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Polyaniline-Coated Polysulfone Membranes as Flexible Optical pH Sensor

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Abstract: A new optical pH sensor based on Polysulfone (PSU) and Polyaniline (PANI) was developed. The transparent and flexible PSU membrane was employed as a support. The electrically conductive and pH-responsive PANI was deposited onto the membrane surface by *in situ* chemical oxidative polymerization (COP). The absorption spectra of the PANI-coated PSU membranes exhibited sensitivity to pH changes in the range of 4-12, which allowed for designing dual wavelength pH optical sensor. The performance and durability of the membranes were assessed by measuring their response starting from high pH and going down to low pH, and vice versa. The effect of synthesis conditions and film thickness were investigated. The effect of the membrane's storage conditions on the reproducibility of the results was also investigated.

Keywords: Optical pH sensor membrane; flexible pH sensor; polysulfone; polyaniline; chemical oxidative polymerization.

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1. Introduction

Polymeric membranes have been widely utilized as immobilization matrices for various types of sensors including optical chemical sensors [1, 2], biosensors [3, 4] potentiometric sensors [5-7], and amperometric sensors [8, 9]. Solid polymeric membrane supports offers advantages such as fast response time, minimal calibration requirement, flexibility, low cost and possibility for deposition into various types of substrates [10]. The performance of polymeric membranes can be enhanced by surface functionalization/ grafting with hydrophilic/ hydrophobic sites for obtaining maximum interaction with specific analyte [6, 11].

Optical sensors have been employed commercially for determination of pH, heavy metal ions, CO_2 and O_2 gases and clinical parameters such as glucose and bacteria in blood [12]. Optical pH sensors are used for measurement and control of pH for applications in chemistry [11], biochemistry [13], clinical chemistry [14, 15] and environmental sciences [16]. In this paper, we report a novel, simple and cost effective method for preparation of optical pH sensor based on polyaniline-coated polysulfone (PANI-coated PSU) membranes with a well-defined pH response and reproducibility in the pH range of 4-12.

2. Experimental Section

Polysulfone membranes were casted from chloroform with different concentrations. The *in situ* chemical oxidative polymerization was carried out by placing PSU membranes into various concentrations of aniline/1M HCl solutions, followed by addition of APS/1 M HCl solutions (Table 1). After a certain period of reaction time, the resulted PANI-coated PSU membranes were removed and washed repeatedly with methanol and 1M HCl to insure the removal of unreacted monomer, oligomer and initiator species. The spectra for PANI-coated PSU membranes were recorded in the range of 400-1000 nm with different standard pH solutions using Cintra 2020 spectrometer.

3. Results and Discussion

3.1 Optimization of the reaction conditions

Polysulfone membranes were coated with polyaniline by *in situ* COP of aniline monomer in the presence of ammonium persulfate (APS) as redox initiator**.** After the coating process, the transparent PSU membranes turned into green due to precipitation of conductive polyaniline on the surface of PSU membranes. In order to obtain a maximum absorbance response of the coated membranes, the reaction conditions were optimized by variation of the reaction time, **Table 1**.

Table 1 Reaction conditions during the OCP. (Aniline: APS) molar ratio was fixed to (1:1.25). All reactions were carried out at room temperature using 1 M HCl as solvent.

Membrane Code	**Monomer Concentration (mole/L)**	**Reaction time (min)**	**Absorbance at pH 4 (λ_2= 825 nm)**
M1	0.05	10	0.63
M2	0.05	20	1.08
M3	0.05	180	2.60

3.2 Performance of PANI-coated PSU Membranes as Optical pH Chemical Sensor

The prepared membranes were tested as optical pH chemical sensor in the visible and Near Infra-Red (NIR) regions, in the range of 400-1000 nm. As shown in Fig. 1, PANI-coated PSU membrane exhibits well-defined pH sensitivity in the pH range of 4-12. The experiments were conducted from pH 4 to 12, with 1 pH unit increment. After each experiment, the coated membrane was rinsed twice with distilled water, placed in the new pH buffer solution and the corresponding spectrum was recorded immediately without further delay or additional equilibration time. The response of the membrane to the newly added buffer solution occurred within a period of less than 10 s. As can be inferred from Fig.1, increasing the pH from 1 to 12 leads to the shift of absorption maxima of coated PANI from 825 nm (at pH 4) to 600 nm (at pH 12). The protonated form of polyaniline Emeraldine Salt (ES) have green color in acidic solutions, which turns into blue colored deprotonated polyaniline Emeraldine Base (EB) in basic solutions *via* doping/dedoping process [17, 18].

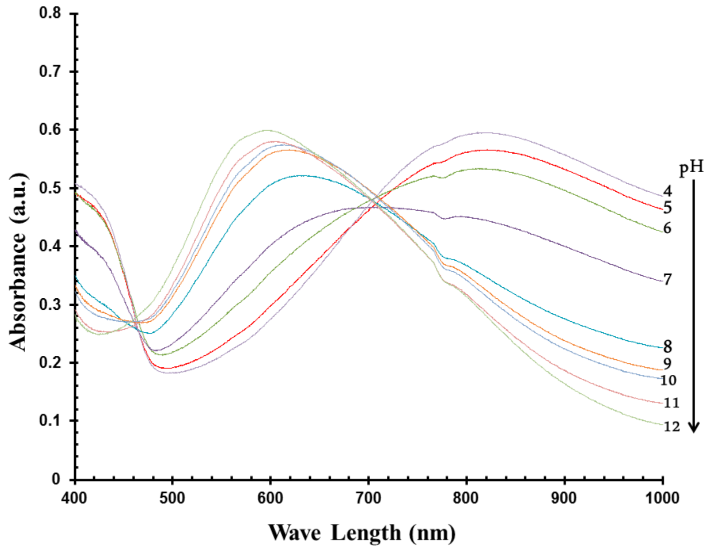

Figure 1. Absorption spectra of the PANI-coated PSU membranes at different pH**.**

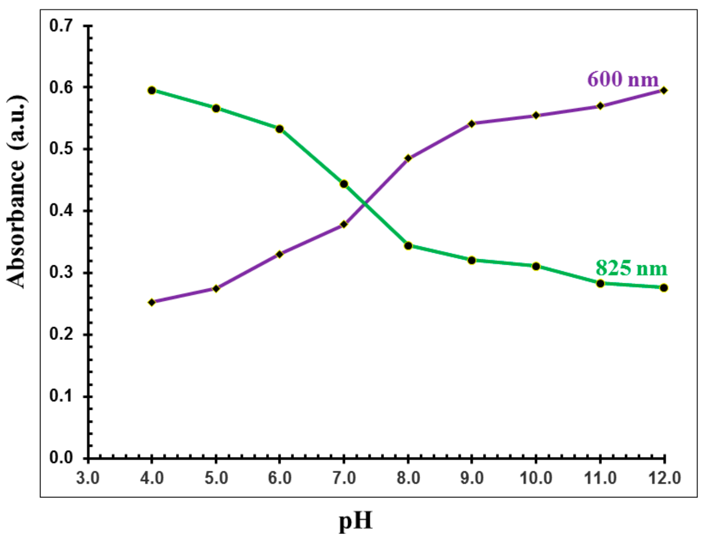

Figure 2. The absorbance change of PANI-coated PSU membranes vs. pH at 600 and 825 nm**.**

The dual wavelength calibration curve was constructed by plotting the pH dependence of the absorptions at 600 and 825 nm, Fig. 2. The apparent pK_a value of the PANI coating is 7.35, representing the pH value where the two sigmoidals intersect (concentration of ES is approximately equal with the concentration of EB). A sigmoidal curve with similar trend was obtained for polyaniline films coated in the inner walls of polystyrene cuvettes, at 600 and 840 nm, with apparent pK_a value of 7.38 [19]. Florea *et al.* [20] reported the absorbance *vs*. pH dependence curve with similar sigmoidals pattern for the PANI-coated optical pH sensor integrated into microfluidic device, with apparent pK_a value of ≈ 5. In a different behavior, the curves obtained for polyaniline-polyvinyl alcohol (PANI-PVA) composite membrane did not exhibit similar sigmoidal pattern, with an observed intersection point at approximately pH 4 [21].

3.2 Effect of the PSU membranes thickness

PSU membranes with different thicknesses in the range of 40-400 μm were coated with polyaniline and tested for its optical pH sensitivity. The effect of the membrane thickness on the optical response was found to be insignificant, even at thickness of 400 μm. This result is important for the feasibility of the practical applications that require tough membranes with superior mechanical properties.

3.3 Storage, stability and reproducibility of PANI-coated PSU membrane

All membranes were stored in 1 M HCl solution for more than 6 months without any observed mechanical disintegration/ deterioration of the stored membranes. The response of the tested membranes after one month storage period in 1M HCl solution was found to be consistent with ≤ 0.02 change in the recorded absorbance values.

4. Conclusions/Outlook

The above obtained results are promising for the development of novel, reliable and free standing optical pH sensor based on polyaniline-coated PSU membranes. The obtained membranes are flexible and exhibit a well-defined and fast pH response in the pH range of 4-12. The optical pH sensor membranes can be stored in 1 M HCl solution for long periods without performance deterioration and with consistent reproducibility behavior.

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Conflicts of Interest

The authors declare no conflict of interest.

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