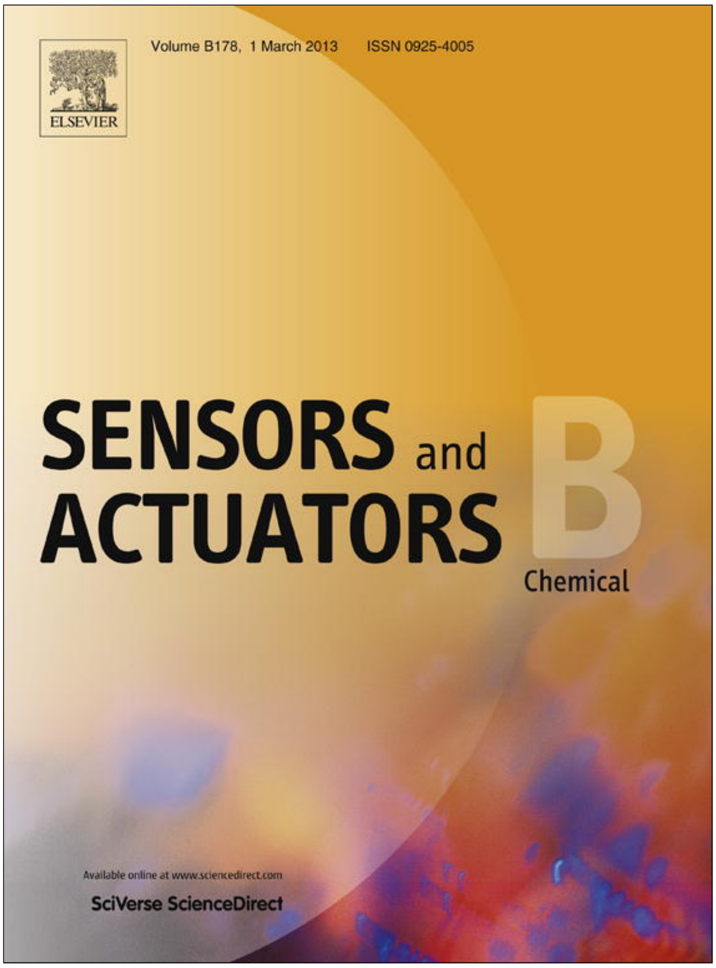
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Absorption-type optical pH sensitive film based on immobilized purple cabbage pigment

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ABSTRACT

A new absorption-type optical pH sensitive film was prepared by immobilizing purple cabbage pigment (PCP) in sol–gel film. For preparation of the pH sensitive film, PCP was entrapped in sol–gel film and then coated on glass slides by dip-coating method. The sensing properties of the PCP-pH sensitive film were examined by ultraviolet–visible spectrophotometer and *p*-polarized reflectance method. The results indicate that the film responds rapidly (within 1–2 min) over a wide pH range of 2–11 with linearly calibration. The relative standard deviation (R.S.D.) of its reproducibility is less than 0.3%. In addition, the refractive index n_f and the thickness d_f of the film are not changed with different pH values. However, the extinction coefficient k_f of the film changes regularly as pH changes, tendency of which is consistent with that of the film absorbance at 633 nm. Therefore, PCP-pH sensitive film is proved to be an absorption-type film, which is promising to design absorption-type pH sensor.

1. Introduction

pH measurement and control has attracted attention of many researchers, since it is widely required in biomedical, chemical, environmental science and engineering [1–3]. Compared to traditional pH detective methods, optical pH sensor has many advantages, such as immunity to electrical interference, fast response, safety and possibility of micro-area measurement [4,5].

Optical pH sensor is based on pH-induced reversible change in optical or spectroscopic properties. Its key part is pH sensitive film, which is usually prepared by immobilizing acid–base indicators or fluorescent indicators in appropriate support materials. In previous works, pH indicators such as neutral red, bromophenol blue, bromocresol green [6–8] have been used for preparing pH sensitive films. However, most indicators are sensitive over a narrow pH range of 3–4 pH units. To widen pH range, attempts have been made by employing several indicators with different dissociation constants (pK_a) or indicators with two or three pK_a values [9].

Purple cabbage pigment (PCP) is a kind of natural pigment extracted from purple cabbage, which is an environmental friendly pH indicator and sensitive in a broad pH range [10,11]. Its main component is anthocyanin. The structure of anthocyanin undergoes transformation as pH changes, which is shown in Fig. 1. It is predicted that preparing pH sensitive film using PCP may have broad useful dynamic range for pH measurement.

The immobilization process can be performed using different support materials, including agarose membranes, ionic polymers, hydrophilic polymers and sol–gel films [12–14]. The sol–gel method is the relatively popular and simple technique, which forms a porous silica matrix providing easy access to entrap the indicator molecules. It has been reported that immobilizing pH indicators in sol–gel matrix could yield a stable reversible and highly sensitive film [15].

It is important for designing pH sensors to measure the optical parameters of sensitive film, including refractive index n_f, extinction coefficient k_f and thickness d_f. Compare to ellipsometer, *p*-polarized reflectance method is simpler in principle, more convenient in measurement and higher resolution about more than 10^{-4} in extinction coefficient, which is more suitable for measuring the optical parameters of sensitive film [16].

In this work, natural indicator – PCP was immobilized into sol–gel film to prepare pH sensitive film, which was different from previous work that used several indicators together to broaden pH range [17]. The absorbance spectra and the optical parameters of the PCP-pH sensitive film were monitored by ultraviolet–visible spectrophotometer and *p*-polarized reflectance method, respectively. It was found that the PCP-pH sensitive film worked well over a wide dynamic range of 2–11 with linear calibration curve. *p*-Polarized reflectance experimental results further suggested that the film was an absorption-type sensitive film that had a great application to fabricate pH sensor.

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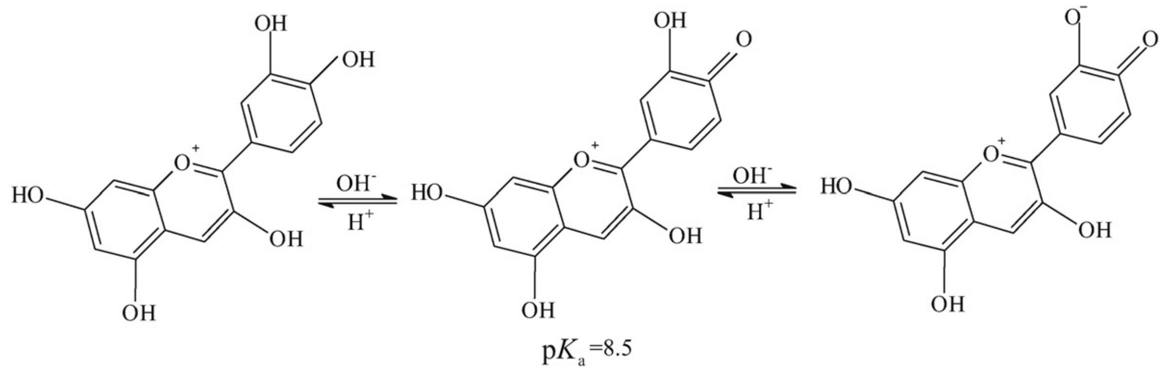

Fig. 1. The structure of anthocyanin at acid–base conditions.

2. Experimental

2.1. Reagents (chemicals and solutions)

All reagents were of analytical reagent grade. PCP was obtained from Anhui Sunshine BIO-tech Co. The following chemicals were supplied by Sinopharm Chemical Reagent Co. Ltd.: tetraethoxysilane (TEOS), anhydrous ethanol (EtOH), Triton X-100, hydrochloric acid (HCl) and sodium hydroxide (NaOH). Test solutions were adjusted by 0.1 mol/L HCl and 0.1 mol/L NaOH to the desired value. All aqueous solutions were prepared with deionized water supplied by UP ultrapure water purification system with resistivity of 18 MΩ cm.

2.2. Preparation of sol–gel pH sensitive film

The sol–gel film was deposited on the glass slide by dip-coating method. The glass slides with 9 mm width and 1 mm thickness as well as K9 optical glasses with diameter of 35 mm and thickness of 4 mm were used as coated substrate to prepare pH sensitive film sample. The former samples were used to test the absorption spectra and the later ones were for measuring the optical parameters of the film. The surfaces of the K9 optical glasses were polished and the parallelism was better than 1′. All the glasses were ultrasonically cleaned in 10% HCl, deionized water and 7% NaOH for 30 min, respectively. Then all the glass slides were further cleaned by deionized water and ethanol.

The sol was prepared at room temperature using 15 ml TEOS, 45 ml EtOH, and 12 ml deionized water mixed with 3% Triton X-100, along with 0.42 g PCP. The sol was briskly stirred using the magnetic stir bar at room temperature for 2 h. After aged three days, the PCP composite sols were ready for coating.

The cleaned glass slides were vertically dipped into and withdrawn from the sol with a uniform velocity of 10 cm/min. After coating, the samples were dried in loft drier at 30 °C for 10 days. Then the coated glass slides were washed under flowing water to remove the excess and unbound indicators.

2.3. Instruments

A Bante 920 pH meter with a combined glass electrode was used for monitoring pH adjustment. A JASCO V-570 UV–VIS spectrophotometer was used for recording the visible spectra and absorbance measurement. The experimental set-up for testing the optical parameters of the film in different pH solutions is shown in Fig. 2. A 632.8 nm He–Ne laser with the power of 2 nW was used as the light source, and a Glan–Taylor prism with an extinction ratio of 10^{-5} was used to generate *p*-polarized light. For a *p*-polarized laser beam with the intensity I_0 falling onto the surface of the sample at incident angle θ_i, two reflected beams I_a and I_b, from the front and back surfaces, were received by CCD. The sample and CCD were set up on a mechanical rotating stage with a precision within 2′. The intensity ratio γ ($\gamma = I_a/I_b$) is dependent on the θ_i and the optical parameters of the film. After monitoring experimental $\gamma - \theta_i$ curve for θ_i from 50° to 60°, it was straightforward to obtain the optical parameters of the film by means of data fitting [16].

3. Results and discussion

3.1. Absorbance spectra properties of PCP pH sensitive film

The spectral change is the result of an acid–base equilibrium of indicators. These changes are completely reversible with variation of pH value. Spectral measurement was made by ultraviolet–visible spectrophotometer. To measure the absorption spectra, the film was immersed in solutions with different pH values. The spectrum was scanned several times in the wavelength range of 400–800 nm for each pH value until the absorbance spectra of the film get stable.

Fig. 3(a) shows the absorption spectra of dissolved PCP at different pH values. The spectral characteristic of PCP shows a distinct maximum absorbance in the visible region at 529 nm, and the absorbance of PCP decreases with pH value increasing. The absorption spectra of PCP sensitive film at different pH levels are shown in Fig. 3(b). The maximum absorbance of the film appears at 533 nm, which shows a small red shift compared to that of the dissolved form. Furthermore, the extent of variations of absorbance with different pH is also diminished for the film. These differences may be attributed to establishment of hydrogen bonds between silicon–oxygen bond in the sol–gel support and the oxygen ion of PCP, which changes its optical properties. Similar observations have been reported by others [18,19]. The absorbance of the film at 533 nm is used for quantitative measurements.

Fig. 4 shows a typically calibration curve derived from absorbance measurement of the film at 533 nm in pH range of 2–11. As the pH increases, the absorbance decreases. The absorbance of PCP sensitive film varies almost linearly, with an equation of

$$A = -0.00314\,\mathrm{pH} + 0.15474$$

And the coefficient of determination (R^2) is 0.99236. It shows that PCP film has a wide dynamic range with straight line fitted to the experimental data. We also measured the absorbance of PCP sensitive film at pH value lower than 2 and higher than 11. Both the absorbance of these two regions at 533 nm are not matched the tendency mentioned above. There is no obvious absorbance change at pH value lower than 2. When the film immersed in the solution with pH value of 12 and 13, the maximum absorption wavelength

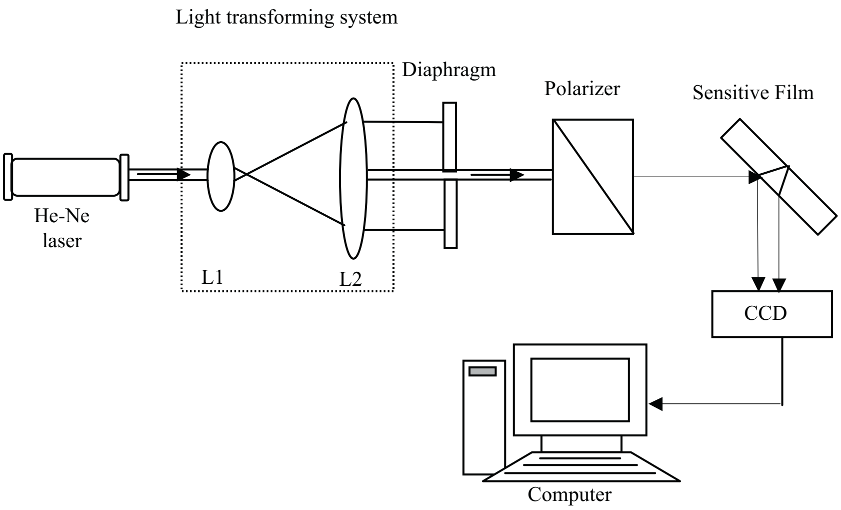

Fig. 2. Schematic diagram of the *p*-polarized reflectance experiment.

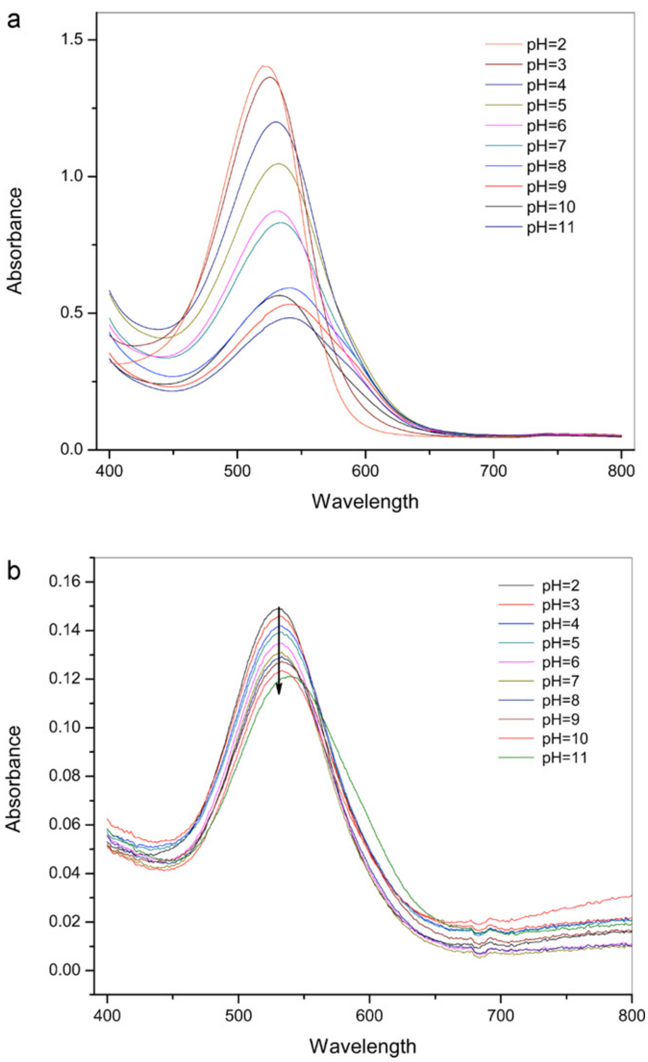

Fig. 3. Absorbance spectra of PCP pigment in pH range of 2–11 for different forms. (a) Dissolved form and (b) immobilized form. The PCP concentration was 3.45×10^{-5} mol/L and 1.92×10^{-5} mol/L in aqueous solution and the film, respectively.

of the film shifted to 597 nm and 609 nm respectively, corresponding to the color change of the film from pink to mauve and blue. The reason is that anthocyanin ionization equation shown in Fig. 1 shifts rightward as pH increases, and the structure change leads to the color change. Furthermore, the sensitive film will loss efficacy when the pH of solution is higher than 13, which leads to the absorbance of the film reduces or even vanishes. Therefore, this film is inapplicable for measurement at strong alkaline condition. All the experiments were conducted in sealed room at room temperature about 25 °C, maintained by air-condition. The temperature fluctuant is tiny (about ±0.5 °C), which has a negligible effect on pH film response [20].

The reproducibility and the response time are important features of the sensitive film. The reproducibility of the PCP sensitive film was evaluated by alternating the pH several runs between 2, 7 and 11. The reversible response of the PCP sensitive film is depicted in Fig. 5. The results demonstrate that the response of this film is fully repeatable in the test pH range of 2–11. The relative standard deviation is less than 0.3% for the both pH level. The response time of the sensitive film was measured less than 2 min.

Therefore, the pH sensitive film based on immobilized PCP has a fast response in a wide pH range of 2–11. Additionally, this liner calibration method makes the practical operation of the pH film simpler and more practicable than that of non-linear multivariate calibration methods in previous works [21].

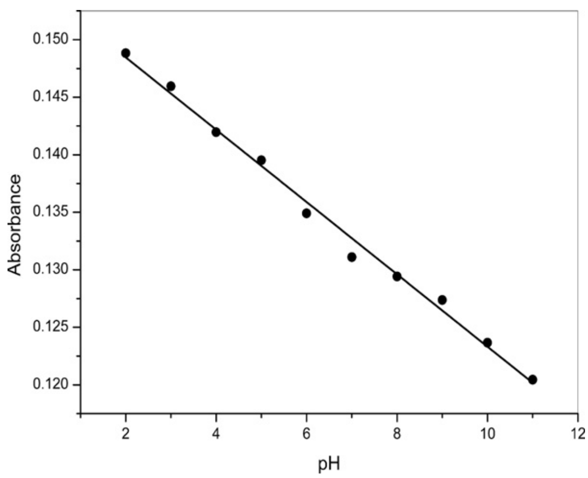

Fig. 4. Calibration curve of PCP sensitive film at 533 nm in a pH range of 2–11.

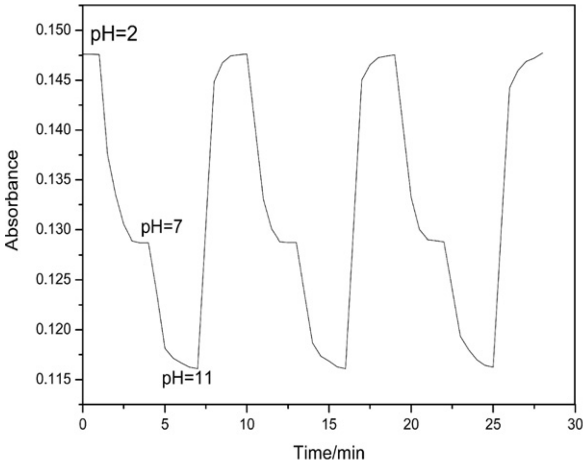

Fig. 5. Variation of the absorbance of the film at 533 nm for alternating the pH value between 2, 7 and 11.

3.2. Optical parameters of PCP pH sensitive film

We measured the angular modulation curves of the reflectance ratio of *p*-polarized reflectance under incident angle range of 50–60° and did numerical curve fitting to obtain the film optical parameters at the pH range of 2–11. Fig. 6 shows typically experimental $\gamma - \theta_i$ curve and theoretical fitting line for pH value of 2 and 3. Table 1 shows the optical parameters of the film in the pH range of 2–11. From the table, it can be seen that the film reflective index almost unchanged with pH value increasing. It is likely that the reflective index of the film mainly depends on the structure of silica matrix. pH solutions merely react with the PCP indicator entrapped in the silica matrix, which has little effect on the reflective index of the film. In addition, no obvious change on the thickness of the film indicates that swelling or shrinking processes would not happen on the film as pH changes and the film has good thickness uniformity.

Whereas, the film extinction coefficient changes with the variation of pH value. This is because the reaction between pH solutions and PCP indicator changes molecular structure of PCP, which manifests as color changing. It will evidently influence the extinction coefficient of the film. The relative value of the extinction coefficient and the absorbance of the film at 633 nm in the pH range of 2–11 was also calculated and shown in Fig. 7. Through the comparison, the extinction coefficient and the absorbance of the sensitive film has the same trend with pH increasing, which is in agreement with Lambert Beer law. A tiny difference shown in Fig. 7 may be attributed to minor differences in wavelength of light source. Therefore, the rationality and correctness of the optical pH sensitive model by *p*-polarized method is obvious.

The PCP sensitive film is proved to be an absorption-type film, which has a great potential application in designing pH sensor. The pH solutions merely affect the film extinction coefficient, showing as the change of signal intensity. This can be applied in pH sensor which simply requires detecting the signal intensity at a given wavelength. The pH sensors based on *p*-polarized reflectance, absorbance measurement and optical fibers are typical models. In *p*-polarized reflectance experiment, the signal intensity changes mainly show as the variation of maximum reflectance ratio at different pH solutions, which can be seen in Fig. 6 obviously. In addition, we can apply our film in the sensing system proposed by Hashemi et al. [12]. In his sensing system, a flow through cell was used for flow absorption measurement. A peristaltic pump was used for pumping solutions through the flow cell automatically. The pH value of the solution can be simply detected by measuring the absorbance of the film at given wavelength. Furthermore, the film

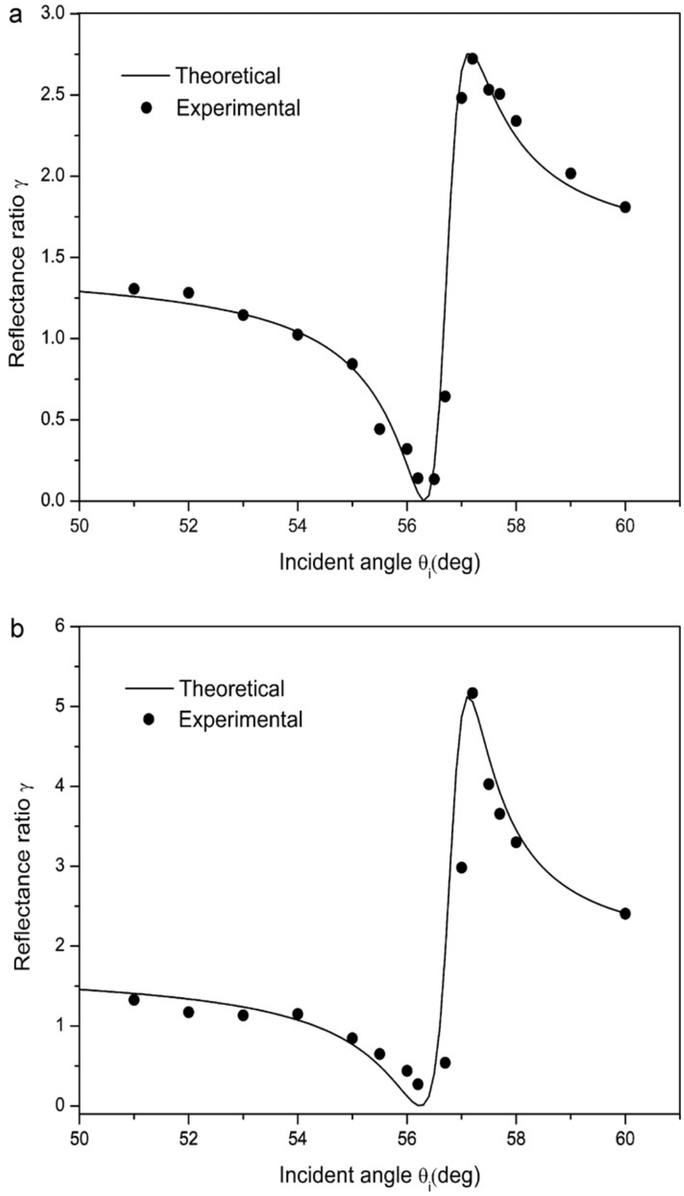

Fig. 6. Experimental $\gamma - \theta_i$ curve and theoretical fitting line of film optical parameters at different pH values. (a) pH = 2 and (b) pH = 3.

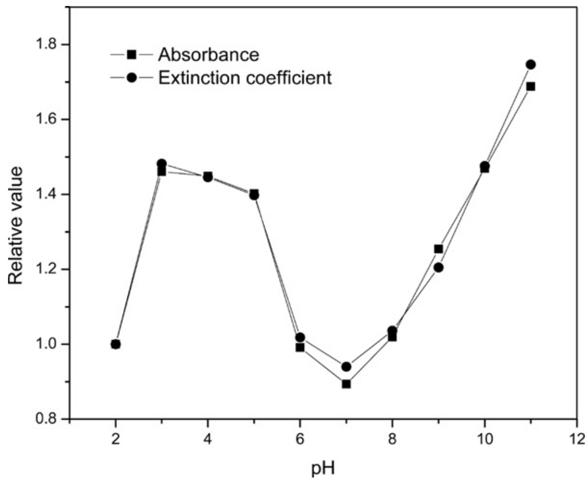

Fig. 7. The relative value of extinction coefficient and absorbance of PCP sensitive film at 633 nm in a pH range of 2–11.

Table 1
The optical parameters of the sensitive film in the pH range of 2–11.

pH value	2	3	4	5	6	7	8	9	10	11
Refractive index n_f	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47
Extinction coefficient k_f	0.0166	0.0246	0.024	0.0232	0.0169	0.0156	0.0172	0.02	0.0245	0.029
Thickness d_f/nm	241.2	241.3	241.2	241.2	241.2	241.2	241.2	241.2	241.5	241.5

can be applied on optical fiber sensor. Dong et al. have proposed an optical fiber sensing model [17], which is useful for actual measurement. We can measure the transmitted power of the sensor to detect the pH value of the solution.

4. Conclusions

An absorption-type optical pH sensitive film based on immobilized PCP in sol–gel film has been demonstrated. The PCP sensitive film linearly responds over a broad dynamic pH range of 2–11 within 2 min and its reproducibility is less than 0.3%. The refractive index n_f and thickness d_f of the film is not changed with variation of pH value. While the film extinction coefficient k_f changes regularly as pH increasing, tendency of which is in agreement with that of the film absorbance at 633 nm. It is suggested that the sensing model based on *p*-polarized reflectance method is reasonable and this PCP-pH sensitive film is an absorption-type film. Our preliminary results show that the natural indicator PCP is promising in preparing pH sensitive film, and the PCP sensitive film has a great application in fabricating absorption-type pH sensor.

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