Sensitive Elements of Gas Sensors Based on Poly-O-Toluidine/Silica Nanoparticles Composite

Yu. Horbenko[a,*], B. Tsizh[b,c], M. Dzeryn[b],
I. Olenych[a], O. Aksimentyeva[a] and V. Bogatyrev[d]

[a]*Ivan Franko National University of Lviv, 6/8 Kyryla & Mefodia str., 79005 Lviv, Ukraine*
[b]*Stepan Gzytsky Lviv National University of Veterinary Medicine and Biotechnologies,*
50 Pekarska str., 79010 Lviv, Ukraine
[c]*Kazimierz Wielki University, 30 Chodkiewicza str., 85-064 Bydgoszcz, Poland*
[d]*O.O. Chuiko Institute of Surface Chemistry NAS of Ukraine,*
17 Henerala Naumova str., 03164 Kyiv, Ukraine

In this work, the thin films of conducting polymer composites of poly-*o*-toluidine with incorporated modified silica nanoparticles on optically transparent substrates were manufactured. The influence of gas vapours (HCl, H_2S, NH_3) on the absorption spectra of the experimental samples was studied. It has been found that only ammonia molecules cause the appearance of an additional optical absorption peak at 610 nm, confirming that the polymer composite can be used as sensitive elements of optical sensors for selective detection of NH_3. In addition, it has been established that the specific surface resistance of the obtained films increases significantly under the action of H_2S and NH_3 gases. The incorporation of the silica nanoparticles provides greater surface area of the sensors and their high sensitivity to toxic gases of different nature.

topics: gas sensor, poly-o-toluidine, silica nanoparticles, optical absorption, resistivity

1. Introduction

Conducting polymers have received considerable interest because of the unique electrical, chemical and physical properties, reasonable price, simple preparation, small dimensions and large surface area. Thus, they have been broadly researched for use in supercapacitors, solar cells, batteries, biochemical applications, electrochromic devices and sensors [1–5]. The use of conductive polymers as a sensitive material in the production of the sensors offers numerous advantages, such as high sensitivity, short response time, room temperature operation, and the possibility of tuning both chemical and physical properties by using different substituents [6, 7]. Combining conducting polymers with other components, especially nanomaterials such as inorganic oxides, due to the synergistic effects, can improve some characteristics, like high electrical conductivity and large surface area [8–10]. Poly-o-toluidine (PoT) is one of the most promising conducting polymers. It is known humidity sensing by PoT/TiO_2 nanocomposite films [11]. It was previously reported that the introduction of modified silica nanoparticles helps to stabilize the resistivity of polyaniline nanocomposites in high humidity

and enhance their sensitivity to hydrogen chloride vapours [12]. In both these cases, *in situ* chemical oxidation polymerization was used, but the electrochemical approach to prepare the new polymer composites can easily control conductivity, compound state, morphology and thickness [13].

The present article focuses on studying properties of nanocomposites based on PoT and modified SiO_2 nanoparticles as sensitive elements for gas sensors. Ammonia is one of the main sources of air pollution released from the decomposition of organic nitrogen-containing materials of animal and plant origin, from industrial effluents and vehicles [14]. Amonia cause burns and swelling in the respiratory tract, damage to the lungs, skin and eyes [15]. Due to the toxic properties of HCl in both gaseous and aqueous forms, there is a great need to detect and establish the concentration of gas particles [16]. H_2S is known as a highly toxic gas with foul odor, which can strongly damage human health, corrode equipment and harm the environment by producing acid rain [17]. Therefore, it is extremely important to detect the lowest concentrations of these harmful gases and control their content in the atmosphere of residential, office and industrial premises.

2. Experimental

Ortho-toluidine (99.5%) was distilled before use. Nanoparticles of SiO_2, modified with phosphorus(III) chloride — grade P-2.1, specific surface area $124 \ m^2/g$, developed at the Chuiko Institute of Surface Chemistry National Academy of Sciences of Ukraine were used as fillers of composites. The technology of their production and properties are described in [18]. Before synthesis of composites, SiO_2 powder (4% by weight) was added to 0.1 M solution of ortho-toluidine in 0.5 M sulfuric acid and sonicated for obtaining homogeneous colloidal dispersion. The solutions were prepared with bi-distilled water.

Thin films of conducting polymer composites of PoT were synthesized electrochemicaly by incorporation of silica nanoparticles on optically transparent substrates under cyclic voltammetric conditions using potentiostat–galvanostat MTech PGP-550M with programmatic control via USB-interface. A double-wall one-compartment cell with a three-electrode configuration was used. A purified and skimmed glass plate, covered with a semiconductor layer SnO_2 (active surface $10 \times 30 \ mm^2$), platinum wire and Ag/AgCl electrodes were used as the working, auxiliary and reference electrode. The films were deposited with 40 or 60 cycles by applying a sequential linear potential scan rate of 50 mV/s between 0 and 1.35 V versus the Ag/AgCl electrode. The resulting polymer films were then washed with distilled water and dried in air at room temperature.

The optical microscopy of the samples was performed on the microscope "Micromed" XS-2610 with a digital camera "Nicon-2500", magnification — 150×. The optical absorption study of all synthesized films was carried out using the Vis-spectrophotometer (KFK-3). All the spectra were recorded in the wavelength range 400–990 nm.

In order to investigate the sensory properties, the obtained thin film elements were kept for a fixed time in a hermetic glass chamber with a volume of $50 \ cm^2$, the required amount of analyte gas was supplied. All tests were performed at 293 ± 1 K. For the resistivity measurement, contacts on the surface of the samples were deposited using a conductive paste Kontaktol Keller (Germany). The resistance during gas vapors influence was controlled with a digital multimeter DT9208A.

3. Results and discussion

Since it is known that SiO_2 particles have a negative surface charge and the PoT chains are polycations, then during electrochemical polymerization of the monomer in the presence of SiO_2, nanoparticles are incorporated to the polymer matrix due the electrostatic attraction force and thus formed the PoT/SiO_2 composite [19]. It was demonstrated that the o-toluidine behaves typically for
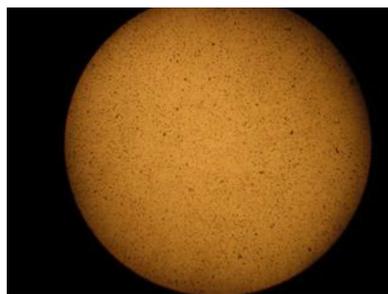

Fig. 1. Photo of the surface of the PoT/SiO_2 film, ×150.

conjugated polymers grown electrochemically and it undergoes oxidation at the potencial ~ 0.60 V vs Ag/AgCl [20]. With increasing number of cycles, the oxidation peak shifted to higher potential values. The cyclic voltammograms for the synthesis of PoT/SiO_2 seem to be identical in shape, but show a slightly higher peak intensity. This effect may be caused by an increase of the total conductivity of the nanocomposite structure due to the large surface area of SiO_2 [21].

The PoT/SiO_2 films obtained on the surface of the conductive glass have a light green color and a homogeneous surface structure. According to optical microscopy, an amorphous–crystalline microstructure of composite films is observed — crystalline PoT/SiO_2 formations, quite uniform distributed in the amorphous polymer matrix (Fig. 1). This developed surface of polymer films determines their ability to adsorb various gases.

The optical absorption spectra of the obtained PoT films are characterized by two bands (Fig. 2). The first peak at $\lambda = 410$–420 nm corresponds to electronic π–π^* transitions in the band gap. The second broad band with a peak at $\lambda = 740$–750 nm is probably the superposition of (i) the band attributed to the n–π^* transition in imino-quinoid structures of polyaminoarenes and (ii) the band caused by absorption of delocalized charge carriers in polaron–bipolaron zone [22]. The incorporation of SiO_2 nanoparticles in the PoT matrix causes significant changes in the intensity of optical absorption. However, the result depends on the thickness of the polymer films, which is regulated by the number of cycles of electrochemical deposition. A decrease in the adsorption values is observed for the thinner composite film in almost whole wavelength range, with the exception of the 420–550 nm region. Increasing the thickness of PoT/SiO_2 causes an increase in the intensity of absorption in the entire wavelength range and a shift of the second peak to 860 nm due to additional doping of polymer.

The influence of gas vapors — HCl, H2S, NH3 — on the PoT/SiO_2 absorption spectra was studied (see Fig. 3). It is established that under the action of HCl vapors there are no changes in the shape of the absorption spectrum and a slight decrease
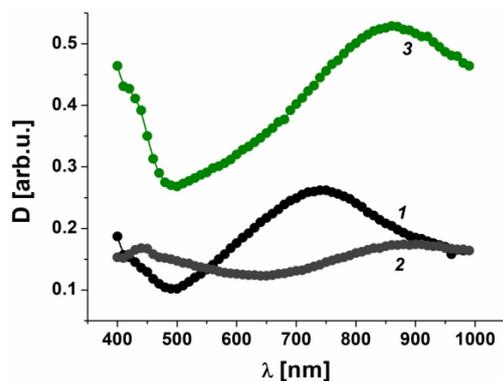
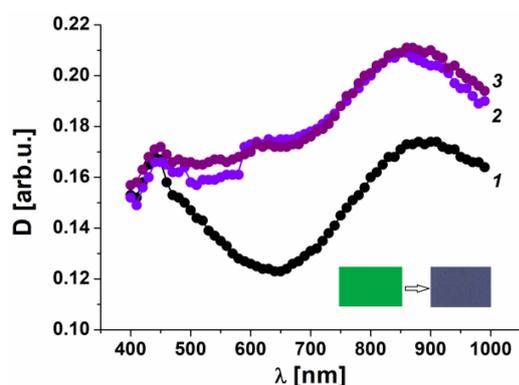Fig. 2. Absorption spectra of films: 1 — PoT, 2 — PoT/SiO$_2$ (40 cycles), 3 — PoT/SiO$_2$ (60 cycles).

Fig. 3. Absorption spectra of films: 1 — PoT/SiO$_2$, upon exposure to ammonia for 2 — 30 s and 3 — 60 s.

Fig. 4. Surface resistance of PoT/SiO$_2$ films upon exposure to (a) ammonia, (b) hydrogen sulfide.

TABLE I

Sensory sensitivity of polymeric films.

Sample	Gas	λ [nm]	τ [s]	$\Delta D/D$ [%]
PoT [23]	NH$_3$	600	600	42.9
PoT/SiO$_2$	NH$_3$	650	30	42.3
	H$_2$S	490	600	18.1
	HCl	490	30	5.9

in absorption is observed in the entire wavelength range. In the case of H$_2$S, the decrease in the absorption intensity in the range of $\lambda = 400$–590 nm and the increase in the absorption intensity in the range of $\lambda = 640$–900 nm are detected. There is also a shift of the second absorption peak from 860 to 840 nm. It has been found that only the ammonia molecules significantly change optical properties of the obtained composites, causing the appearance of an additional optical absorption peak nearby 610 nm. This can be explained by an increase in the percentage of the reduced fragments in the aminoquinone structure of the polymer chain [22] caused by interaction with gas molecules. It should be noted that the composite film changed color from green to purple due to the action of NH$_3$. Thereby PoT/SiO$_2$ films can be used as sensitive elements of optical sensors for selective detection of ammonia.

The sensory sensitivity of the films, calculated at wavelengths corresponding to the maximum sensitivity of the PoT/SiO$_2$ at room temperature, was also determined and compared with pure polymer (Table I). It was found that in the case of ammonia detection, the maximum values of sensory sensitivity for the PoT/SiO$_2$ composite and PoT films almost do no differ. However, the response
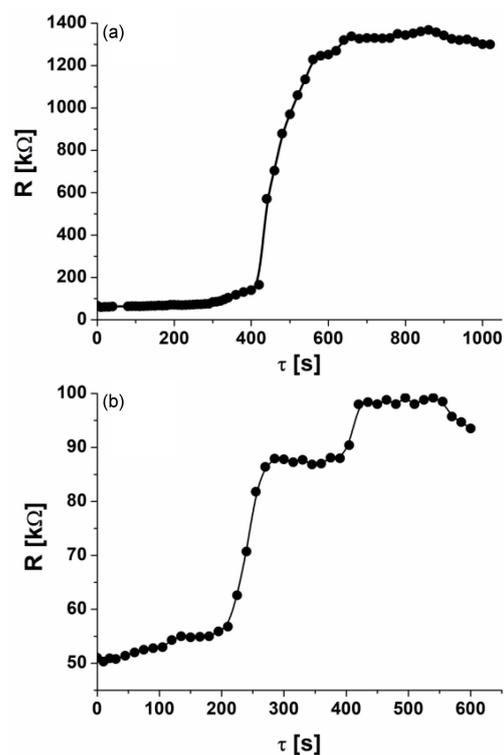
time for PoT/SiO$_2$ is much shorter, which is probably due to the increase in the specific surface area of sensitive films due to the incorporation of silica nanoparticles, and will definitely be an advantage of a composite for use in gas sensor design.

Moreover, it has been established that the specific surface resistance of obtained PoT/SiO$_2$ composite films significantly increases under the action of H$_2$S and NH$_3$ gases, respectively 2 and 26 times (Fig. 4). Such a significant change in resistance is probably due to the combination of gas molecule interactions with polymer via proton exchange mechanism and electron-donating adsorption of gas molecules on the silica surfaces.

4. Conclusions

The electrochemical formation of poly-o-toluidine/modified silica nanocomposite films on an optical transparent substrate was successively performed by cyclic voltammetry. The incorporation of SiO$_2$ nanoparticles causes an increase of

the optical absorption of the polymer and a shift of the second peak towards long wavelengths. The influence of gas vapours — HCl, H_2S, NH_3 — on the PoT/SiO_2 absorption spectra was studied and the sensory sensitivity of composite films were calculated. It has been found that ammonia molecules gave rise to an additional peak of optical absorption of PoT/SiO_2 at 610 nm. It has been revealed experimentally that the adsorption of NH_3 and H_2S molecules significantly increases surface resistance of obtained composites.

The PoT/SiO_2 nanocomposite films exhibit gas sensing properties such as good sensitivity and fast response time. Based on the obtained data, the possibility of using electro-deposited thin films of PoT/SiO_2 in gas sensors production, both optical and resistive, for monitoring the state of environments in real conditions of atmosphere was shown.

References

[1] S.A. Alqarni, M.A. Hussein, A.A. Ganash, A. Khan, *BioNanoScience* **10**, 351 (2020).

[2] L. Luo, W. Huang, C. Yang, J. Zhang, Q. Zhang, *Front. Phys.* **16**, 33500 (2021).

[3] K.R. Reddy, B. Hemavathi, G.R. Balakrishna, A.V. Raghu, S. Naveen, M.V. Shankar, in: *Polymer Composites with Functionalized Nanoparticles*, Eds. K. Pielichowski, T.M. Majka, Elsevier, 2018, p. 357.

[4] H. Palza, P. Zapata, C. Angulo-Pineda, *Materials* **12**, 277 (2019).

[5] S.O. Hacioglu, H.Z. Kaya, Y.A. Udum, L. Toppare, *RSC Smart Mater.* **2019**, 51 (2019).

[6] Y. Wang, A. Liu, *Polym. Int.* **69**, 7 (2020).

[7] R. Song, Z. Wang, X. Zhou, L. Huang, L. Chi, *ChemPlusChem* **84**, 1222 (2019).

[8] R. Arancis, N. Joy, P. Aparna, R. Vijayan, *Polym. Rev.* **54**, 268 (2014).

[9] P. Kunzo, P. Lobotka, E. Kovacova, K. Chrissopoulou, L. Papoutsakis, S.H. Anastasiadis, Z. Krizanova, I. Vávra, *Phys. Status Solidi A* **210**, 2341 (2013).

[10] V. Svitkova, I. Palchetti, *Bioelectrochemistry* **136**, 107590 (2020).

[11] T. Zhou, X. Xie, J. Cai, L. Yin, W. Ruan, *Polym. Bull.* **73**, 621 (2015).

[12] Yu.Yu. Horbenko, B.R. Tsizh, O.I. Aksimentyeva, I.B. Olenych, V.M. Bogatyrev, M.R. Dzeryn, *Sci. Messenger LNUVMB Ser. Food Technol.* **21**, 29 (2019).

[13] O.I. Aksimentyeva, O.I. Konopelnyk, M.Ya. Grytsiv, G.V. Martyniuk, *Funct. Mater.* **11**, 300 (2004).

[14] S. Aarya, Y. Kumar, R. K. Chahota, *J. Inorg. Organomet. Polym. Mat.* **30**, 269 (2019).

[15] R. Cope, *Vet. Toxicol.* **48**, 629 (2018).

[16] S.C.K. Misra, P. Mathur, M. Yadav, M.K. Tiwari, S.C. Garg, P. Tripathi, *Polymer* **45**, 8623 (2004).

[17] Y. Liu, Y. Wang, *Energy & Fuels* **33**, 10812 (2019).

[18] V.M. Bogatyrev, A.A. Chuiko, *Ukr. Chem. J.* **50**, 831 (1984).

[19] A.-N. Chowdhury, M.R. Rahman, D.S. Islam, F.S. Saleh, *J. Appl. Polym. Sci.* **110**, 808 (2008).

[20] E. Ekinci, *Polym. Bull.* **42**, 693 (1999).

[21] A.A. Ganash, N.A. Alhebshi, N.H. Alyoubi, *J. Appl. Electrochem.* **50**, 1019 (2020).

[22] O.I. Konopelnyk, O.I. Aksimentyeva, *Mol. Cryst. Liq. Cryst.* **719**, 19 (2021).

[23] B. Tsyzh, M. Dzeryn, Y. Horbenko, *Sci. Messenger LNUVMB. Ser.: Food Technol.* **19**, 59 (2017).