HIGHLY SENSITIVE CHITOSAN-BASED OPTICAL FLUORESCENT SENSOR FOR GASEOUS METHYLAMINE DETECTION

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Abstract

An optical fluorescent sensor based on a chitosan thin film co-doped with Eu^{3+} and a bromothymol blue pH indicator has been developed. Near-UV to visible (350–400 nm) excitation of the europium (III) chelate complexes with 1,3-diphenyl-1,3-propanedione exhibits a typical lanthanide emission with maximum at 618 nm. Luminescent spectra of the Eu^{3+} complex were found to be insensitive to the presence of methylamine gas. Therefore, bromothymol blue, a non-fluorescent pH indicator with an absorbance maximum of deprotonated form close to the Eu^{3+} emission band was added to the film to provide a non-fluorescent reversible response to different methylamine concentrations, which can be detected by measuring the Eu^{3+} emission.

Key words*: composites, optical materials, thin films, luminescence*

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1. Introduction

Development of green approaches for different applications involves the use of renewable natural resources, among which polysaccharides represent highly available multifunctional materials. Recently, the fabrication of biopolymer-based nanocomposites for environmental applications [1], sorption, catalysis and sensing [2–4] have been reported. No less promising is the application of natural polymers as an alternative to synthetic ones in optical sensors for the detection of hazardous chemicals [5–7] or humidity [8,9]. In contrast to many synthetic polymers, whose application frequently requires the utilisation of organic solvents [10], natural film-forming polysaccharides are water soluble, easily processable and offer a simple and environmentally friendly method for fabrication of optical sensors with a chemosensitive polymer layer.

The development of sensors for monitoring of hazardous gases, such as ammonia [10–13], hydrochloric acid [13,14] and volatile organic compounds, is an increasingly expanding field of research and development due to the high human health and environmental risks caused by the use of these substances in industry. Among many detection methods, a fast response time, good reproducibility and high electromagnetic interference immunity of optical sensors [7,15] make them one of the most prospective [10,12,14,16,17]. A general approach to develop optical sensors for volatile acids and bases consists in the fabrication of thin chemochromic films doped with pH-sensitive dyes, whose optical properties change depending on the presence and concentration of an acid–base analyte. The dyes can be incorporated into the sensing layer via covalent immobilisation, the sol–gel method [12] and entrapment in polymeric film [10] or self-assembled multilayers [13,18].

In this paper, we demonstrate a new fluorescent methylamine gas sensor based on the natural polysaccharide chitosan. An optical fluorescent sensor based on a chitosan thin film co-doped with Eu^{3+} and a bromothymol blue pH indicator has been developed. Near-UV to visible (350–400 nm) excitation of the europium (III) chelate complexes with 1,3-diphenyl-1,3-propanedione exhibits a typical lanthanide emission, with a maximum of 618 nm. The luminescent spectra of the Eu^{3+} complex were found to be insensitive to the presence of methylamine gas. Therefore, bromothymol blue, a non-fluorescent pH indicator with an absorbance maximum of deprotonated form close to the Eu^{3+} emission band was added to the film to provide a non-fluorescent reversible response to different methylamine concentrations, which can be detected by measuring the Eu^{3+} emission.

2. Materials and methods

2.1. Chitosan film fabrication

Chitosan stock solution at a concentration of 1% was prepared by dissolution of 1 g of polymer (high molecular weight chitosan, Sigma) in 100 ml of 1% acetic acid. The solution was stirred under heating for 6 hours, centrifuged at 4400 rpm for 180 min and filtered through a 0.45 μm membrane. To obtained thin films, chitosan solution was spun onto the 2.5 x 2.5 cm glass substrates using Laurell WS-400B-6NPP-LITE spin-coater at 1000 rpm. After drying in ambient atmosphere for 10 minutes, chitosan films were deprotonated by immersion into 3% ammonia solution for 10 minutes, followed by rinsing with distilled water. The thicknesses of the obtained coatings were controlled with optical reflectometry (Sentech SE500adv, Germany) and were 620±30 nm.

2.2. Doping chitosan film with europium dibenzoylmethanate ($Eu(dbm)_3$)

To dope the coating with luminophore, the 0.1 M $Eu(dbm)_3$ alcohol solution was placed onto the substrate, followed by spinning at 1000 rpm until dry. During this step, the chitosan film swells in alcohol, and the luminophore molecules diffuse into the film, while the subsequent rotation removes the excess of solution from the substrate by applying a centrifugal force.

2.3. Doping chitosan film with bromothymol blue (BTB)

After doping of $Eu(dbm)_3$, the substrate was immersed in BTB solution (dye content 0.5 g/L, pH 5.0) for 30 minutes. After dye entrapment, the substrate was thoroughly rinsed with deionised water and air-dried. The scheme of chitosan film deposition and doping with $Eu(dbm)_3$ and BTB is presented in Figure 1.

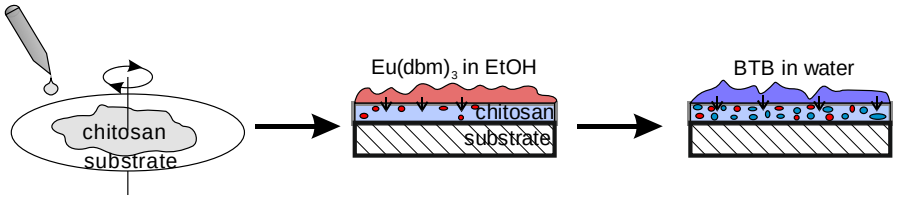

Figure 1. The scheme of chitosan film deposition and doping with optically active dopants

Optical study. The study of coating sensor characteristics were performed using a Horiba Fluorolog 3 spectrofluorimeter equipped with a specially designed sealed chamber (V = 700 cm^3). The required concentration of methylamine was obtained from pre-calibrated gas mixtures of methylamine and laboratory air. The exact value of the methylamine concentration was determined by a commercial gas analyser (Kollion 1B).

The luminescence spectra were recorded with 1 nm step and a 0.1 second average time. Kinetics studies were carried out at the maximum emission of the complex λ = 618 nm, and the excitation radiation wavelength λ = 395 nm.

The measurement cycle consisted of an inlet of analyte into the chamber until termination of the output signal change and subsequently blowing the chamber with clean air to restore the initial output signal level.

3. Results and discussion

From the literature, it is known that luminophores are characterised by excitation and emission spectra. Organic phosphores tend to absorb and emit radiation over a wide spectral range with minimal Stokes shift between absorption and emission peaks, which significantly overlap. Development of precise sensor systems based on organic luminophores requires, in many cases, to separate the exciting and emitting radiation, which can be realised by using bandpass filters or diffraction gratings. In the current work, we used an Eu^{3+}-based luminophore, which is characterised by a significant Stokes shift and narrow emission peak. Thus, europium dibenzoylmethanate was excited by radiation with a wavelength of 395 nm and emission was recorded at a wavelength of 618 nm. The presence of bromothymol blue indicator determined the coating sensitivity to the vapours of volatile amines. In the presence of gaseous methylamine, absorbance of the indicator increased and overlapped the emission of the europium complex (Fig. 2a). Proximity of

the BTS and $Eu(Dbm)_3$ molecules promoted efficient energy transfer and produced modulation of the sensor signal (Fig. 2b).

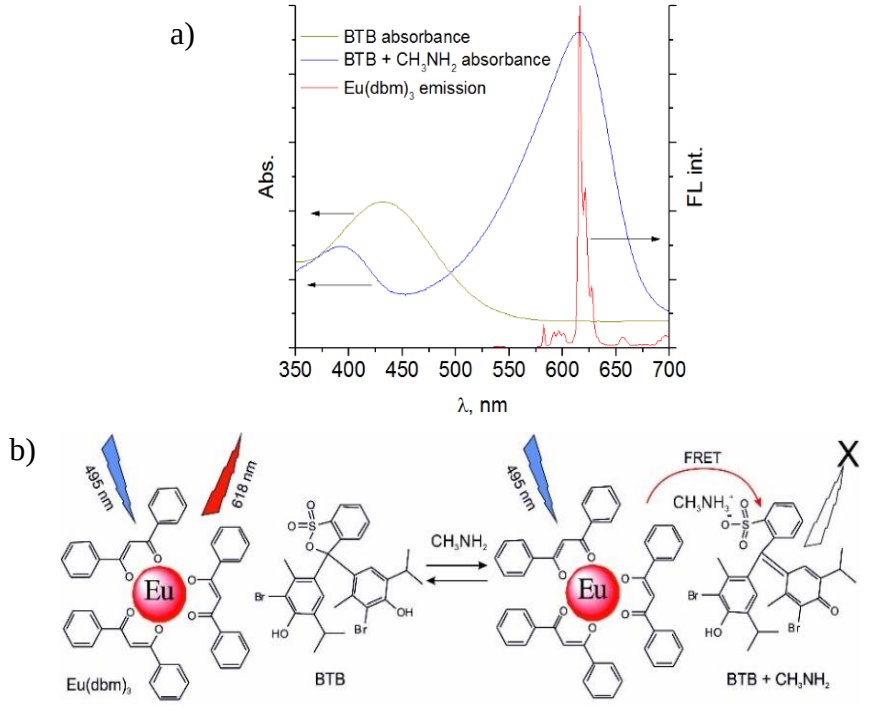

Figure 2. (a) UV-vis spectra of protonated and deprotonated forms of bromothymol blue and fluorescent spectrum of europium dibenzoylmethanate and (b) the scheme of reversible formation of sensor response onto presence of methylamine

Figure 3a shows the luminescence spectra of the composite coating in the air and in the presence of methylamine. As can be seen, the presence of the analyte leads to quenching of coating luminescence at 618 nm.

Upon progressive increase of the methylamine concentration, a gradual decrement in the fluorescence at 618 nm was observed. Figure 3b shows the dependence of signal quenching on the concentration of methylamine in the analysed air (fluorescent response toward analyte was normalised as $R = 1-I_i/I_{max}$, where I_{max} is the fluorescence intensity of the sensor without analyte and I_i is the fluorescence intensity of the sensor with analyte). The working sensitive range of the coating was from 0.1 to 100 ppm. On the basis of the signal-to-noise ratio of three, the detection limit was estimated to be 0.06 ppm or 0.08 MAC.

Response time and signal stability are important parameters that determine the kinetic characteristics of the sensor. The response time was investigated by monitoring the fluorescent emission intensity at an excitation wavelength of 395 nm. Presented in Figure 4, a sensogram demonstrating the quick registration of analyte concentration changes and the complete restoration of the basic signal level after purging the system with clean air is shown.

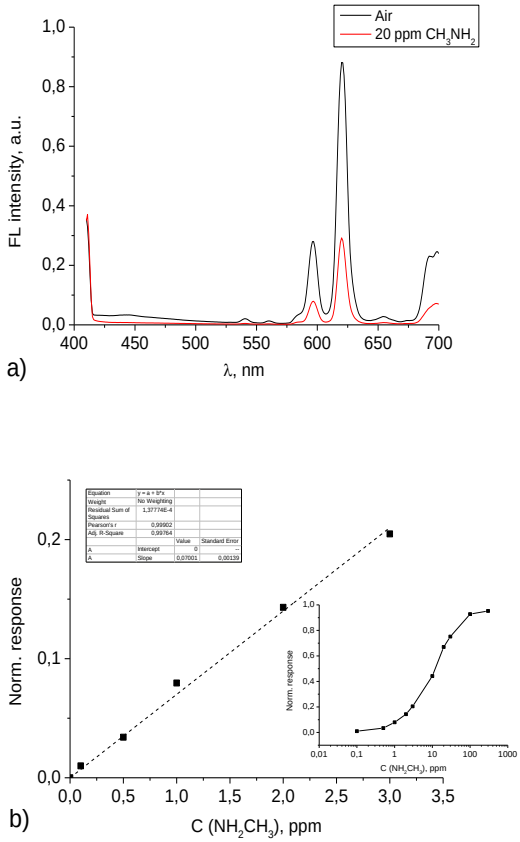

Figure 3. (a) Fluorescence spectra of the sensitive coating in laboratory air and in the presence of 20 ppm CH_3NH_2, (b) dependence of normalised response signal on concentration of methylamine

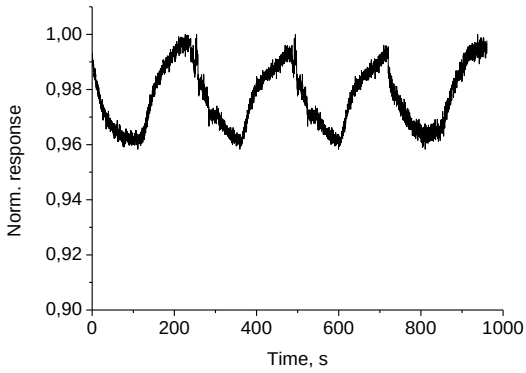

Figure 4. Time dependent periodic response of coating sensitive to gaseous CH_3NH_2

4. Conclusions

In summary, we report a new chemosensor based on a chitosan thin film co-doped with Eu^{3+} and a bromothymol blue pH indicator for the selective detection of methylamine concentration in air. The sensing properties of the developed chemosensor were examined by fluorescence spectroscopy. Near-UV to visible (350–400 nm) excitation of the Eu^{3+} chelate complexes with 1,3-diphenyl-1,3-propanedione exhibits a typical lanthanide emission with a maximum of 618 nm. Bromothymol blue, a non-fluorescent pH indicator with an absorbance maximum of deprotonated form close to the Eu^{3+} emission band was added to the film to provide a non-fluorescent reversible response to different methylamine concentrations, which can be detected by measuring the Eu^{3+} emission.

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