Fiber-optic sensor for butylamine

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Abstract. Fiber-optic chemical sensor for butylamine was realized. The sensor includes a thin layer nanostructure on the end of optical fiber with a diameter of 600 µm. It consists of luminescent silica nanoparticles modified with pyrylocyanine dye, silver nanoparticles and photonic-crystal film. The sensitivity of the sensor is increased tenfold due to an additional covering of the film with photonic crystal as a porous mirror and the injection of silver nanoparticles with a diameter of 5-7 nm.

1. Introduction

Fiber optics is one of the most dynamically developing field of physics. The application of fiber optics in a range of sensors has several important advantages. Insensitivity to electromagnetic and radiation interference, chemical and thermal stability, remote sensing, relatively low cost makes these types of sensors indispensable in some cases [1]. The coating of the thin-film nanostructures based on silica nanoparticles on the surface of optical fiber allows significantly extend the scope of fiber-optic sensors [2-5]. It is known that amines are usually toxic and in some cases are strong carcinogens. One of the significant shortcomings of existing chemical sensors for amine-type compounds is the lack of selectivity. This paper reports the results of experimental studies of selective sensor for butylamine based on nanostructure thin-film coated at the end of an optical fiber. This film consists of silica nanoparticles of 8-10 nm modified by polymethine dyes [6]. It is well known that pyrylocyanine dyes interact with primary amines to form pyrydocyranines. Pyrydocyranines exhibit luminescence, which is different from the luminescence of the starting pyrylocyanines. This effect was inventive incentive for the synthesis of pyrylocyanine 2 and pyrylocyanine 3 dyes [6], which selectively react with butylamine. It is also well known that the luminescence properties of organic dyes are enhanced in the mesoporous nanostructures of silica and the radiation resistance of the dyes increased [7,8]. Therefore, the binding of luminescent functional dyes with silica nanoparticles is promising for the use of optical chemical sensors. The pyrylocyanine dye may have a covalent bond with the skeleton of silica nanoparticles. The method of chemical modification of silica nanoparticles in a sol-gel synthesis is described in [6].

2. Materials and methods

«Avantes AvaSpec-2048TEC» spectrometer with a spectral resolution of 1 nm was used in the studies of luminescence properties of the thin films, which are consist of modified silica nanoparticles (MSN). «Newport LQC 405 - 85E» semiconductor laser was used as a source of exciting light with a wavelength of 407 nm (figure 1). The thin-film nanostructure is deposited on the end of a freshly
cleaved optical fiber with a diameter of 600 µm by dropping into the solution of MSN or deposition and subsequent drying a drop of the solution at the end of the fiber. We have experimentally found that the film of MSN is durable to the various kinds of mechanical effects and demonstrates a high radiation resistance.

Figure 1. The optical scheme of measuring; a – semiconductor laser, b - reflection probe, c – spectrometer.

A typical luminescence spectrum of the MSN film modified by pyrylocyanine 3 dye has a pronounced peak at 660 nm. The film gives a green-yellow luminescence with a maximum at 560 nm after a treatment with 10% solution of butylamine (figure 2).

Figure 2. The luminescence spectrum of the MSN thin-film by pyrylocyanine 3 before (1) and after (2) treatment with butylamine solution.

It should be noted that the luminescence effect of the MSN film after the treatment with other amino liquids leads only to the quenching of luminescence in the red spectrum, while the yellow-green luminescence does not appear. The minimum concentration of butylamine in ethanol was $10^{-3}$ mol/l in which possible to record the luminescent responses from the MSN film modified by pyrylocyanine 3 dye. In contrast to the MSN film modified by pyrylocyanine 3 dye, the films modified by pyrylocyanine 2 do not have the luminescence before the treatment. The maximum of luminescence at 580 nm was exhibited after treatment with butylamine solution (figure 3, curve 1). On exposure to other amino substances, the luminescence peak does not appear which also shows selectivity for the analyte.

To increase the amplitude of the luminescence response from the MSN film coated on the end of optical fiber as a porous selective mirror was applied. The mirror is an artificial opal photonic-crystal (PhC) film. The maximum of reflection of this mirror coincides with the peak of pyrylocyanine luminescence in MSN after the treatment with butylamine solution (figure 3, curve 2).
The luminescence spectrum of the MSN thin-film by pyrylo cyanine 2 after treatment with butylamine solution (1) and the reflectance spectrum of «PhC mirror» (2).

It was achieved by choosing the diameter of monodisperse silica spheres (MSS) of about 260 nm. The porosity of PhC film allows butylamine and other substances easily penetrate into the MSN film. The PhC opal film was grown by moving meniscus method on the end of the optical fiber [9]. For this purpose optical fiber is fixed in the suspension of MSS on the surface under an angle of 15 degrees. The reflection spectrum of «PhC mirror» deposited on the end of the optical fiber is practically coincided with the luminescence band of pyrylocyanine 2 dye in the region of 580 nm.

3. Results

The experiments have demonstrated that the coating of the «PhC mirrors» on the MSN film leads to an increase in the amplitude of the reflected signal in 3 - 4 times (figure 4). The PhC film was a highly ordered hexagonal close-packed structure of the MSS, and the crystallographic direction (111) was normal to the surface. The presence of «PhC mirror» does not affect the rate of change of the optical response of sensory film.

The further increase in the amplitude of a luminescence of MSN might be enhanced due to the presence of nearby metallic nanoparticles such as Ag or Au [10]. We have found that the addition of
Ag nanoparticles with a diameter of 5 - 7 nm into the MSN film leads to an increase the luminescence in 2 - 3 times (see figure 5).

**Figure 5.** The luminescence spectrum of MSN by pyrylocyanine 3 before (3,4) and after (1,2) treatment with butylamine solution; with (1,3) and without (2,4) injection of silver nanoparticles.

4. Conclusion

This paper proposed an optical fiber butylamine chemical sensor based on selectively altering the luminescent properties of MSN thin-film. The sensor component is a MSN covalently bound with pyrylocyanine dye and deposited at the end of the optical fiber. We confirmed that our sensor has high sensitivity for actual use, and 10% solution of butylamine concentration less than $10^{-3}$ mol/l can be detected. It was shown that the addition of silver nanoparticles into the film of MSN and the coating it the PhC film as a porous selective mirror on the end of the fiber can increase the sensors sensitivity about 10 times. We assumed that the improving the sensing element by doping it in PhC film with metallic nanoparticles allow us to develop a highly sensitive selective optical chemical sensors remote monitoring.

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