Synthesis of polyaniline/carbon nanotubes nanocomposites and their sensing properties to methylamine

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Abstract

Novel nanocomposites of polyaniline (PANI) doped by dodecylbenzenesulfonic acid with multi-walled carbon nanotubes (PANI/CNT) were synthesized for methylamine sensing. FTIR and Raman spectroscopy, XRD and TEM methods proved their composition and nanostructure. The gas sensing ability of their thin films (10-30 μm) was investigated at methylamine concentrations from 570 ppb to 10 ppm through the change of the films electrical resistance. The composites showed high performances in terms of reversibility and detection limit. Specifically, the last parameter was below 600 ppb. However, the response times increased drastically when the concentration of the methylamine decreased. At 9.5 ppm concentration the response time was around 10 minutes while it reached 25 min and 80 min at 2.5 ppm and 570 ppb respectively.

Key words: nanocomposites, polyaniline, carbon nanotubes, synthesis, sensing, methylamine

Introduction

Amines are an important family of compounds used in great quantity in industrial process in chemical, pharmaceutical, polymer and rubber industries. They are used as components of some paints, adhesives, textiles as well as in pharmaceutical preparations. Thus, one can find materials with amines in buildings (phonic insulation, furniture), in cars, trains or planes (foams used for seats etc.). Amines can cause cutaneous irritation, respiratory disorder or cancer in some cases and therefore are subject to rules for health and work safety. Methylamine is the simplest primary amine and is used e.g. to produce pharmaceuticals "ephedrine" and "theophylline", the pesticides "carbofuran" and "metham sodium"; solvents N-methylformamide and N-methylpyrrolidone. It is an irritating for the eyes, nose and larynx even for a short duration of exposure at concentration between 20 to 100ppm. Non-published reports relate a case of allergic or chemical bronchitis for workers exposed to methylamine at levels below 10ppm. At the same time it is not classified as carcinogenic [1] and is also a product of decomposition of some food proteins [2]. Nevertheless, this substance is highly toxic; its detection is, therefore, of great importance for the environment. A variety of analytical methods have been developed for this purpose but most of them need expensive and complicate techniques [2,3].

On the other hand, due to a basic nature of methylamine, as well as of other amines, doped conducting polyaniline (PANI) is highly suitable for its detection [4] and can be used in simple and inexpensive electrical resistance schemes. Chemical background of this approach stems from the doped PANI reversible ability to share its acid-dopant with basic substances and, therefore, to decrease its conductivity during this interaction [5]. To the best of our knowledge, application of PANI-based materials to methylamine sensing is not enough developed yet. This motivated us to create solution-processable conducting PANI-carbon nanotube (CNT) composites with a high surface area (due to presence of CNTs) and capable to form thin robust films on interdigitated electrodes due to using a plasticizing dopant dodecylbenzenesulfonic acid (DBSA).

Materials and Methods

PANI/CNT nanocomposites were synthesized through chemical aniline polymerization when using oxidant $(NH_4)_2S_2O_8$ in a presence of multi-walled carbon nanotubes and DBSA in the

reaction water medium with initial aniline concentrations of 20 %, 60 % and 70 %. This procedure resulted in formation of the nanocomposites containing PANI doped with DBSA. By previous tests the PANI/CNT nanocomposite with the intermediate PANI base loading was chosen for the sensing measurements. The polymerization yield analysis, FT-IR and Raman spectroscopy techniques, XRD, transmission and scanning electron microscopy (TEM and SEM) methods were used to study the nanocomposites' composition and morphology.

To prepare sensor devices, ultrasonically treated dispersions of the nanocomposite in chlorobenzene were drop-cast on Au interdigitated electrodes. The thickness of the formed films varied in the range of 10 to 30 micrometers. The sensor device was put in a dynamic exposure chamber, in which the temperature and relative humidity (RH) were controlled for all experiments (T = 25°C and 50% RH). The sensor response was determined in the methylamine concentration range 0.57 ppm-9.5 ppm as a relative variation of the resistance R of the sensor exposed to the methylamine-air gas mixture compared to the initial resistance value R_0: $(R/R_0 - 1) \times 100\%$.

Characterization

The FT-IR spectra confirm a presence PANI-DBSA in the nanocomposites. Specifically they contain typical bands at 2923, 2852, 2360 cm^{-1} of stretching vibrations of aliphatic CH_2, CH_3 groups (DBSA); as well as characteristic vibration modes of PANI: 1570 cm^{-1} and 1465 cm^{-1} (C=C stretching of quinoid and benzenoid rings), 1398 cm^{-1} (C-N^+ stretching), 1285 cm^{-1} (C-N stretching of secondary aromatic amine), 1136 cm^{-1} (–$NH^{+\cdot}$-), 1124 cm^{-1} (C-H bending); 1021, 999 cm^{-1} (SO_3^-); 871 (C-H bending) etc.

The Raman spectra of the nanocomposites contain D and G bands of CNT at 1310 and 1580 cm^{-1} respectively. The bands corresponding to PANI in a doped state can be detected at 1170 and 1260 cm^{-1} (C–H bending of the quinoid and benzenoid rings respect-tively), 1340 cm^{-1} (C-N stretching), 1480 cm^{-1} (C=N stretching vibration) and at 1630 cm^{-1} (C–C stretching of the benzene ring).

The XRD patterns (Fig.1) demonstrate that PANI-DBSA in the PANI/CNT nanocomposite is in almost completely amorphous state. This can be concluded from a broad peak at 2Θ = 19.1º near the CNT's characteristic peak of at 2Θ = 25.85º observed for a nanocomposite (curve 1),

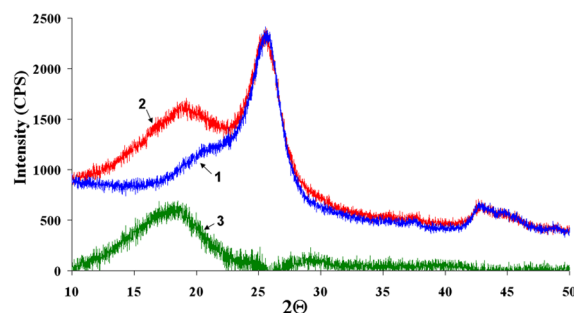and more precisely by the broad peak at 2Θ = 18.4º in the differential spectrum (curve 3).

Fig. 1: XRD patterns of CNT (1), the PANI/CNT nanocomposite and their difference (3) displaying PANI-DBSA input.

Additional weak reflections at 2Θ = 24.5º and 29.5 º can be probably assigned to a small amount of the crystalline phase [6]. The left shoulder at the CNT (002) peak can be assigned to amorphous silica [7].

Microscopy images of the nanocomposites did not display clear difference between PANI and CNT phases. Thus, SEM image in Fig. 2 shows highly porous agglomerated nanoparticle morphology of the PANI/CNT nanocomposite produced at the intermediate 60 wt% concentration of aniline.
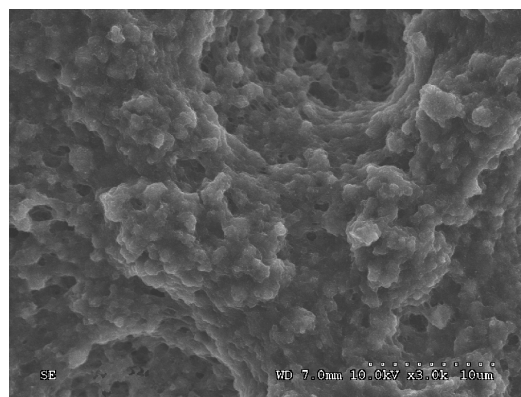

Fig. 2: SEM image of the PANI/CNT composite.

This suggests that CNTs are completely coated with PANI-DBSA nanoparticles and their separate phase cannot be observed. The observed high porosity of the nanocomposite suggests easy accessibility of the sensing clusters for a gas analyte.

Sensing properties of the PANI/CNT nanocomposites

Fig. 3 shows typical response data of the nanocomposite sensors. At a concentration of 4.7 ppm of methylamine the resistance film increases by more than 8% from its initial value after 10 minutes (Fig.3a). The responses are reversible in the sense that the resistance

increases under the methylamine exposure and then decreases when fresh air environment is restored (Fig. 3b).
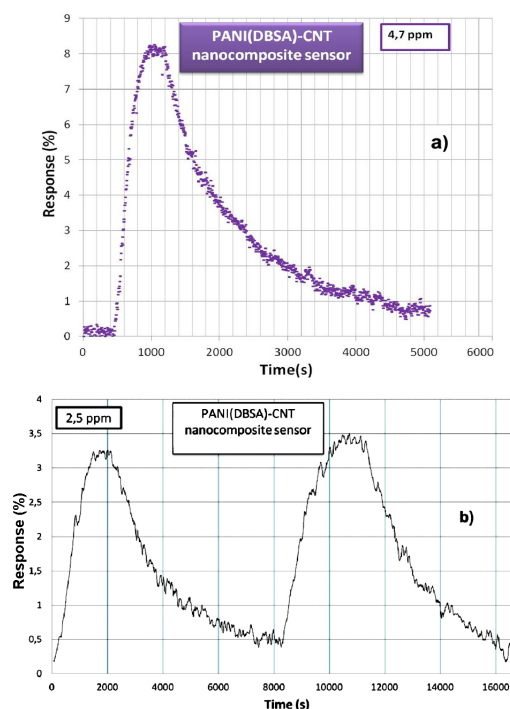

Fig. 3: Sensor responses of the PANI/CNT nanocomposite to methylamine at 4.7 ppm (a) and 2.5 ppm (b).

The composites showed detection limit as low as 570 ppb. However, the response times increased drastically when the concentration of the amine gas decreased 10 min at 9.5 ppm the response time was around while it reached 25 min and 80 min at 2.5 ppm and 570 ppb respectively (Tab. 1). The mechanism of the observed changes can be understood as a deprotonation of the amine groups in the emeraldine salt (PANI-DBSA) converting it to emeraldine base. The deprotonation rate depends on the methylamine concentration leading to a drop of the electrical resistance of the sensor material. As this reaction is reversible, the initial degree of doping of PANI is restored and the sensor returns at its initial resistance when it is exposed to fresh air.

Table 1: Metrological parameters of the PANI-CNT nanocomposite sensor

Concentration (ppm)	Response (%)	Response time (min)
9.5	9.95	10
4.7	8.00	10
2.5	2.75	25
0.57	1.75	80

Conclusions

PANI-CNT nanocomposites were prepared and studied as the sensing layer for an electronic methylamine gas sensor operating at room temperature. Simple methylamine gas sensor devices were constituted of interdigitated gold electrodes patterned on a ceramic substrate and coated with the nanocomposite PANI-CNT films. The sensors had a significant response at methylamine concentration as low as 570 ppb with response time between 10 and 80 min depending on the analyte concentration.

Acknowledgments

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