Fluorescence pH probe based on microstructured polymer optical fiber

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Abstract: A kind of optical pH sensor was demonstrated that is based on a pH-sensitive fluorescence dye-doped (eosin) cellulose acetate (CA) thin-film modified microstructured polymer optical fiber (MPOF). It was obtained by directly inhaling an eosin-CA-acetic acid mixed solution into array holes in a MPOF and then removing the solvent (acetic acid). The sensing film showed different fluorescence intensities to different pH solutions in a pH range of 2.5–4.5. Furthermore, the pH response range could be tailored through doping a surfactant, hexadecyl trimethyl ammonium bromide (CTAB), in the sensing film.

OCIS codes: (060.2370) Fiber optics sensors; (060.4005) Microstructured fibers; (300.2530) Spectroscopy, laser-induced; (280.1415) Biological sensing and sensors.

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1. Introduction

Microstructured optical fibers (MOFs) as a new class of optical fibers have received increasing interest in recent years for their great potential from an application point of view [1, 2]. Their optical properties are primarily determined by the distribution, diameter, and shape of the air holes [3-5]. In addition to these uses, the holes in MOFs can be channels for gas or liquids to flow through, and functional materials can be immobilized simultaneously in them [6-9]. The MOFs have been used to develop new types of fiber-based sensors that can be classified into three types. The first type is fiber optic chemical sensors that are based on evanescent-wave probing for gas- or liquid-phase analyte sensing [10-13]. The second is surface-modified fiber sensors, such as fibers with thin metal or polymer coatings [14, 15]. The third is optoelectronic functionalized fibers, which include metals or semiconductors that allow both optical and electrical transport [16].

In this paper, we describe a new potential of MOFs in the field of pH sensing. In many diverse fields such as medicine, environmental sciences, agriculture, food science, or biotechnology, pH monitoring is an important concern [17]. Several kinds of pH sensors have been proposed, such as field-effect sensors, nanomaterials sensors, and recently, optical fiber sensors [18-22]. Among them, optical fiber-based pH sensors display appreciated features associated with fiber optics, such as electromagnetic immunity, small size, capability of remote measurements, and absence of electrical power at the sensing end. Up to now, most of the reported optical fiber pH sensors have been based on pH-indicator or pH-sensitive fluorescent-dye modified conventional fiber made from glass or polymer [23, 24]. Among them, polymer optical fiber used in sensor fabrication exhibits a higher numerical aperture; this facilitates the launching of a light source and coupling with other optical apparatus or detectors better than the use of silica fiber. Polymer materials such as polymethyl methacrylate (PMMA) show favorable chemical stability, acid resistance, alkali resistance, and biocompatibility, which make them perfect carriers for sensing films. In the case of glass-based fibers, the pH sensing heads are often very fragile, since the unprotected fiber core (normally below 100 µm) is exposed to its surroundings in order to obtain an overlap between the optical field and the analyte sample. Also, pH sensors based on conventional fiber geometries are difficult to use for microanalysis and for *in vivo* measurements, such as in the stomach and blood vessels of the human body, requiring higher sensitivity [25].

The MPOF as a pH-sensing probe is endowed with the advantages of both the POF and the MOF. They are flexible, and their microstructure greatly enhances the specific surface area of sensing. Because the sensing process is carried out in the air holes, microanalysis is possible, and simultaneously damage to the sensing layers can be avoided.

Here, eosin and CA were chosen as the pH-indicator and its carrier, respectively, since the CA has a high permeability for water and ions, and the hydrophobic eosin shows favorable compatibility with CA. By forming eosin-doped CA film on the side wall of holes in the MPOF, a highly sensitive pH sensor probe with a short response time could be fabricated.

2. Experimental

In order to construct this evanescent-wave-based pH sensor, a 2–3 cm length of homemade PMMA MPOF was prepared [26, 27]. The MPOF had 18 air holes arranged in 2 circles with an outer diameter of 760 µm and a hole diameter of 100 µm [Fig. 1(a)].

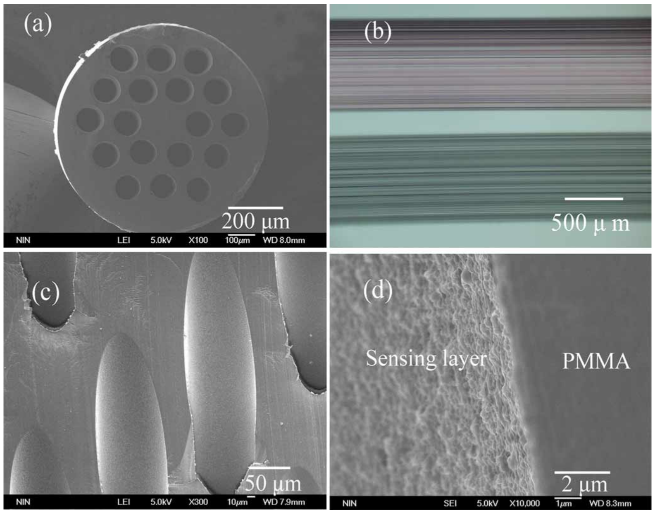

Fig. 1. SEM and photograph of MPOFs. (a) Cross-section of MPOF. (b) Comparison of CA film modified (above) and unmodified (below) MPOFs. (c) CA layer viewed from inclined orientation. (d) Microscopic morphology of a hole surface of the eosin-CA-MPOF.

This larger diameter could ensure the subsequent polymer solution flowing easily through the MPOF. 0.25 g of CA was dissolved in 10 ml of acetic acid (HAc) while stirring at 80°C to form a transparent solution. 10 mg of indicators of eosin were added to the solution. The eosin-CA solution was inhaled into holes of MPOF under pressure of 0.09 MPa, and it immediately spread on the side walls of the holes in the MPOF. An eosin-doped CA film formed on the side walls of the MPOF holes after removal of the acetate acid molecules by blowing on them for 0.5 hour. Finally, the modified holes in the MPOF were washed with a basic aqueous solution at pH 12 for 10 minutes to remove possible dissociative eosin molecules.

The eosin-CA-film modified MPOF presented a pink color owing to the existence of eosin [Fig. 1(b)]. The morphology of the eosin-CA film was observed by scanning electron microscopy (SEM). Figure 1(c) was obtained by cutting the sample in the inclined orientation. From the local magnified SEM [Fig. 1(d)], the morphology of the eosin-CA layer was continuous, homogeneous, and highly porous, as is the nature of CA film. The film thickness was about 100 nm.

3. Characterization and discussion of fluorescence pH probe

In order to test the sensitivity of the proposed design, the eosin-CA-MPOF probe was inserted in a number of given potassium chloride-hydrochloric acid or phosphate pH buffer solutions. The holes were filled immediately with the solution by capillarity. The setup for sensor response monitoring was sketched in Fig. 2 .The excite source was a laser diode. To obtain high sensitivity and to avoid dye bleaching caused by high energy density, a laser beam at 532 nm was extended from 2 mm to 1 cm in diameter with a columniform lens, and the laser beam was orthogonal to the cross-section of the analyte solution-contained eosin-CA-MPOF probe [28, 29]. Emitted fluorescence tunneled through the evanescent field into two cross-sections of the probe. Then the end faces of the analyte solution-contained probe and the end-fiber of the detector were tightly connected in an immobilized connector. The detector end-fiber was a commercial POF with a larger diameter of 1 mm, and it was coaxial with the MPOF, which sufficiently ensures the collection of the fluorescence of the whole probe end. The probe was placed in a dark chamber to prevent it from exposure to external light noise. We measured refractive indices of the analytes using a V-prism refractometer at a temperature of 14.5°C and a wavelength of 589.3 nm (sodium light). Their refractive indexes were 1.3357, 1.3369, 1.3373, 1.3376, and 1.3365, respectively. The refractive index of pure water was also measured, and it was 1.3335. It could be seen that the addition of inorganic salts brings about very weak refractive index changes, and there were very little changes among those of different pH solutions. The PMMA refractive index was 1.49. So, the very little refractive index changes would not influence obviously the evanescent wave guiding in the MPOF probe.

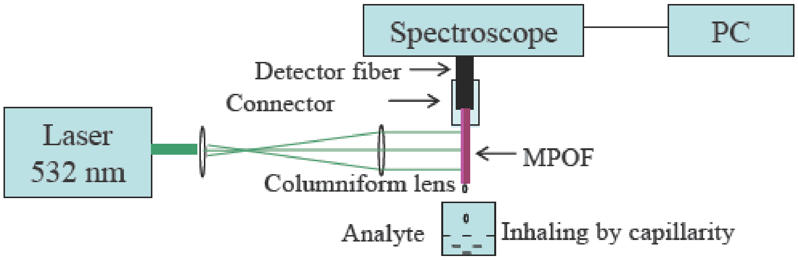

Fig. 2. Sketch of experimental setup for pH sensor probe characterization.

Spectra in the range of 540–650 nm gathered on different pH solutions were shown in Fig. 3. Dynamic tests revealed that the eosin-CA-MPOF probe exhibited a rapid response below 1 second owing to the nanoscale thickness of the film and its favorable hydrophilicity. The intensity of fluorescence exhibited high stability at each pH value. Furthermore, from this figure we could clearly note that the fluorescence intensity increased as the pH value

#89044 - $15.00 USD Received 26 Oct 2007; revised 8 Nov 2007; accepted 8 Nov 2007; published 28 Nov 2007

increased for all wavelengths. The maximum fluorescence peak was located at 570 nm, and no peak shifts were observed during the changing of the pH solutions. The insert in Fig. 3 shows the fiber excited at pH=12, whose strong fluorescence was observed and compared with a low pH value below 1.

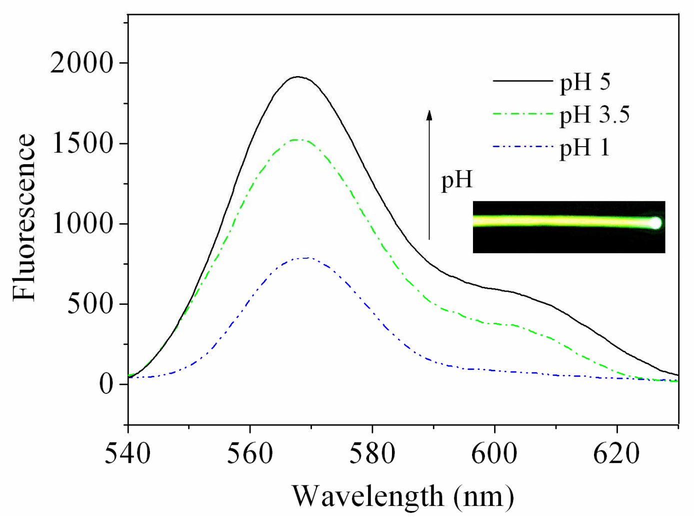

Fig. 3. Fluorescence spectra of eosin-CA-MPOF responding to the different pH of aqueous solutions. Insert: photo of eosin-CA-MPOF excited at pH=12.

The fluorescence intensity at a 570 nm wavelength was plotted against the pH levels in Fig. 4. It was found that when the pH values changed from 2.5 to 4.5, the intensity increased linearly. In the ranges below pH=2.5 and above pH=4.5, there were no remarkable intensity changes. This should be ascribed to the chemical structure change of eosin at different pH values. At a pH level below 2.5, the carboxyl of eosin mainly existed in form of inner ester. Low fluorescence of eosin was observed in this form. Oppositely, with the increase of pH, its structure was changed into an ionic form molecule and presented higher emission intensity. When the pH was above 4.5, eosin completely transformed into its ionic form and gained maximum intensity, 110% of the inner ester form.

It has been reported that immobilizing surfactants on sol–gel matrices could affect the chemical and spectral properties of co-entrapped pH indicators [30]. Based on this point, we also investigated the effect of co-entrapment of surfactants with eosin on the pH response in the CA matrix of a pH sensor probe.

The co-entrapment of eosin in a CA matrix with cationic surfactants, hexadecyl trimethyl ammonium bromide (CTAB), was investigated for pH sensing (mole ratio 1:1, CTAB to eosin). The plots of the emission intensities versus pH-exhibited S-shaped calibration graphs like a pure eosin-doped response curve (Fig. 4). Notably, the CTAB co-entrapment shifted the pH response range to a more acidic value as compared with CA film that was not co-entrapped. Apparent pKa values were calculated via equation:

$$\mathrm{p}K_a = \mathrm{pH} - \log \frac{I_{\mathrm{acid}} - I_{\mathrm{x}}}{I_{\mathrm{x}} - I_{\mathrm{base}}}, \quad (1)$$

where I_{acid} and I_{base} were signal intensities of eosin in their acid and conjugate base forms, respectively. I_{x} was the defined pH signal intensity [31]. In this condition, the pKa value was found to be reduced to 2.8 from the original 3.5 in the condition that was not co-entrapped. This result would produce an active phase for monitoring lower pH values than the range of above eosin-CA-MPOF. It should be pointed out that the eosin seemed to be in a different environment when the surfactant co-entrapment took place. Because eosin (ionic form) had an

#89044 - $15.00 USD Received 26 Oct 2007; revised 8 Nov 2007; accepted 8 Nov 2007; published 28 Nov 2007

opposite charge to the co-trapped cationic surfactants (hexadecyl chain), the main interaction between them was ionic [32]. Then, a higher proton concentration was needed to compete with the strong interaction between the CTAB and the indicators as well as to overcome repulsions from the cationic surfactant headgroups. Additionally, though the CTAB caused the sensitivity to reduce from 470 a.u./pH to that of 231 in value, each curve gave enough of an intensity change above 80% (relative to minimal values) to ensure the sensing process.

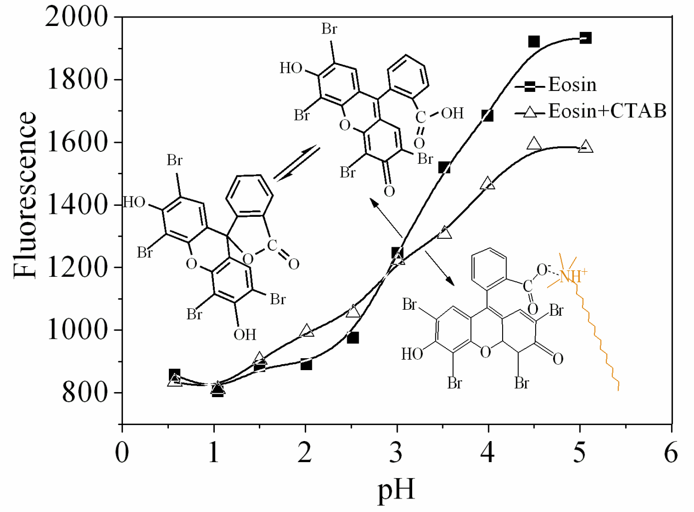

Fig. 4. Response curve of the pH sensor probe and effect of co-entrapment of CTAB on the response results.

In order to check reproducibility of the new pH probe, three pieces of the same MPOF were deposited with sensing films under the same conditions. These MPOF probes then were filled with the same pH buffer solution and inserted into the connector separately. Results showed the fluctuation of fluorescence intensity was below 2%.

4. Conclusions

In summary, we have successfully prepared a pH-sensitive dye-doped CA-film-modified MPOF probe by using a liquid-phase coating method. By tailoring the pH response range with surfactants CTAB, the eosin-CA film-modified MPOF or eosin-CTAB-CA film-modified MPOF as an optical pH sensor probe showed both a short response time and a wide response range from pH 1.5 to 4.5. The present work demonstrates new possibilities for applications of MPOF in the fields of optical microanalysis or *in vivo* biosensing, such as acidity detection in the human body.

Acknowledgments

This work was supported by the National Natural Science Foundation of China project 60437020 and the High-Tech Research and Development Program of China number 2007AA032452.

#89044 - $15.00 USD Received 26 Oct 2007; revised 8 Nov 2007; accepted 8 Nov 2007; published 28 Nov 2007