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IMMOBILIZATION AND PHOTOCHEMICAL STUDIES OF BROMOCRESOL PURPLE IN SOL-GEL MEMBRANE

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Abstract. pH-sensitive indicator bromocresol purple was immobilized in sol-gel membrane. Inorganic silicate TEOS was utilized as a precursor during experiments. Different factors influencing the properties of final material were studied. Spectral characteristics of the indicator were also investigated.

Keywords: indicator, sol-gel, absorption, immobilization, pH-sensor.

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1. Introduction.

The sol-gel technology has been becoming one of the most attractive methods in materials science and analytical chemistry. Unlike traditional silica glasses, sol-gel derived glasses have numerous of advantages: tunable pore size and surface chemistry (versatility), extended composition ranges, better homogeneity, less energy consumption – more greener, uses simple lab equipment (low cost) and can be used to immobilize less thermal unstable molecules and even biomolecules.

In most experiments tetraethoxysilane (TEOS) and organically modified silicates are used because of many attracting properties [1-3]. Because silicate based precursor are more tunable in contrast to d-block metal containing counterparts. Sol-gel based membranes was successfully utilized in multianalyte sensor and shown great advantageous [4]. Ammonia sensor was also proposed using bromocresol purple and fast response time of 10 s was achieved [5]. TEOS based sensors also used in not only preparation of optic sensors, but also electrochemical sensors [6].

In this paper we present results of immobilization a pH-sensitive indicator bromocresol purple in TEOS based sol-gel membrane. We also studied pH-response of final materials and proposed optimal preparation parameters. Prepared pH-sensitive membranes were studied using different physicochemical techniques and discussed.

2. **Experimental**.

2.1. Materials and methods.

Tetraethoxysilane (TEOS) was purchased from Haihang Industry Co.,Ltd (PRC); ethanol (EtOH), bromocresol purple (BCP), hydrochloric acid (HCl) and nitric acid (HNO_3) were analytical grade and used without any purification. All buffers and solutions prepared using chemical pure grade reactants and doubly distilled water used as solvent.

2.2. Preparation of sol-gel membranes.

Sol-gel solutions were prepared mixing 4 ml of TEOS, 4.1 ml of EtOH (2.88 ml of MtOH) for 15 minutes. 1.3 ml 0,01M HCl aqueous solution was added in order to start hydrolysis and condensation reactions. pH of the final solution was adjusted to 2 since this solution was found to be optimal. Resulting solution was mixed for 4 hours at room temperature. Then 40 μl of 0.1M BCP in EtOH solution was added and another 30 minutes was mixed. In order to study water to alkoxide ratio *R* several sol cocktails were prepared and the content is given in Tab. 1.

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Table 1.

Content of solutions used in experiment

No	Alkoxide	Solvent	R ratio	Catalyst
1	TEOS	C_2H_5OH	1:1	HCl
2	TEOS	C_2H_5OH	1:2	HCl
3	TEOS	C_2H_5OH	1:3	HCl
4	TEOS	C_2H_5OH	1:4	HCl
5	TEOS	C_2H_5OH	1:5	HCl
6	TEOS	C_2H_5OH	1:6	HCl
7	TEOS	CH_3OH	1:1	HCl
8	TEOS	CH_3OH	1:2	HCl
9	TEOS	CH_3OH	1:3	HCl
10	TEOS	CH_3OH	1:4	HCl
11	TEOS	CH_3OH	1:5	HCl
12	TEOS	CH_3OH	1:6	HCl

Solution of sol then remained for 24 hours for aging. Microscope slides were taken and cut into 0.6x4 cm pieces. All glasses were activated in nitric acid for 1 hour and rinsed with ethanol and copious amount of water before dip coating process. Preparation steps of samples are given in Fig. 1.

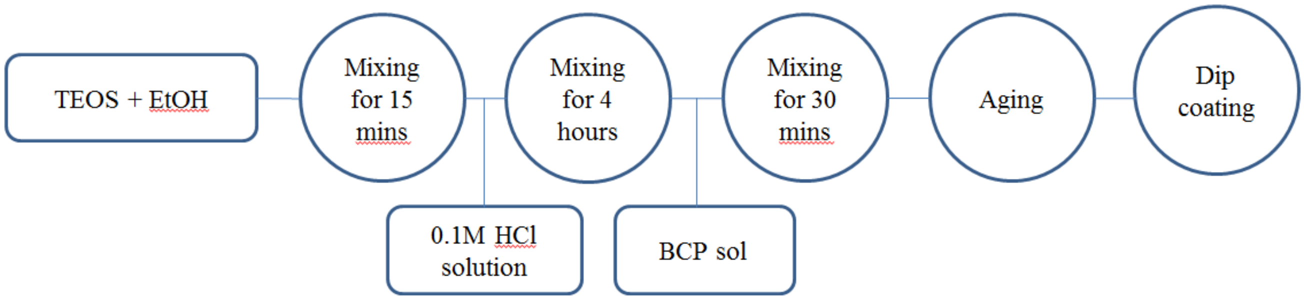

Fig. 1. Schematic diagram of sample preparation steps.

2.3. Spectroscopic studies of prepared membranes.

Absorption measurements was done on the UV-vis spectrophotometer EMC-30PC-UV (EMC Labs Germany) and surface of prepared membranes was investigated using the light microscope Optika (Germany). Sensor membranes was rinsed in distilled water and dried before each experiment.

ISSN 2320-9186

3. Results and discussion.

Preparation of BCP@TEOS optical membrane was prepared and investigated. During the experiment several sol cocktails with different contents were prepared and we found that the most optimal result achieved at pH=2 sol solution and R ratio of 4 (Table 1). When using more basic solutions, sensor film shown more distinct cracks and the homogeneity of films deteriorated.

In order to study optimal indicator concentration, we also prepared series of sol-gel solutions and found BCP concentration has to be around $4 \cdot 10^{-4}$ M. Decrease in concentration reduces the sensitivity and increase diminishes the homogeneity of membrane.

Figure 2 show the absorption spectra of BCP in acidic media. As shown there is a maximum around 433 nm. The intensity of the peak decreases as the pH of solution increases. In neutral solution BCP has two peaks at 433 and at 588 nm. Absorption spectra of BCP in basic solutions are given in Figure 3. Increase pH makes the second peak more intense and the solution turns violet immediately. Isosbestic point was observed at 490 nm. The spectral characteristics of BCP in very acidic and basic solution is given in Figure 4.

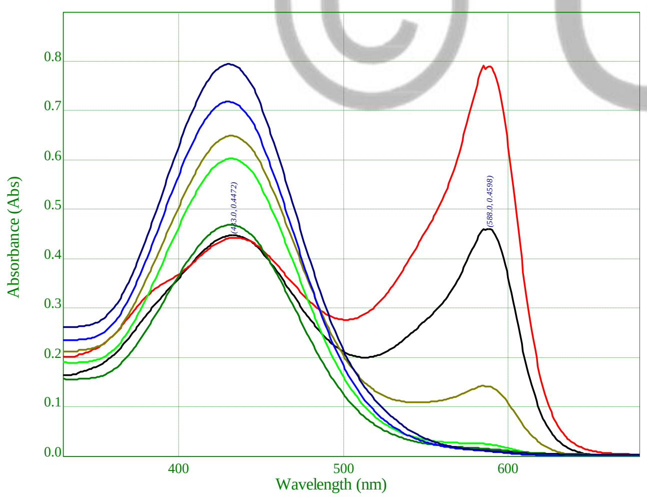

Fig. 2. Absorption spectrum of BCP in acidic solution. Intensity at 433 nm decreases as pH increasing. The black line is in distilled water.

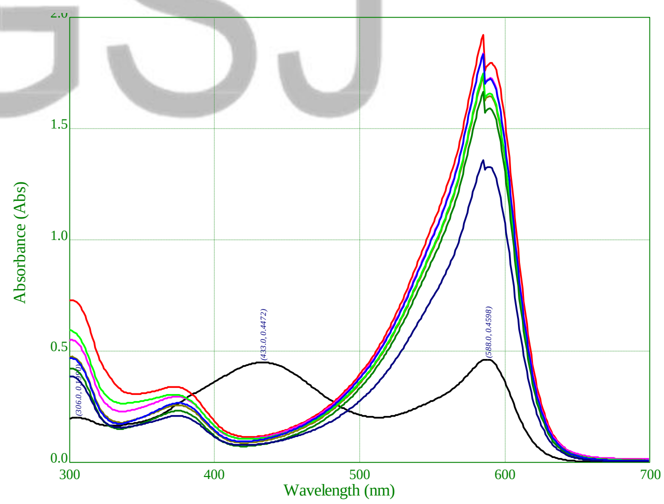

Fig. 3. Absorption spectrum of BCP in basic solution. Intensity at 588 nm increases as pH increasing. The black line is in distilled water.

Fig. 5 shows the spectra of BCP doped in sol–gel glass. The absorption spectra of BCP doped sol–gels reassembles to the spectra of BCP in aqueous solutions (Fig. 2-4). At low pH, the absorbance maximum is at 433 nm, and this peak decreases as solution pH increases. There is only a slight red shift of the absorbance maximum in the sol–gels comparing to the aqueous solutions, e.g. the absorbance maximum are

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436 in acidic solutions. In aqueous solutions, comparison of spectra in aqueous solutions and in the sol-gel matrix has striking differences in case of intensity of peaks. This phenomenon causes because of strong acidic media in pore of matrix. But film has very fast response without a heat treatment.

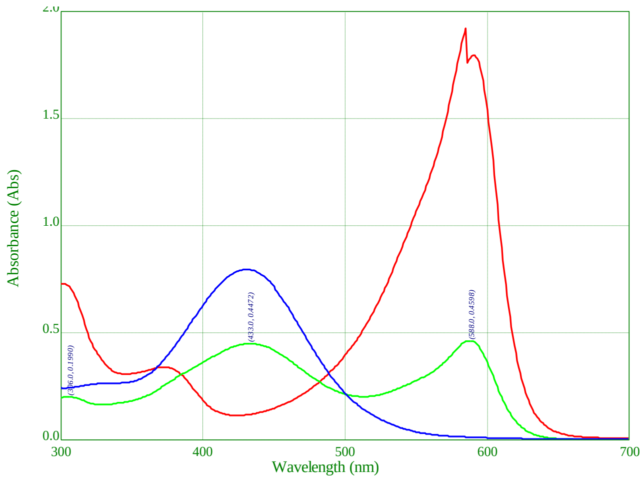

Fig. 4. Absorption spectrum of BCP at pH=1 (blue line) acidic solution, at pH=7 (green line) neutral solution, and at pH=13 (red line) basic solution.

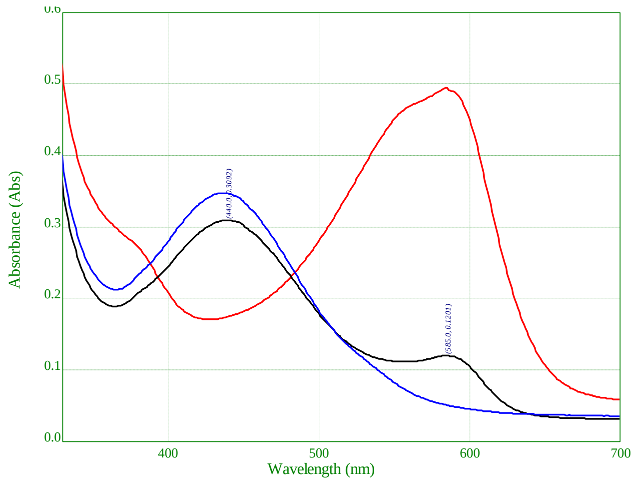

Fig. 5. Absorption spectrum of BCP@TEOS membrane at pH=1 (blue line) acidic solution, at pH=7 (black line) neutral solution, and at pH=13 (red lone) basic solution.

Films prepared using MtOH as a solvent show similar behavior, but the surface shown more cracks and we decided to use EtOH as a solvent.

Conclusions.

pH indicator BCP was immobilized in optical film using the sol-gel technology. The spectroscopic properties of prepared film to pH at room temperature were investigated. The response of the sensor is fast, exhibits good reversibility and repeatability. These experimental results have shown that a fast response optical fiber evanescent pH sensor can be constructed using the sol-el process.

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