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pH-indicators doped polysaccharide LbL coatings for hazardous gases optical sensing

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ABSTRACT

Sensitive layer-by-layer (LbL) coatings for optical detection of gaseous NH_3 and HCl were prepared by self-assembly of oppositely charged polysaccharides (chitosan and λ-carrageenan) followed by doping LbLs with pH-sensitive dyes – bromothymol blue (BTB) and Congo red (CR). It has been shown that CR, being an amphoteric dye, diffuses into LbL films regardless of the charge of the outermost polyelectrolyte layer, and the dye loading increases linearly with the LbL film thickness, whereas BTB diffuses into LbL films only when the outermost layer is positively charged, and linearity between dye loading and film thickness holds only up to 8–12 double layers (DLs) deposited. Formation of dye-doped LbL coatings at the surface of K^+/Na^+ ion-exchanged glass has allowed fabrication of composite optical waveguide (OWG) gas sensor for detection of ammonia and hydrochloric acid vapors. The response time of BTB-doped composite OWG for ammonia detection was below 1 s, and the detection limit was below 1 ppm. CR-doped OWG sensors have shown high sensitivity to HCl vapor but slow relaxation time (up to several hours for 12 DL LbL films).

1. Introduction

Development of green approaches for versatile applications is closely related to utilization of renewable natural resources, among which polysaccharides represent widely abundant and multifunctional raw materials. Recently, aside from the booming biomedical field, biopolymer assisted fabrication of nanocomposites for environmental applications (Zhao et al., 2011) and synthesis of metals and metal oxide nanoparticles for sorption, catalysis, and sensing (Sarkar, Guibal, Quignard, & SenGupta, 2012) have been reported. Not less promising is the application of natural polymers as an alternative to synthetic ones and even inorganic materials in optical sensors for the detection of hazardous substances (Kurauchi, Ogata, Egashira, & Ohga, 1996) and humidity (Arregui, Ciaurriz, Oneca, & Matias, 2003). In contrast to many synthetic polymers, whose application in optics frequently requires utilization of organic solvents (Courbat, Briand, Damon-Lacoste, Wöllenstein, & de Rooij, 2009), natural film-forming polysaccharides are water soluble, easy to process, and offer a green way for fabrication of the sensors for environmental applications.

Real-time sensing of hazardous gases such as ammonia (Courbat et al., 2009; Khan, Baig, & Khalid, 2011; Malins, Butler, & MacCraith, 2000), hydrochloric acid (Norena-Franco & Kvasnik, 1996; Yang, Ma, & Yang, 2011), and volatile organic compounds (Yuan, Yeom, Lim, & Kang, 2011) is an increasingly expanding field of research and development due to high human health and environmental risks posed by generation and utilization of these substances in technological processes. Among numerous detection methods, fast response time, good reproducibility, and high electromagnetic interference immunity of optical sensors (Corres, Arregui, & Matias, 2007) make them the most booming area of research in the recent years (Courbat et al., 2009; Malins et al., 2000; Shang, Wang, Xu, Tong, & Wu, 2011; Yang et al., 2011; Yimit, Itoh, & Murabayashi, 2003). One of the simplest but efficient approaches to develop optical sensors for volatile acids and bases consists in 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. Optical fibers (Tao, Xu, & Fanguy, 2006) or planar waveguides (Courbat et al., 2009) can be used as a support for polymeric sensing layers. The dyes can be incorporated to the sensing layer via covalent immobilization (Trupp et al., 2010), sol–gel method (Malins et al., 2000), and entrapment in polymeric film (Courbat et al., 2009) or self-assembled multilayers (Goicoechea, Zamarreno, Matías, & Arregui, 2008). Despite relative simplicity of the thin film fabrication by dip-coating or spin-coating solutions of sol–gel precursors or polymers, the fine control of the resulting film thickness, and, therefore, the quantity of the embedded dye, is not feasible (Corres et al., 2007). This limits the possibility to fabricate sensors with highly reproducible

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properties and results in the necessity of individual calibration procedures, since the thickness of a sensing layer and the content of a dye have a strong effect on the response time and sensitivity (Courbat et al., 2009; Shang et al., 2011).

The problem of fabrication of sensing layers with highly reproducible and finely controlled film thickness and dye content can be solved using layer-by-layer (LbL) electrostatic self-assembly of oppositely charged polyelectrolytes. This method introduced by Decher, Hong, and Schmitt (1992) was extensively used ever since to produce different functional materials with a nanoscale control of the polyelectrolyte layer thickness at the surfaces of arbitrary shape and size. The important advantages of LbL films for optical sensor applications are high optical homogeneity, very low scattering losses (Corres et al., 2007), adjustable gas permeability (Wang, Stedronsky, & Regen, 2008), and easily tuned content of functionalizing additives, including dyes (Nicol, Habib-Jiwan, & Jonas, 2003).

The optimal polyelectrolyte pair for LbL build-up of a polymer layer doped by pH-sensitive dye for optical sensor applications is expected to yield rapidly growing transparent films with high affinity to dye molecules and thickness of a few dozens to hundreds nanometers (Courbat et al., 2009), which can be formed at a reasonable number of adsorption steps. We have recently shown that LbL films of the required thickness can be easily obtained by the assembly of natural polysaccharides – chitosan and κ-carrageenan (Bratskaya et al., 2007) under controlled pH and ionic strength conditions. The efficient entrapment of pH-sensitive dyes in such films is possible due to high sorption capacity of chitosan to anionic and amphoteric dyes (Kurauchi et al., 1996; Phaechamud, Koizumi, & Ritthidej, 2000) that have been already used in several optical sensor applications based on spin-coated or dip-coated chitosan films as a dye support (Kurauchi et al., 1996; Shang et al., 2011).

In this work the formation of chitosan–λ-carrageenan LbL coatings doped with pH-sensitive dyes – bromothymol blue (BTB) and Congo red (CR) and their application as sensitive layers on the optical waveguide (OWG) for detection of gaseous ammonia and hydrochloric acid have been investigated.

2. Experimental

2.1. Materials

Chitosan with a deacetylation degree of 80.5% and a molecular weight of 5×10^5 Da and λ-carrageenan were purchased from JSC "Bioprogress" (Russia) and Fluka, respectively. Analytical grade water soluble pH-sensitive dyes – bromothymol blue (BTB), and Congo red (CR) – were purchased from "Reachim" (Russia). All other reagents were of analytical grade.

Microscopic glass slides (Menzel GmbH, Germany), highly polished single-crystal silicon wafers with a native SiO_2 layer of 1.8 ± 0.4 nm (Semiconductor Processing, Germany), and K/Na ion exchange sodium silicate glass planar OWG (optical waveguides) with a refractive index of the core layer of 1.521 were used as substrates for preparing LbL coatings. Prior to polyelectrolytes deposition, substrates were cleaned in $H_2O_2/NH_3/H_2O$ (1:1:1, v/v/v) mixture at 80 °C in an ultrasonic bath, thoroughly washed with distilled water, and dried at 120 °C.

2.2. LbL build-up and entrapment of pH-sensitive dye

LbL coatings were prepared by a successive immersion of a substrate to solutions of chitosan and λ-carrageenan (polymer content 1 g/L, 0.15 M NaCl, pH 5) for 10 min with the intermediate careful rinsing under running deionized water. To avoid acidic degradation of carrageenan, only freshly prepared solutions were used for LbL build-up. Subsequently, self-assembled layers of chitosan and λ-carrageenan were further referred to as double layers (DL). To obtain LbL coatings of various thicknesses, the number of DL was varied from 1 to 20.

To dope LbL coatings with pH-sensitive dyes, the substrates with the fixed number of DL were immersed in BTB or CR solutions (dye content 1 g/L, pH 5.0) for 18 h. In kinetics studies, the contact time was varied from 30 min to 72 h. After the dye entrapment by LbL coatings, substrates were thoroughly rinsed with deionized water and air-dried.

2.3. Surface characterization

The LbL coatings topography was investigated on a scanning force microscope DI-3100 (Digital Instruments, Santa Barbara, USA) in the tapping mode. The thickness and refractive index of the polymer layers (in dry state on the surfaces of silicon wafers) were measured at $\lambda = 633$ nm and an angle of incidence of 70° with a null-ellipsometer in a polarizer compensator-sample analyzer (Multiscope, Optrel Berlin) microfocus ellipsometer. Initially, the thickness of the native SiO_2 layer was calculated at refractive indices $n = 3.858 - i \times 0.018$ and $n = 1.4598$ for the Si wafer and the SiO_2 layer, respectively.

2.4. UV–vis spectroscopy

The absorption spectra of LbL coatings with and without pH-sensitive dyes built on the surface of microscopic glass slides were recorded in the wavelength range of 300–700 nm with steps of 1 nm using an UV–vis spectrometer UV-1650PC (Shimadzu, Japan) with a sealed glass cell equipped with a film holder. Spectra of LbL coatings doped with BTB or CR in ammonia or hydrogen chloride atmosphere were recorded after 30 min blowing the cell with a constant flow of vapor produced by bubbling air through 25% aqueous ammonia or 37% aqueous HCl solutions, respectively (absorbance of the substrates was set as a baseline). All spectra were recalculated for a single LbL film, assuming that the recorded spectra corresponded to two LbL films formed at both sides of the substrate.

2.5. Optical waveguide (OWG) chemical sensor fabrication and investigation of its sensing properties

OWG chemical sensor was fabricated by a deposition of 12 DL of chitosan/λ-carrageenan onto a 10 mm long central part of K^+/Na^+ ion-exchanged glass OWG and subsequent entrapment of pH-sensitive dye as described in Section 2.2. The chemochromic films were deposited only on a 10 mm long central part of the OWG. The experimental setup for investigation of pH sensor properties was similar to that described in (Yimit et al., 2003). The original sealed chamber was mounted on a goniometric platform. Input and output prisms were made of flint glass with a refractive index at the working wavelength $n = 1.76412$. A He–Ne laser ($\lambda = 633$ nm) with an average output power of $I = 11$ mW was used as a radiation source. A power meter Newport 2935c was used as photodetector. Gaseous ammonia concentration was varied by bubbling air through the aqueous ammonia solutions. The real ammonia gas concentration was determined by a commercial ammonia gas solid-state analyzer Kollion-18 (Russia). The sensor response to acidic gas was investigated in a chamber containing 1 ppm of HCl generated by bubbling air through 1% HCl solution. All measurements were made at room temperature and relative humidity 50%.

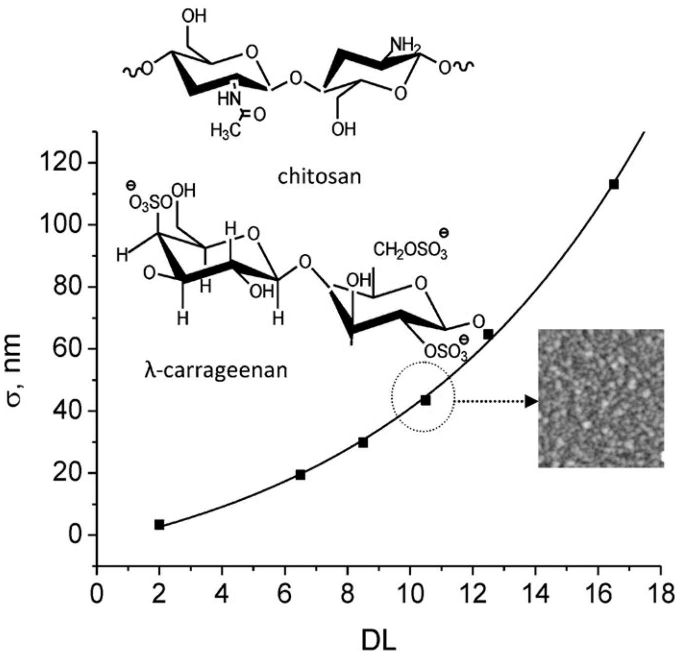

Fig. 1. Dependence of chitosan–λ-carraggenan LbL film thickness (σ) on the number of DL deposited. The surface topography (image size 1 μm × 1 μm) is given for the 10 DL chitosan–λ-carraggenan film.

3. Results and discussion

3.1. LbL film formation and pH-sensitive dye entrapment

Although an overwhelming majority of studies on LbL films formation and properties have reported experimental data for synthetic polyelectrolytes, there is an increasing interest to LbL assembly of natural polyelectrolytes, whose tunable conformational states or biological activity allow obtaining functional coatings with specific properties (Bratskaya et al., 2007; Richert et al., 2004; Schoeler et al., 2006). An important feature of many natural polyelectrolytes for fabrication of sensing layers in optical devices is a fast exponential growth of their LbL films (Bratskaya et al., 2007; Richert et al., 2004; Schoeler et al., 2006). The optimal thickness of the polymer films used as responsive layers in OWG sensors is limited to a few hundred nanometers corresponding to the penetration depth of evanescent field (Courbat et al., 2009) and, therefore, can be easily obtained by a reasonable number (up to 20) of alternative adsorption steps using a pair of natural polyelectrolytes (Bratskaya et al., 2007; Richert et al., 2004) or their combination with synthetic polyelectrolytes (Schoeler et al., 2006).

According to the data presented in Fig. 1, chitosan–λ-carrageenan LbL films with the thickness suitable for fabrication of OWG sensing layers can be obtained by deposition of 4–20 DL. The topography analysis of the LbL films of intermediate thickness (10 DL) showed a homogeneous surface coverage with a RMS roughness of 7.2 ± 0.6 nm. Compared to the previously investigated chitosan/κ-carrageenan system (Bratskaya et al., 2007), λ-carrageenan, as a non-gel-forming polysaccharide (de Velde & de Ruiter, 2002) yields slightly thinner, less rough LbL coatings with a lower number of aggregates that is very important for optical applications due to the possible contribution of aggregates to the scattering losses of OWG that worsen overall performance of the optical sensor.

To impart to chitosan–λ-carrageenan films optical sensing properties toward gaseous ammonia and hydrochloric acid, the preformed LbL coatings can be doped with pH-responsive dyes (pH indicators). Chitosan readily interacts with water soluble anionic and amphoteric dyes; however, the efficiency of interactions significantly depends on the dye structure and hydrophilicity (Kurauchi et al., 1996; Phaechamud et al., 2000). For the optimal performance of the composite OWG, pH-sensitive dyes entrapped into the polymer layer shall meet the following criteria: (i) difference in absorption of acid and base form of the indicator in the polymer layer must be significant at the wavelength of commercially available lasers, e.g. He–Ne-laser (λ = 633 nm); (ii) no phase separation in the polymer film shall be induced by entrapment of the indicator to prevent optical losses; (iii) indicator shall have low pK_a value (for detection of bases) and high molar absorption coefficient to assure the lowest detection limit (Werner, Klimant, & Wolfbeis, 1995). Using these criteria, BTB (pK_a = 7.2, molar absorptivity 16,380 M cm^{-1} at 430 nm (Qi et al., 2003)) and CR (pK_a = 4.1, molar absorptivity 42,000 M cm^{-1} at 488 nm (Kuhr, Licklider, & Amankwa, 1993)) were chosen to dope polysaccharide LbL coatings for the detection of gaseous ammonia and hydrochloric acid, respectively. These dyes belong to the groups of sulfonephtalein (BTB) and azo (CR) dyes, which are often used in optical sensors (Courbat et al., 2009; Goicoechea et al., 2008; Malins et al., 2000; Yimit et al., 2003).

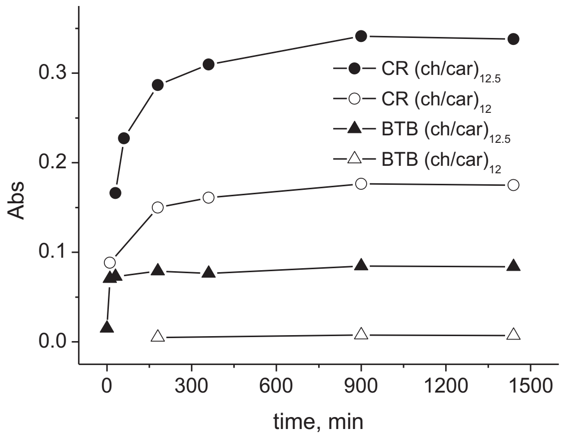

Fig. 2. Kinetics of BTB and CR dyes entrapment into chitosan/λ-carrageenan (ch/car)$_{\text{DL}}$ LbL coatings of 12 and 12.5 DL. Optical density (abs) was recorded at 420 nm for BTB and 500 nm for CR.

Kinetics studies of the dyes entrapment into LbL coatings revealed significant differences in the behavior of BTB and CR dyes. Anionic dye BTB diffuses to LbL layer only when the top layer is formed by the oppositely charged chitosan. The equilibrium state of BTB diffusion into (ch/car)$_{12.5}$ LbL coatings is reached within several minutes of contact regardless of the dye concentration in solution (0.1–1 g/L) – (Fig. 2). The limitation of dyes diffusion into LbL films with the likely charged outermost layers was previously observed for many systems (Caruso, Lichtenfeld, Donath, & Mohwald, 1999; Chung & Rubner, 2002; Nicol et al., 2003) and related to the electrostatic potential barrier. In contrast to BTB, the amphoteric dye CR diffuses into LbL when the top layer is formed by either of polyelectrolytes, and the diffusion process is much slower reaching saturation after several hours of contact (Fig. 2). It should be mentioned that the dye displacement by a subsequent polyelectrolyte layer adsorption, which is typical for LbL due to the stronger interactions of polyanion–polyanion than polyanion–dye (Caruso et al., 1999; Nicol et al., 2003), was observed only in the case of BTB while CR was irreversibly entrapped into the LbL structure, most likely, due to a strong cross-linking of chitosan with sulfo groups of the dye. The intensity of dye–LbL film interactions is also evidenced by a very significant red-shift over 50 nm for the CR acid form spectrum (Fig. 3(b)). For comparison, 6 nm and 15 nm blue-shift was detected for the spectra of base and acid form of BTB, respectively (Fig. 3(a)).

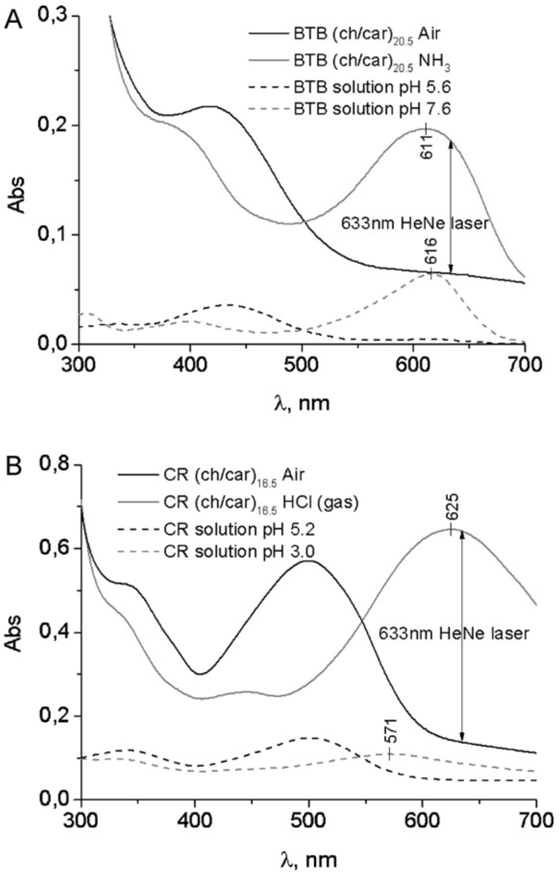

Fig. 3. Absorption spectra of pH-indicators in solution and in chitosan/λ-carrageenan (ch/car)$_{DL}$ LbL films exposed to air and NH_3/HCl atmosphere: BTB (a) and CR (b).

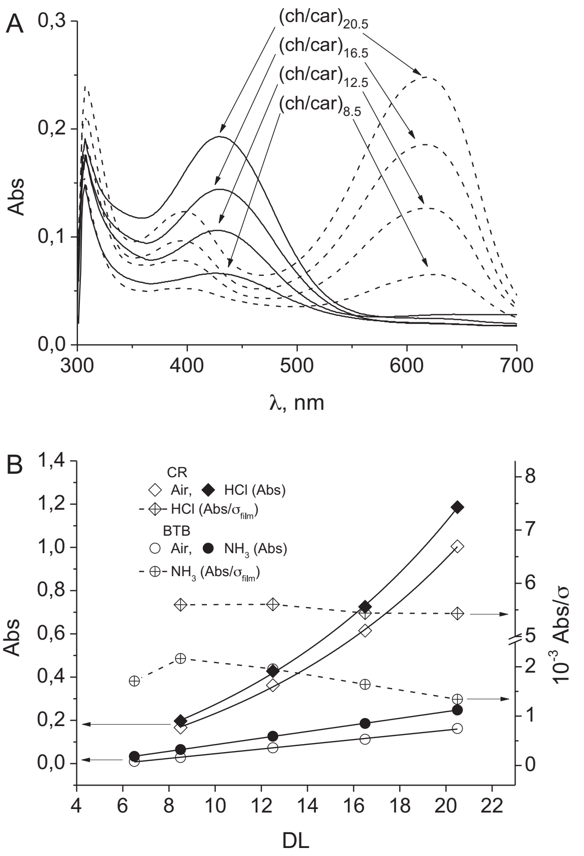

Fig. 4. Absorption spectra of BTB-doped chitosan/λ-carrageenan (ch/car)$_{DL}$ LbL coatings in air (solid lines) and in NH_3 atmosphere (dash lines) (a). Dependence of dye-doped LbL coatings optical density (abs, solid lines) at λ_{max} and specific optical density (abs/σ, where σ is the thickness of LbL coatings in nanometer, dash lines) on DL number. λ_{max} = 500 nm (CR, Air); 625 nm (CR, HCl); 420 nm (BTB, Air); 610 nm (BTB, NH_3) (b).

One of the main parameters to optimize for the sensitive layer fabrication is the dye content in the polymer film (Courbat et al., 2009). An important advantage of LbL structures is the possibility to strictly control the amount of dye in a polymer layer by adjusting the LbL film thickness. Previous studies have shown that the amount of dye entrapped into linearly growing LbL films increases linearly with the DL number (Caruso et al., 1999; Chung & Rubner, 2002) due to the increase of the number of sites available for binding of the oppositely charged dyes. It is also known that the number of functional groups available for polyion–dye interaction is higher in LbL films with lower ionic cross-linking degree, which are built-up at pH corresponding to only partial ionization of weak polyions forming LbL assembly (Yoo, Shiratori, & Rubner, 1998). Here to increase the dye loading and, therefore, the films sensitivity, we built up chitosan/carrageenan LbL films at pH 5, when a weak polycation chitosan (pK_a 6.5) is not fully protonated. Such films, when compared to those assembled at lower pH, have looser structure and are characterized by higher thickness increment per DL (Bratskaya et al., 2007).

3.2. Response of the pH-indicator doped LbL films and OWG pH-sensor to gaseous NH_3 and HCl

One can see that significant changes in absorption of acid and base form of CR and BTB at the wavelength of He–Ne laser (633 nm) are preserved upon the entrapment of dyes into the LbL film (Fig. 3) that allows application of such coatings for fabrication of OWG gas sensors. When CR-doped films are exposed to HCl atmosphere, red color of the films rapidly turns to deep blue, the color of the BTB-doped film changes from yellow to blue in the presence of ammonia gas (Fig. 1S). Analysis of the absorption spectra of dye doped LbL films shows (Fig. 4(a)) that the dye content increases with the increase of DL number for both (acid and base) forms of the pH-indicator, but the dependence is exponential for CR and close to linear for BTB (Fig. 4(b)).

In contrast to dyes entrapment into the linearly growing film (Caruso et al., 1999; Chung & Rubner, 2002; Nicol et al., 2003) for exponentially growing chitosan/carrageenan LbL films, one can expect an exponential dependence of the optical density on the DL number, if the ability of the dye to diffuse through the bulk of the film is assumed (Caruso et al., 1999; Chung & Rubner, 2002). Fig. 2S shows that the optical density of CR-doped LbL films and the optical response to HCl vapor indeed increases linearly with the film thickness in the studied interval of the DL number, while for BTB the deviation from linearity starts for the film with thickness over 60 nm (12 DL) suggesting that the dye loading is lower than can be expected from the number of binding sites within the LbL film. This tendency can be clearly seen in Fig. 4(b) illustrating changes in specific optical density per nanometer of the LbL film, while for CR dye loading per DL only slightly decreases with the increase of the film thickness, for BTB it notably decreases upon deposition of 12 DL.

Similar deviation from the linearity of dye loading with the increasing film thickness was previously observed (Caruso et al., 1999) for the dye entrapment into much thinner LbL films and was related to the ability of the dye penetrate through the limited number of DL. Here, most likely, with the increasing DL number BTB diffusion is hindered by the exponentially increasing

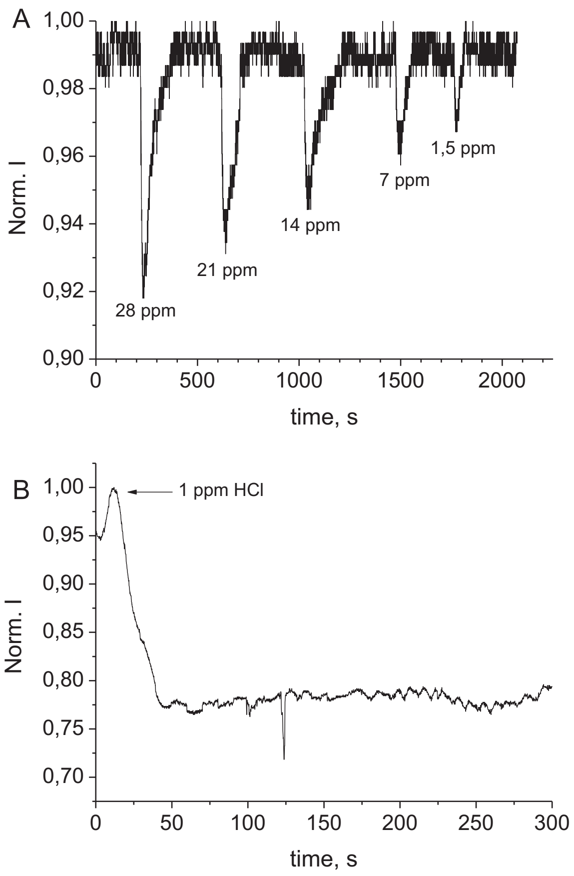

Fig. 5. Response of the composite OWG with BTB-doped sensing layer to gaseous NH_3 (a), and CR-doped sensing layer to gaseous HCl (b).

thickness of negatively charged carrageenan layer, which represents an electrostatic barrier for the anionic dye. Thus, a number of chitosan/carrageenan DL deposited for fabrication of OWG sensors shall be limited to 8–12 DL to balance the thickness and dye content of the polymeric sensitive layer. It should be also mentioned that AFM has not detected the formation of dye solid particles even at high dye loading for the films over 12 DL, while for spin coated dyes (Yimit et al., 2003) and dyes adsorbed from highly concentrated solutions (Shang et al., 2011) scattering losses arise from the particle formation or non-uniform distribution of the dye in the sensing layer and worsen the optical response.

Planar waveguide optical sensors based on evanescent field have been previously discussed in detail in literature (Courbat et al., 2009; Yimit, Rossberg, Amemiya, & Itoh, 2005), the general scheme of the OWG composite pH-sensor is given in Fig. 3S. The principle of the absorption optical sensors is based on the changes in power transmitted by the waveguide when the evanescent field interacts with the absorbing medium, which is in our case represented by the pH-indicator entrapped into LbL film. When the He–Ne laser (633 nm) is used as a light source for optical sensor, the pH-indicator doped LbL coatings are transparent in air but absorb light in the presence of gaseous NH_3 (BTB-doped LbL) and HCl (CR-doped LbL) that results in a decrease of the power transmitted by OWG.

As seen in Fig. 5(a), the interaction of BTB-doped LbL films with NH_3 is fast and completely reversible. The response time was below 1 s for the studied interval of NH_3 concentrations that is significantly faster than that of the optical sensors with sulfonephtalein dyes entrapped into plasiticized synthetic polymer films (Courbat et al., 2009) and sol–gel glass films (Malins et al., 2000). Since the analyte diffusion rate and the solvatation of ammonia are the factors controlling the initial phase of the response curve (Malins et al., 2000), hydrophilic LbL coatings with the thickness of a few dozens nanometer are more favorable for the dyes entrapment than hydrophobic polymer films or inorganic porous substrates. Although in the latter case the effect of humidity on the optical response is eliminated, very slow kinetics of such sensors is a significant drawback. At the same time, the immunity of faster optical sensors with more hydrophilic sensing layers, including LbL coatings, to humidity can be increased, for example, by using optical sensor arrays instead of a single sensor (Hutter, Horesh, & Ruschin, 2011).

Fig. 5(a) shows that BTB-doped LbL coatings on the OWG allow detection of ammonia below 1 ppm level. It should be mentioned that the lowest detection limit, which can be achieved with composite OWG, does not depend only on the sensing layers quality. Since the accuracy of the optical measurements is often limited by the laser stability and the detector signal-to-noise ratio, which was rather high for the type used here, there is still room for improvement of the overall performance of the device using the same sensing element. The optical response of the OWG sensor based on BTB-doped LbL films formed by 12 DL was linear for NH_3 concentrations at least up to 150 ppm, but the linearity range can be adjusted by varying the amount of dye entrapped into the sensing layer (Malins et al., 2000), which in its turn is determined by the number of DL deposited (Fig. 4(b)).

In contrast to many studies on pH-indicator doped optical sensors for the ammonia detection (Courbat et al., 2009; Shang et al., 2011; Yimit et al., 2003), the attempts to fabricate sensors for gaseous acids are very limited. Yimit et al. (2003) tried to use a BTB-based optical sensor for hydrochloric acid detection, but no change in the light intensity output was found due to optical inactivity of the acid form of the pH-indicator at the He–Ne laser wavelength. Here to fabricate an optical sensor for gaseous acids, a CR dye was entrapped into LbL coatings on the same OWG as was used for the ammonia sensor. The typical response curve of this sensor to HCl vapor is shown on Fig. 5(b). One can see that CR entrapped into LbL reacts with HCl vapor somewhat slower than BTB with NH_3 that can be related to high cross-linking of the film with the dye, however response time is still below 30 s for 1 ppm HCl that is sufficiently fast for the optical sensor. The sensitivity of the sensor obtained is very high and allows detection of acid at the level below 1 ppm. However, a significant drawback of the CR-doped sensor consists in its very slow relaxation time (up to several hours for 12 DL LbL films), while the recovery time for the BTB-doped ammonia sensor is below 5 min in the closed chamber (Fig. 5(a)) and virtually immediate at the open air. Thus, composite OWG with CR-doped LbL coatings can be used only as optical switches for the detection of minor quantities of acids in the atmosphere.

4. Conclusions

Exponentially growing LbL films of a thickness up to 120 nm have been built-up by self-assembly of natural polysaccharides – chitosan and λ-carrageenan – at the glass surface and the surface of K^+/Na^+ ion-exchanged glass optical waveguide (OWG) at pH 5. To impart chitosan–λ-carrageenan LbL films with optical sensing properties toward gaseous ammonia and hydrochloric acid, the preformed LbL coatings have been doped with pH-responsive dyes (pH indicators) – bromothymol blue (BTB) and Congo red (CR) – via dye diffusion process.

Kinetics studies of the dyes entrapment into LbL coatings revealed a significant difference in the behavior of BTB and CR dyes. Amphoteric dye CR diffuses into LbL when the top layer is formed by either chitosan or λ-carrageenan, while anionic dye BTB diffuses only to LbL films with the positively charged outermost layer. Since with increasing LbL the film thickness linearity between BTB loading and film thickness becomes broken due to the hindering BTB diffusion by exponentially increasing thickness of the negatively charged carrageenan layer, the number of DL deposited for fabrication of sensing layers shall be limited to 8–12 DL to balance the thickness and dye content of the polymeric coating.

UV–vis spectroscopy investigation of the dye-doped LbL films in the air and HCl or NH_3 atmosphere has revealed a significant change in absorption of acid and base form of CR and BTB at the wavelength of He–Ne laser (633 nm) that makes them applicable for fabrication of optical waveguide (OWG) gas sensors. The optical response of a composite OWG sensor based on BTB-doped LbL films (12 DL) was linear for NH_3 concentrations at least up to 150 ppm with the lowest detection limit below 1 ppm. The response time of such a sensor was below 1 s that is significantly faster than that of optical sensors based on BTB embedded into plasticized films of synthetic polymers. CR-doped LbL films as an element of OWG sensors showed very high sensitivity to HCl vapor but, due to the very slow relaxation time, can be applied only as optical switches but not as real-time sensors.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.09.076.

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