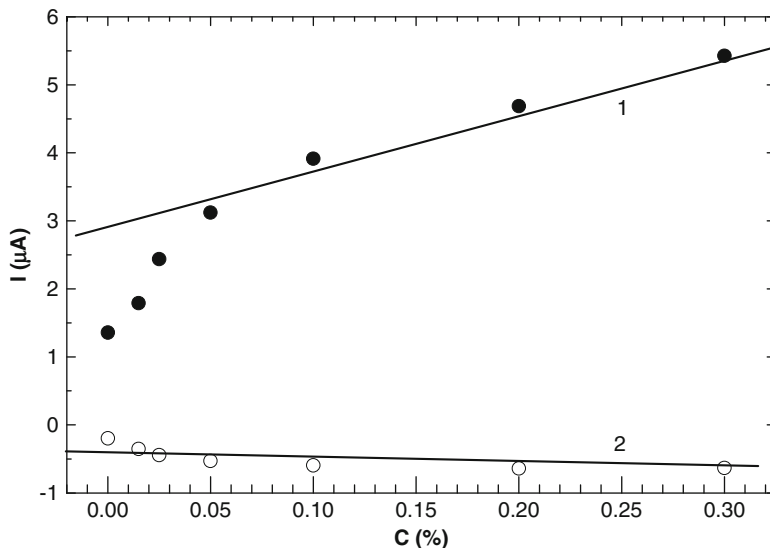


Fig. 12.3 The dependence of the value of the current I at applied voltage $U = +5$ V (I) and $U = -5$ V on the concentration of ammonia solution C

(see Fig. 12.2, curve 1). During the exposition to ammonia vapors the nonlinearity of $I(U)$ characteristics started at lower voltages and effect of the rectification increased from 2.2 to 8.6 at voltage $U = 5$ V (see Fig. 12.2, curve 2). As it is shown in Fig. 12.2, curve 3, the reversibility of the values of current takes place. Unfortunately, after exposition to 0.3% ammonia vapor the reversibility was slow about 24 h.

The dependences of value of the current on concentration of ammonia solution are presented in Fig. 12.3. In range of ammonia concentration from $C = 0.05\%$ till 0.3% the linear dependence of the forward current takes place whereas the reverse current is linear in all studied concentration range.

12.3 The Oxygen Content Sensitive Luminescence of Zirconia Nanocrystals

The development of oxygen sensors is an important problem for today energetics since most of energy is obtained via different burning processes. In its turn, the burning process efficiency strongly depends on the oxygen quantity, therefore, via monitoring oxygen it is possible to realize the control of burning.

The origin of zirconia (ZrO_2) luminescence at room temperature and above is the electron transitions in crystalline lattice defects. The intensity of this luminescence depends on oxygen amount in the material [7, 8]. The exchange of oxygen between zirconia and surrounding gasses takes place at the appropriate temperature.

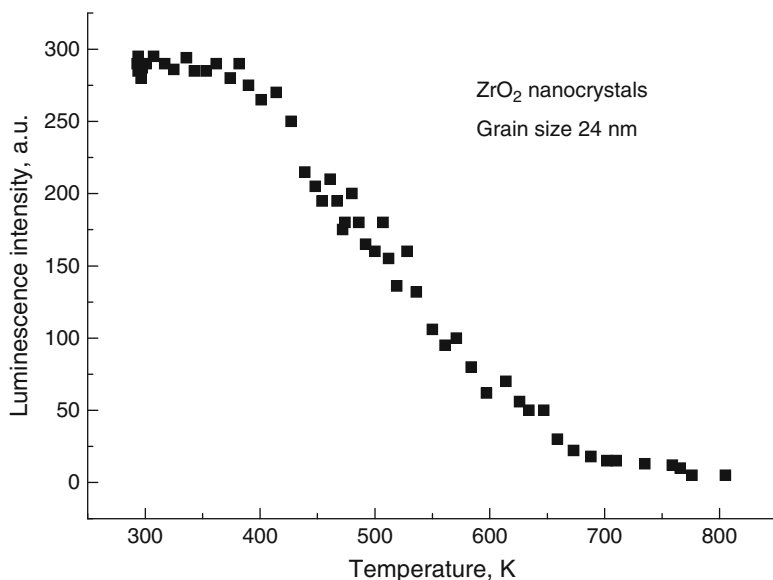


Fig. 12.4 The temperature dependence of zirconia nanocrystals luminescence intensity in the air

Hence the luminescent oxygen sensor could be possible if the oxygen exchange took place at the temperature below luminescence quenching. It has been reported that the luminescence of zirconia is detectable at temperatures [9] up to 540 K and at this temperature the mobility of oxygen is high enough in nanocrystalline zirconia. The experiments carried out have shown that luminescence of zirconia nanocrystals can be measured at least at 650 K (see Fig. 12.4) and somewhat above this temperature. The interaction with surrounding gasses (oxygen exchange) takes place via material surface. The large surface area is more efficient, therefore the nanocrystalline zirconia with grain sizes from 10 up to 120 nm has been used in different experiments.

The oxygen – nitrogen gasses mixtures containing different amounts of oxygen have been experimentally used for determining nanocrystalline zirconia luminescence sensitivity to oxygen. In these experiments the zirconia nanocrystals were slightly pressed into the stainless-steel cell, the cell was placed on the heater, the temperature of the cell was measured by a thermocouple. All the equipment was mounted in the camera with controlled gasses mixture inlet. The camera with optical windows for luminescence excitation and registration was placed in apparatus for luminescence measurements and was used for luminescence spectra and intensity dependence on oxygen concentration registration. The zirconia luminescence band position strongly depends on excitation wavelength [10, 11] if the excitation is within band-gap. Thus, the strongly definite wavelength – the 4-th harmonic of YAG laser (266 nm) – was used for luminescence excitation.

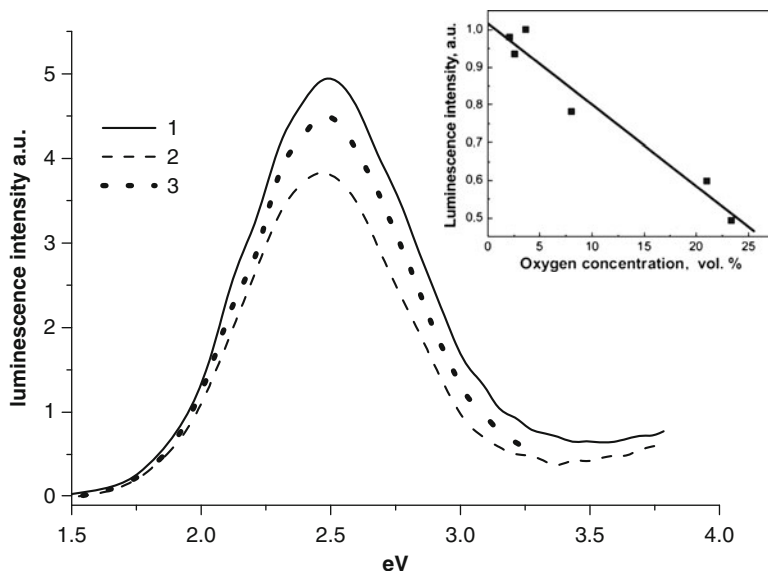


Fig. 12.5 The luminescence spectra of zirconia nanocrystals for different oxygen concentration in surrounding gasses mixture: (1) 5% oxygen; (2) 10% oxygen; (3) 8% oxygen; Inlet – luminescence intensity dependence on oxygen concentration in gasses mixture

The luminescence spectra as well as luminescence intensity dependence for different oxygen concentration in gasses mixture is shown in Fig. 12.5.

The process of reversibility has also been tested – the luminescence intensity has been measured for several cycles' oxygen rich and oxygen poor gasses mixtures in camera and it has been found that the reproducibility of luminescence intensity is good [8], the results scattering is within 6% around the corresponding intensity level.

The other observation has demonstrated that the oxygen exchange between zirconia nanocrystals and gasses mixture takes place even at room temperature. However, the exchange process is slow at room temperature – the stationary level of luminescence is reached within ~40 min.

It is generally known that the nonradiative transitions from luminescence center excited state to ground state are temperature dependent and it is origin for luminescence intensity of any material dependence on temperature. Therefore, an accurate determination of temperature of zirconia nanocrystals used for oxygen sensor is necessary. The luminescence decay time depends on temperature and we propose to exploit this dependence for zirconia nanocrystals temperature measuring using the pulsed excitation of luminescence. The experiment shows that zirconia nanocrystals luminescence decay depends on temperature and this phenomenon is possible to use for temperature determination. The above mentioned results of zirconia nanocrystals luminescence study has led to the conclusion that relative simple oxygen sensor is possible if the pulsed excitation of luminescence is used. The luminescence response

on excitation pulse is also a pulse; the amplitude of this pulse (luminescence intensity) is sensitive to the oxygen concentration and decay time of luminescence pulse is sensitive to the temperature. Thus, within a single measurement both the concentration of oxygen and the temperature of sensing element can be detected [12] due to multifunctionality of zirconia nanocrystals.

12.4 Polymer/Nanostructured Carbon Composites for Application in Volatile Organic Compound (VOC) Detection

12.4.1 Principle of VOC Sensing by Polymer/Nanostructured Carbon Composite

Advanced composites for VOC sensing produced of polymer matrix and nanostructured carbon are described in this chapter. A polymer/nanostructured carbon composite (PNCC) can be produced dispersing electroconductive carbon nanoparticles within an isolator like a polymer matrix. This process is called percolation, when a long-range 3D network of carbon nanoparticles throughout the polymer matrix is formed. As shown by Knite et al. [13], the best PNCC sensitivity is expected above the percolation threshold – a concentration of nanostructured filler, when PNCC electrical resistance significantly decreases. Carbon nanoparticles form an electroconductive 3D network by structuring carbon nanoparticle aggregates into agglomerates within a polymer matrix. It was shown by Balberg [14] that electroconductive contacts between carbon aggregates are indirect – tunneling contacts, where a thin polymer layer exist between particles. It has been demonstrated by Zavickis [15], that in polyisoprene-nanostructured carbon composite (Pi-NCC) 96% of electroconductive contacts between carbon aggregates are tunneling-like and there are only few direct carbon particle contacts. Directly the high extent of tunneling contacts determines Pi-NCC high VOC sensitivity. This is because electrical resistance of PNCC changes exponentially versus thickness of tunneling barrier (polymer layer) [16].

When PNCCs are exposed to VOC, carbon aggregates forming conductive network are withdrawn from each other by VOC induced isolating polymer matrix swelling. Consequently, electrical resistance of the composite increases and the presence of VOC can be detected.

PNCC sensitivity of VOC is primarily determined by PNCC matrix compatibility with VOC. VOC having good compatibility with polymer matrix would cause higher electrical resistance response of PNCC and vice versa. Secondly VOC molecule dimensions determine PNCC sensitivity of VOC as described by Sakale et al. [17].

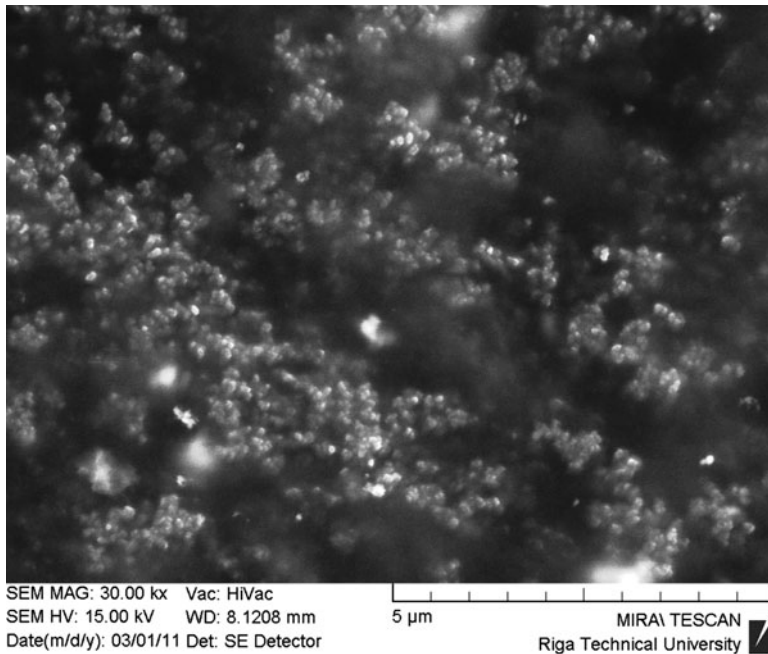


Fig. 12.6 SEM image of Pi-NCC with four parts per hundred rubber carbon nanoparticles taken by Dmitrijs Jakovļevs, Riga Technical University. *Dark grey/cloudy* phase is polymer. *Round particles* are carbon nanostructure formed within the polymer

12.4.2 PNCC VOC Detection

12.4.2.1 Sample Preparation

PNCC samples have been produced by the drop-casting method. Sakale et al. [16, 18] describes the procedure of sample making and sensor material geometrical design in detail. Previously, it has been found that Pi-NCC both sensitivity and response stability greatly influence the filler dispersion method used [16]. It is of essential importance that carbon nanoparticles are homogeneously dispersed and high structured carbon nanostructures within the polymer matrix are formed (Fig. 12.6).

12.4.2.2 VOC Sensing by Pi-NCC

Occupational Safety and Health Administration (OSHA) have determined VOC concentration levels like TWA (time weighted average) and IDLH (immediately dangerous to life and health). TWA indicates the time-weighted average concentration for up to a 10-h workday during a 40-h workweek. TWA concentration level would not cause harmful health effect on employees. IDLH is a concentration

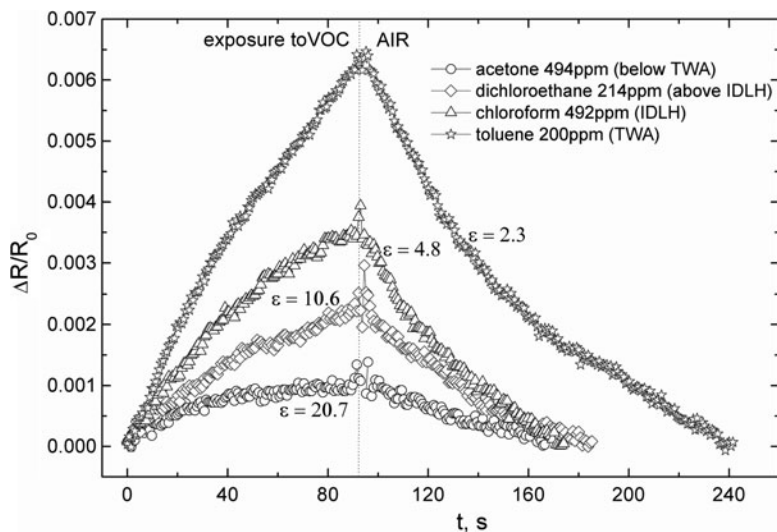


Fig. 12.7 Relative electrical resistance change of Pi-NCC versus time, when sample exposed to different VOC

of VOC; once reached, it would cause significant health problems in people exposed to it.

Pi-NCC electrical resistance response equal to or higher than IDLH level of chloroform and dichloroethane vapour is shown in Fig. 12.7. Pi-NCC capability to detect acetone and toluene vapour at concentrations equal to or smaller than TWA level has been tested as well (see Fig. 12.7). A sample was exposed to vapour for 90 s. As it can be seen from Fig. 12.7, Pi-NCC electrical resistance starts to increase directly at the moment of sample exposition to vapour. In the case of acetone, dichloroethane and chloroform vapour Pi-NCC electrical resistance relaxation time is shorter or equal to the sample exposure time to vapour. Only in the case of toluene vapour relaxation the time is longer than the exposure time.

In Fig. 12.7, dielectric constants of tested VOC are indicated. Dielectric constant (ϵ) of pure polyisoprene is 2.68. The closer is ϵ of VOC to ϵ of pure polyisoprene, the better is vapour compatibility with polymer, and the higher response could be reached by the composite.

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