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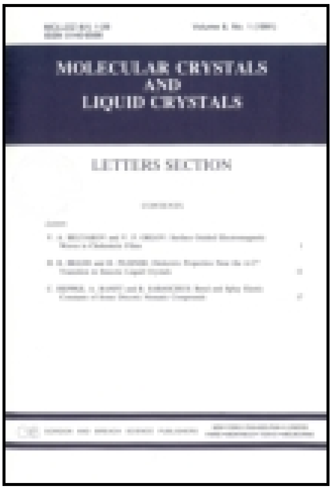

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Effect of Ammonia on Optical Absorption of Polyaniline Films

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Effect of Ammonia on Optical Absorption of Polyaniline Films

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The influence of ammonia on the optical absorption of polyaniline films obtained by the electrochemical method is studied. In the presence of ammonia, the optical spectra of a polymer are found to change due to the appearance of a new absorption band with a maximum at 2.07 eV and a simultaneous decrease in the intensity of bands at 1.57 and 2.91 eV. The kinetics of changes showing the presence of an isobestic point at 2.71 eV is elaborated. The results can be used to optimize the ammonia gas sensors for monitoring the biotechnological processes in the food industry and the environment.

Keywords Polyaniline films; gas sensor; sensitive element; optical absorption.

Introduction

To date, a wide variety of sensor devices and systems to control gas environments have been developed. The films of oxides, as well as various inorganic and organic semiconductors, have been exploited as sensitive elements in these sensors. In recent years, an interest in the use of polymer films [1–19] sensitive to various gases increased due to the better adaptability, easiness of synthesis and use, lower cost, and, in some cases, better performance. Alternatively, despite the successful development and the use of “artificial nose” systems and other gas-sensitive devices, there is a high need in cheap portable sensors for the operational observation of environmental and industrial processes, monitoring the gaseous media in food, especially, control over the freshness of food (meat, fish, dairy, and other products) in the process of the storage and for other purposes. In particular, the loss of freshness (putrefaction damage) of protein-containing food results in the detachment of volatile substances, especially ammonia, due to a degradation of proteins and other nitrogenous compounds. The intensity of detached ammonia corresponds to a level of degradation of proteins, polypeptides, and free amino-acids. Thus, the ammonia concentration is the most accurate reliable criterion of freshness of protein-containing food

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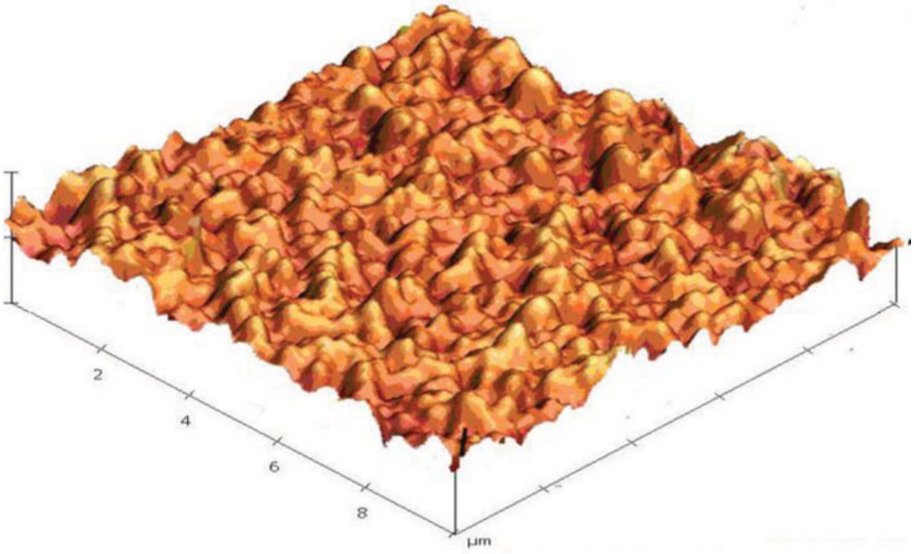

Figure 1. AFM image of the surface morphology for a PANI film obtained on the SnO_2 electrode by the electrodeposition technique. The film thickness is 300 nm.

at various stages of the storage [20]. In this regard, there is an urgent need for simple, reliable, cheap, and accessible sensors of ammonia, and their development is extremely important.

Among a large number of ammonia gas sensors such as semiconductor, chemical, electrochemical, resistive, etc. ones, the optical sensors seem to be the most promising. Whereas, among ammonia-sensitive materials, the organic polymer films of polyaniline (PANI) [1–7,9–14,16–18] are very promising for the optical sensing. At present, the effect of ammonia on the properties of layers of PANI and its derivatives is known, but the detailed behavior was not studied. In particular, the optical properties of PANI films in the presence of ammonia vapor were not investigated enough from the viewpoint of their use in optical gas sensors. This paper presents the results of such studies and shows the fundamental advantages of PANI films as sensitive elements for gas sensors of ammonia.

Experimental

Among the known methods of the deposition of PANI films, such as thermal [12] and electrochemical deposition [4–6,13], dip-, drop-, spin-coating [14–16], Langmuir-Blodgett, and layer-by-layer technique [17,18], vapor deposition polymerization [19], and others [1, 7, 21] to obtain reproducible gas sensitive layers, the electrochemical deposition is a convenient method, because it can effectively control the properties of the films by the process parameters. PANI films were electrochemically deposited from a 0.1 M solution of aniline (monomer) in 0.5-M sulfuric acid at a current density of 0.05–0.20 $mA{\cdot}cm^{-2}$ for 2–10 min, similarly to our previous publications [4–6]. Deposition of PANI films was performed at room temperature in a glass electrochemical cell, in which glass plates ($10 \times 20 \times 0.3$ mm) with a transparent conductive coating (SnO_2) served as a working

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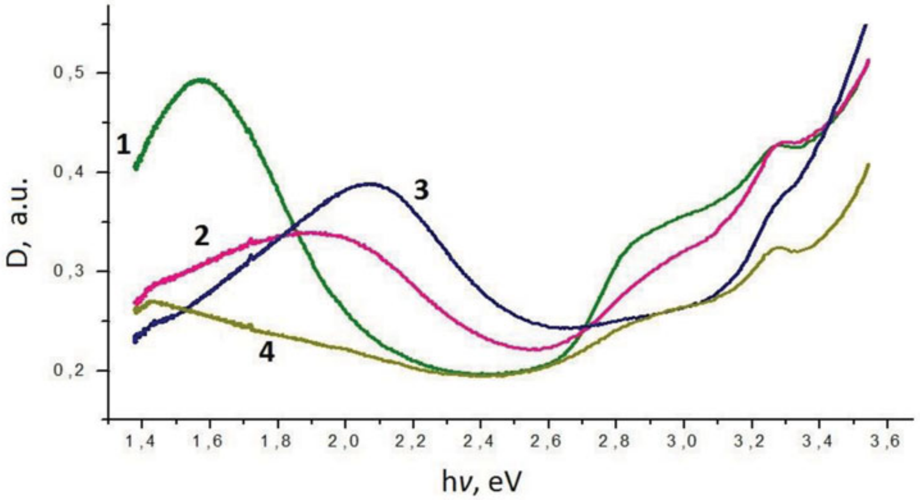

Figure 2. Optical absorption spectra of PANI films before (1) and after the exposure to ammonia for 1 min (2) and 5 min (3) and after the treatment with an acid solution (4). The partial pressure of ammonia, $P_{NH3} = 6.2$ Pa.

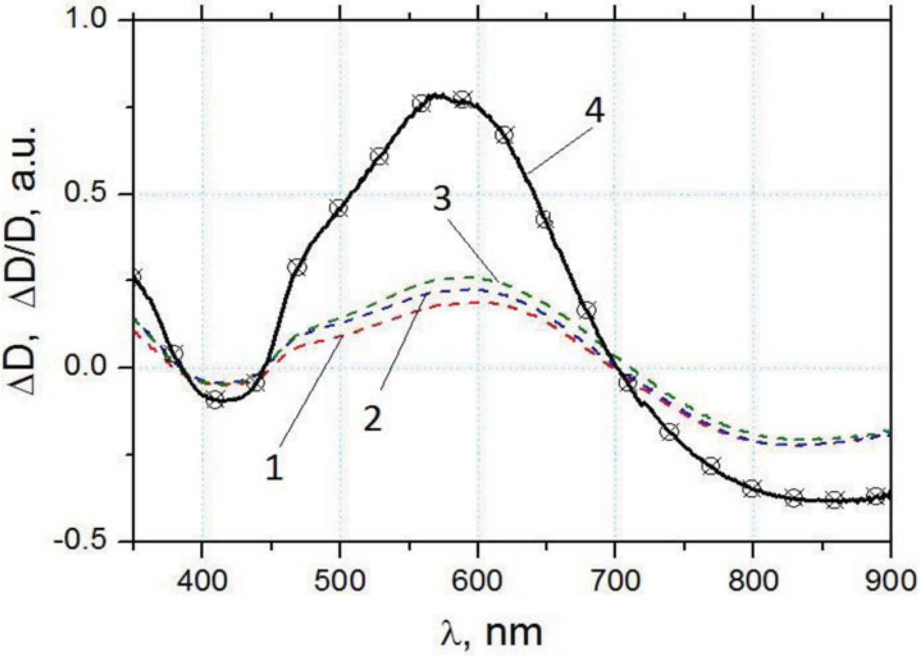

Figure 3. Differential spectra in absolute, ΔD, (1-3) and relative representations, ΔD/D, (4) for changes in the optical absorption of PANI films as a result of the exposure to ammonia for 1 min (1), 2 min (2,4), and 24 min (3).

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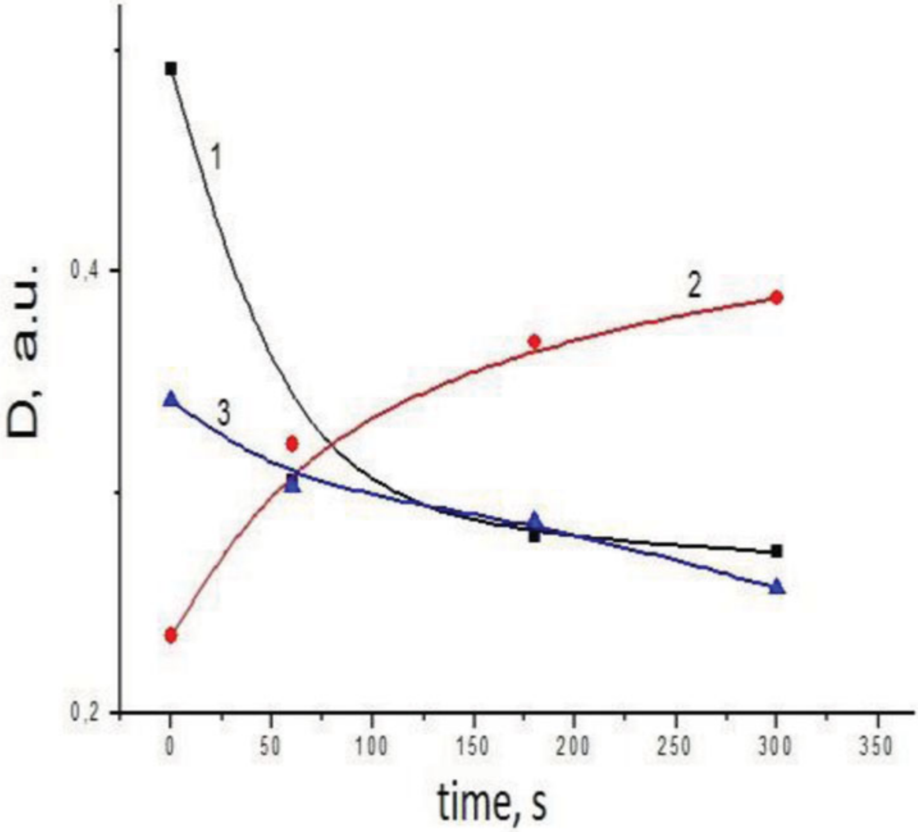

Figure 4. The kinetics of the optical absorption for PANI films on the exposure time to ammonia at 1.57 eV (1) 2.07 eV (2) and 2.91 eV. $P_{NH3} = 6.2$ Pa.

electrode. The antielectrode was a platinum mesh. This deposition technique has allowed us to vary, to a high extent, the composition, topology, thickness, and other parameters of the synthesized layers and to optimize them effectively toward achieving the high stability and the reproducibility for various batches of samples. The recovery of gas sensing in the films has been achieved by the short-time exposure in a 0.5 M aqueous solution of sulfuric acid, rinsing with distilled water and drying in a stream of dry air for 3–5 min. The easiness of this technique allows us to predict its future practical use for the development of reversible gas sensitive elements.

Optical absorption spectra of PANI films were obtained, by using a modified two-beam optical spectrometer Specord M400 applying the following measurement parameters: spectral range −200–900 nm, slit width −1 nm, integration time −1 s, scan step −1 nm, scan speed −10 nm/s. To measure the optical spectra of the films in the ammonia atmosphere, a sealed quartz chamber 50 cm^3 in volume was used, into which the necessary volume of gas (ammonia) was supplied. All measurements were performed at a temperature of 293 ± 1 K. Analysis of the results was performed using the standard correlation program, in which the relative error did not exceed 1.5% in the entire range of measurements.

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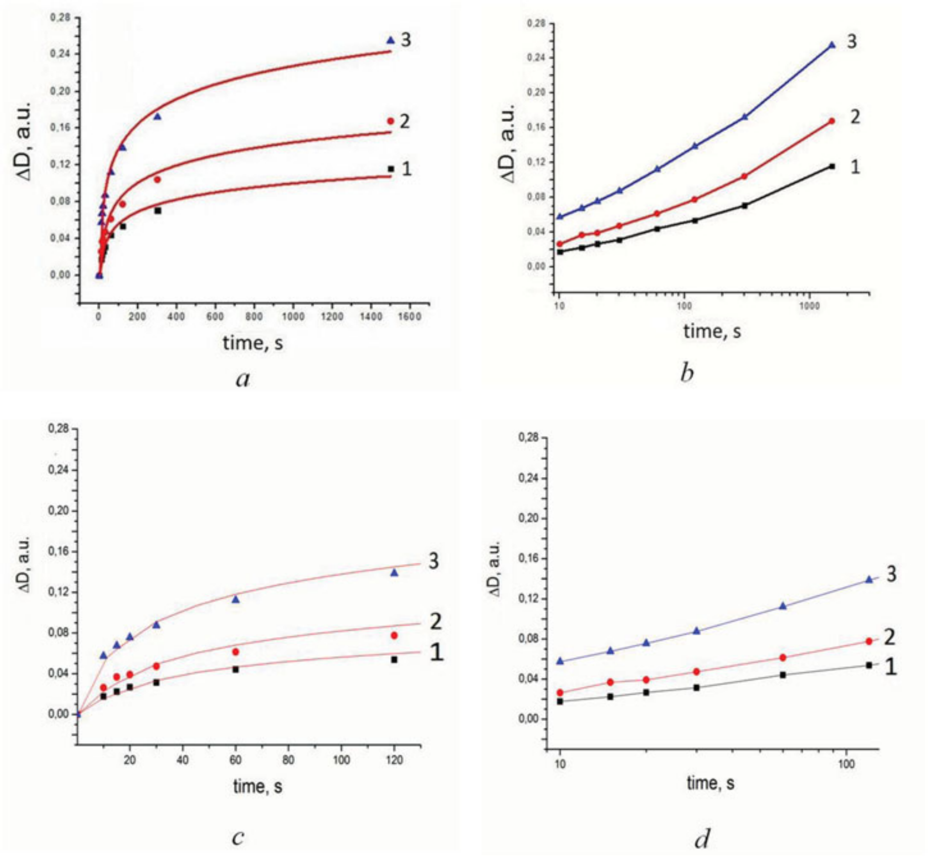

Figure 5. The kinetics of the optical absorption for PANI films on the exposure time to ammonia ($P_{NH3} = 6.2$ Pa) at a wavelength of 570 nm for film thicknesses of 0.4 μm (curve 1), 0.7 μm (curve 2), and 1.3 μm (curve 3) for the time ranges up to 1500 s (a, b) and 300 s (c, d) on the linear (a, d) and logarithmic (b, c) scales.

Results and Discussion

During the electrochemical deposition of PANI films from solutions of monomers in proton acids, a series of physical and chemical processes run. As a result of the electron transfer at the electrode/solution interface, the oxidation of the monomer occurs with the formation of cation radicals of aniline. The process follows with the isomerization of cation-radicals and oxidative coupling reactions leading to the formation of conjugated polymer chains and the deposition of a conductive polymer layer. The formation of a polymer is a bimolecular reaction complicated by heterogeneous conditions of the chain growth, when the reaction product formed near the electrode is not soluble in the reaction medium and forms a film on the electrode surface. A high conductivity of polyaniline permits us to synthesize the films with various thicknesses. The obtained polymer layer has a bright green color being a feature of the acid-doped form of PANI, emeraldine salt. The surface morphology of the films is shown in Fig. 1.

The study of the films by AFM and the statistical analysis of the surface morphologies revealed that the structure of polyaniline in thin films is globular, and the size of globules

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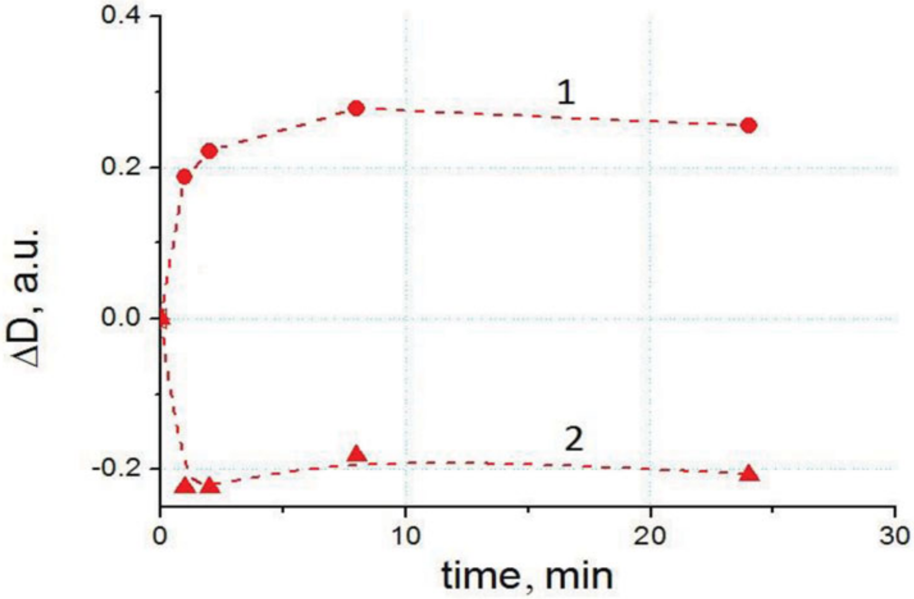

Figure 6. The kinetics of the optical absorption for PANI films on the exposure time to ammonia (P_{NH3} = 6.2 Pa) at wavelengths of 600 nm (1) and 830 nm (2).

is not bigger than 100 nm (Fig. 1). Globules are evenly packed developing a large surface of the films that promotes the adsorption capacity of the polymer.

The obtained PANI films with various thicknesses (from 0.3 to 2.2 μm), as predicted in [4–6], can be characterized by a broad band of optical transmittance (30–60%) in the visible range (ca. 450–700 nm) and by absorption band in the near infrared region (ca. 700–900 nm).

A feature of these films is the presence of a band with maximum at 1.57 eV in their absorption spectra (Fig. 2, curve 1). The band consists of various electronic transitions in the benzoquinoide chain, the polaron and bipolaron zones [22]. The band formed in the electro-synthesis of polyaniline in an acidic medium is absent in the absorption spectra of the films obtained by the thermal deposition in vacuum [23]. In addition, the spectral bands at 2.91 and 3.28 eV were observed (Fig. 2, curve 1), being characteristic of polyaniline and associated with the absorption of cation-radicals in the structures of polyaminoarenes and the π-π^* transition in the conjugated aromatic system [22].

In contact with ammonia, a new band with a maximum at 2.07 eV appears. Simultaneously, the intensities of the bands at 1.57 and 2.91 eV decrease (Figs. 3 and 4). The isobestic point at 2.71 eV (Fig. 2) evidences that the band at 2.07 eV arises from the interaction of ammonia with a protonated nitrogen atom of PANI, having a delocalized charge on the conjugation chain and compensated with anionic dopants to form a new unstable complex. At the interaction with an acid solution, this complex is destroyed, as was evidenced by the disappearance of the band (at 2.07 eV) and the appearance of the absorption at 1.57 eV (Fig. 2, curve 4).

The kinetics of the optical absorption of PANI films in the presence of ammonia shows that the major changes in optical properties occur in the first seconds of the ammonia injection (Figs. 4–6). The same kinetics is observed for all wavelengths under study, particularly in the near infrared spectral range. There, in contrast to the visible range, the

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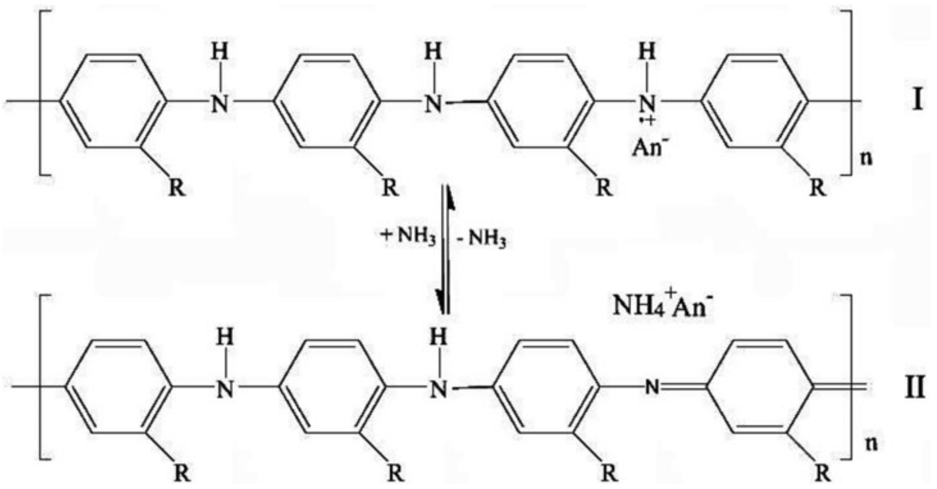

Figure 7. Molecular structure of emeraldine salt of polyaniline (I) before the exposure to ammonia and its transformation to emeraldine base (II) after the interaction with ammonia.

optical absorption in the presence of ammonia does not increase, but decreases (Figs. 4 and 6). However, if we take into account that the absorption spectrum in this region is affected by the formation of polarons [1], specifically cation radicals of protonated polyaniline stabilized with acidic residues (An^-) (see structure I, top of Fig. 7). An interaction of the species with molecules of ammonia results in the deterioration of the An^- concentration due to the formation of $\{NH_4{}^+ \ldots An^-\}$ complexes (see structure II, bottom of Fig. 7). Formation of the $NH_4{}^+$ cation requires the involvement of hydrogen ion (proton) resulting in a decrease of the concentration of protonated cation radicals in a PANI chain. The level of deprotonation for the polymer chain is proportional to the partial pressure of ammonia, adsorbed in a polymer film, which is accompanied by a decrease of the optical absorption in the spectral areas related to the polaron and bipolaron bands.

The PANI films prepared and studied using the above technique have quasilinear behavior of kinetic changes on the logarithmic scale of time (Fig. 5b, d). The dependences are identical for various film thicknesses (Fig. 5, curves 1–3) and reproducible for five different batches of samples used in the experiment. The response from interaction of PANI film with basic competitive substance, ethanol, is one order of magnitude lower than observed one for ammonia vindicating sufficient level of selectivity towards ammonia. All this allows us to recommend the technique for the development of competitive gas sensors or visual indicators, since these changes are accompanied by a pronounced change of the film color from green (emeraldine salt) to blue (emeraldine base), as we reported previously [4,6].

Conclusions

1. In the presence of ammonia, a new absorption band with a maximum at 2.07 eV was found to appear with a simultaneous decrease in the intensity of bands at 1.57 and 2.91 eV in the optical spectra of the polymer. The growth of the new absorption band is mainly resulted in a transformation of the centers of absorption at 1.57 eV, which is confirmed by the presence of the isobestic point at 2.71 eV.

2. The possibility to increase the sensitivity of ammonia sensors based on polyaniline films can be achieved by the comparative measurements of optical absorbance changes at 570 nm relative to the absorption at 800 nm. The results can be used to optimize ammonia gas sensors for monitoring the biotechnological processes in food industry and the environment.

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