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pH sensitivity of emeraldine salt polyaniline and poly(vinyl butyral) blend

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Abstract

pH sensitivity of emeraldine salt polyaniline (ES-PANI) and poly(vinyl butyral) (PVB) blend film was investigated. This blend film can be used as a pH sensing element in new-type pH sensors to replace traditional instruments based on fragile glass electrodes for pH measurement of water in aquaculture farming. Structural and optical characteristic of PANI were studied by Fourier transform infrared spectroscopy (FTIR) and ultraviolet visible spectroscopy (UV-vis). Electrical characterization of ES-PANI:PVB blend films versus pH was performed with chemiresistors fabricated by micro-lithography. A ES-PANI:PVB layer was drop-coated on comb-shaped platinum electrodes patterned on SiO₂/Si substrates. Scanning electron microscope (SEM) and optical microscope were used to investigate morphology of the fabricated platinum electrodes and the coated polymer blend films. *I*-*V* measurements of the polymer-coated chemiresistors were performed at very low relative humidity after the polymer films were exposed to pH 1–8. The results showed that logarithm of electrical resistance of the ES-PANI:PVB films increased almost linearly as pH increased from 1 to 8. The initial results showed that the PANI blend-coated chemiresistors can be used as pH sensors for water quality monitoring.

Keywords: pH sensor, conductive polymer, polyaniline, protonation, chemiresistor

Classification numbers: 2.03, 4.10, 5.10

1. Introduction

pH is one of the important parameters of water that need to be monitored continuously in aquaculture farming. Currently, commercial pH meters with glass electrodes using electrochemical method are popular because they have high accuracy and affordable cost. However, these glass electrodes have fragile structure, large scale and they need calibration before each use. For online monitoring of water and need of data transfer via wireless system, these pH glass electrodes might be not suitable. To replace pH meters using glass electrodes, many research groups have explored many kinds of conductive polymers and their blends as sensing layers for pH sensors [1–7].

Several developed pH sensors have employed these conductive polymers [6, 8–12]. The optical pH sensor is

based on polyaniline (PANI) [8]. The film showed rapid reversible color change upon pH change. Solution pH could be determined by monitoring either absorption at a fixed wavelength or the maximum absorption wavelength of the film. Tsai [10] investigated optical characteristics of poly(diphenylamine) and copolymers of diphenylamine with aniline in a wide pH range of 2–13 using UV-vis spectroscopy and titration curves. Nevertheless, construction of optical sensors is often complicated and bulky. Therefore, electrochemical sensors employing conductive polymer layers have been developed. Lindfors [9] studied potentiometric measurements of a mixture of PANI and plasticized poly(vinyl chloride) in the pH 2–9. Lakard [6, 12] developed five potentiometric pH sensors based on thin polymer films. The polymers were electropolymerized from their respective monomers: 1,3-diaminopropane, diethylenetriamine, pyrrole,



p-phenylenediamine and aniline. These molecules contain amino groups, which are sensitive to proton concentration changes. The potentiometric responses appeared linear in the range from pH 2 to 11. However, electrodeposition of polymers and electroplating of silver are quite complicated and make it difficult for batch fabrication.

Among the investigated conductive polymers, PANI has been proved to be suitable for pH sensing thanks to changing conductivity of PANI films due to protonation as pH is varying [1, 8, 13–15]. For the application in pH monitoring of water in aquaculture farming, the requirements of sensing conductive polymer film include stability in ion-containing water and changing conductivity in pH range of 5–8.

In this study, pH sensitivity of emeraldine salt polyaniline (ES-PANI) and poly(vinyl butyral) (PVB) blend film is investigated. *I*–*V* measurements of the ES-PANI:PVB blend films coated on micro-electrodes were carried out in a controlled environment after these blend films were exposed to pH buffer solutions. The pH dependent resistance of the blend films was then determined. This shows the feasibility of using ES-PANI:PVB blend films for pH monitoring of water quality.

2. Experimental

2.1. Materials

Emeraldine base polyaniline (EB-PANI) (Mw 20 000), poly(vinyl butyral) (PVB) (Butvar® B-98), dimethyl sulfoxide (DMSO) (99.9%) and HCl (37%) were bought from Sigma Aldrich. All the chemicals were used as purchased without further purification. pH buffer solutions were prepared from citric acid ($C_6H_8O_7$) and disodium phosphate ($Na_2HPO_4 \cdot 12H_2O$). After preparation, these pH buffer solutions were checked by commercial pH glass electrodes pH-506 (Apel Instruments, Vietnam).

2.2. Preparation of polymer solutions

2.2.1. EB-PANI solution. Mix 30 mg of EB-PANI with 10 ml DMSO, stir for 24 h with magnetic stirrer at room temperature to obtain EB-PANI solution. The solution was then filtered through filter paper. The obtained polymer solution has dark blue color.

2.2.2. ES-PANI solution. EB-PANI powder was protonated by HCl 1 M solution to obtain ES-PANI (green color). The salt was filtered and rinsed by DI water to remove residual acid. Then ES-PANI was dried under vacuum at 60 °C in a vacuum oven. 30 mg ES-PANI was mixed with 10 ml DMSO to obtain ES-PANI solution. This solution underwent ultrasonication and centrifugal mixing.

2.2.3. Blend solution of ES-PANI:PVB. 30 mg ES-PANI and 30 mg PVB were mixed with 10 ml DMSO to obtain blend solution. This solution then underwent ultrasonication and centrifugal mixing.

2.3. Chemiresistor fabrication

Chemiresistor (with the size of 1×1 cm) includes comb-shaped platinum micro-electrodes with dimensions of $3850\text{--}3980\text{ }\mu\text{m}$ (length) $\times$ $20\text{--}50\text{ }\mu\text{m}$ (width) $\times$ $20\text{--}150\text{ }\mu\text{m}$ (gap). Platinum layers with thickness of 180 nm were sputtered with Univex 350 (Leybold, Germany) and then were patterned on Si wafers coated with 780 nm thick SiO_2 by lithography and lift-off techniques.

2 μl of polymer solutions was drop-coated on platinum electrodes and these polymer-coated electrodes were heated in a vacuum oven at 60 °C for 24 h to completely remove the DMSO solvent.

2.4. Characterization

UV–vis absorption spectroscopy of PANI samples was obtained from a double beam spectrophotometer Cary 100 (Varian, USA) in the wavelength range from 200 to 800 nm. A Tensor 37 (Bruker, USA) was used for Fourier transform infrared spectroscopy (FTIR) of PANI powder in the transmittance mode.

The thickness and morphology of the platinum electrodes and the polymer films after fabrication were characterized by a stylus profiler Dektak 6M (Veeco, USA), optical microscope GX51 (Olympus, Japan) and scanning electron microscope (SEM) JSM-6480LV (Jeol, Japan).

2.5. pH-dependent resistance characterization

The relationship of resistance of the polymer films and pH was investigated by using *I*–*V* measurements. The polymer films coated on micro-electrodes were exposed to different pH solutions which were then removed by a clean filter paper. The polymer films were dried in vacuum at room temperature before *I*–*V* measurements. This procedure followed the method described in reference [7].

I–*V* measurements were done with a semiconductor parameter analyzer 4155C (Agilent, USA) in a home-built measurement setup (figure 1). *I*–*V* measurements were carried out in a closed metal chamber with controlled relative humidity after each exposure to a pH buffer solution of the polymer films. The measurements were done at a low humidity to exclude the effect of humidity on conductivity of ES-PANI which has been known [16]. The low humidity was maintained by purging nitrogen through the chamber during the measurements. The humidity and temperature was measured by a PCMini52 hygrometer (Michell Instruments, The Netherlands), accuracy $\pm 2\%$ RH and temperature ± 0.2 °C. The temperature was 25 °C and relative humidity was kept below 2.5% RH during *I*–*V* measurements.

The polymer chips were mounted on two spring hook type test probe clips (zoom-in photo in figure 1) connected to the analyzer via coaxial cables. Two-point dc resistance was measured when the humidity reached 2.5%. DC voltage (scanning from -1 V to $+1$ V, in 30 s, with steps of 25 mV) was applied to two contact pads of the chemiresistor chips; current going through the polymer layer was measured.

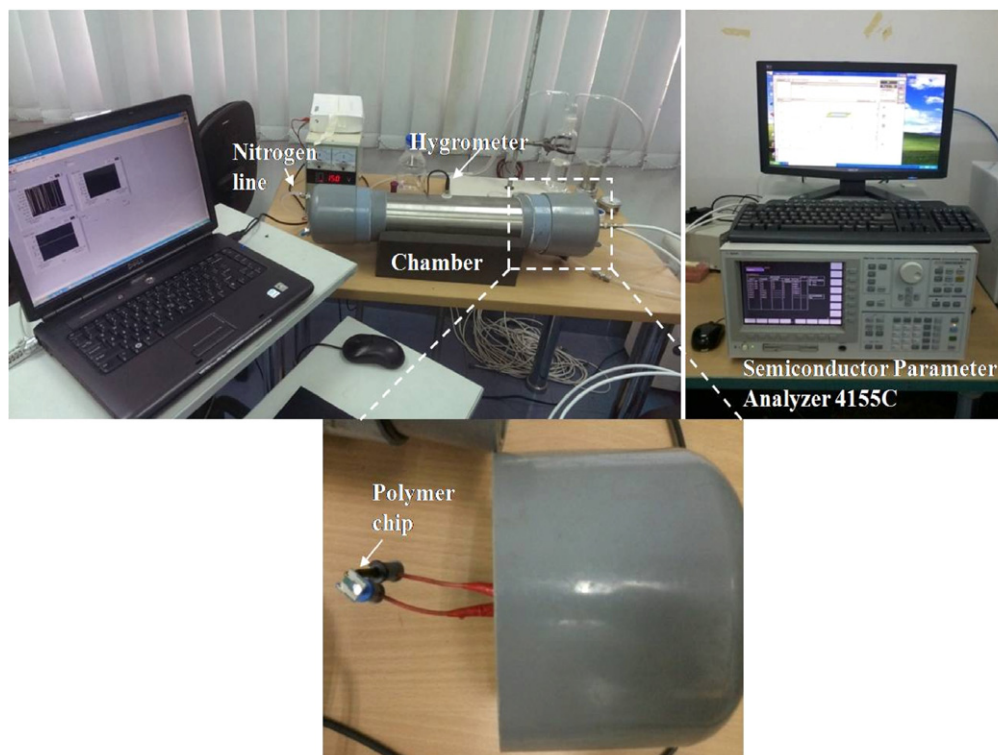


Figure 1. Photo of the measurement setup.

Resistance R was calculated from the collected voltage and current in I - V measurements, $R = \Delta V / \Delta I$.

3. Results and discussion

3.1. Spectroscopy of EB-PANI and ES-PANI

UV-vis spectroscopy of EB-PANI and ES-PANI was carried out with Cary 100 (Varian, USA) in the wavelength range from 200 to 800 nm. UV-vis absorption spectra of EB-PANI and ES-PANI in DMSO are shown in figure 2.

UV-vis spectrum of EB-PANI in DMSO solvent shows clearly two peaks at wavelength of 324 nm (3.9 eV) and 625 nm (2.1 eV). This result is in good agreement with literature values [17–19]. The absorption peak at 324 nm is assigned to the π - π^* transition of the benzenoid rings. The peak at 625 nm originates from the exciton transition of the quinoid rings [19]. The absorption spectrum of HCl-doped PANI in DMSO solvent shows peaks at 289 nm, 456 nm and 663 nm. The two bands have been assigned to the optical absorption of the polaron band [17, 18].

FTIR spectra of PANI and ES-PANI powder were performed with a Tensor 37 (Bruker, USA) in the transmittance mode. Figure 3 shows FTIR spectra of EB-PANI and ES-PANI. The peak assignments (table 1) are in good agreement with the published values [20, 21].

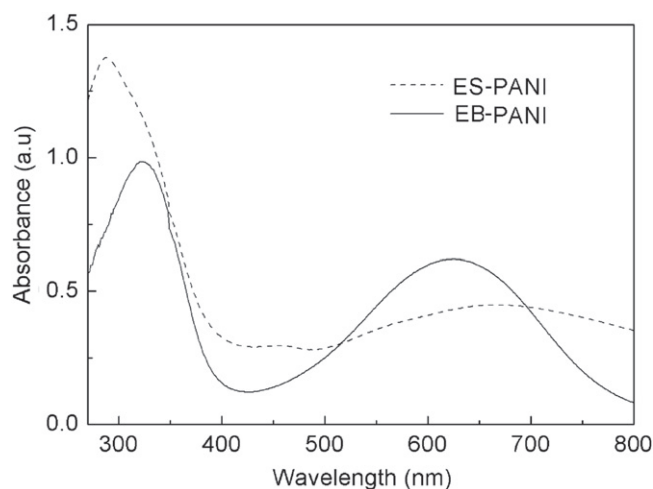


Figure 2. UV-vis absorption spectra of EB-PANI (solid line) and ES-PANI (dash line) in DMSO.

3.2. Metal micro-electrodes

A series of chemiresistor chips with different dimensions of platinum electrodes were fabricated by lithography, sputtering and lift-off processes. Figure 4 shows SEM images of the fabricated platinum electrodes. The metal combs had good morphology; the dimensions were the same as dimensions of electrodes designed on a mask. Figure 5 shows the fabricated platinum electrodes coated with the polymer films.

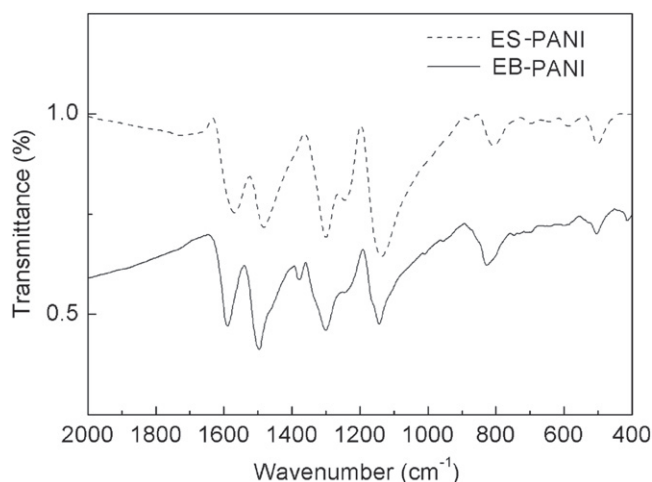


Figure 3. FTIR spectra of EB-PANI (solid line) and ES-PANI (dash line).

Table 1. Peak assignments of the FTIR spectra of EB-PANI and ES-PANI [20, 21].

Peak (cm ⁻¹)	Vibrational mode
1589–1568	C=C stretching-quinoid rings
1496–1483	C=C stretching-benzenoid rings
1377	C-N stretching in quinoid unit-benzenoid unit-quinoid unit
1299–1263	C-N stretching-aromatic amine
1141–1136	C-H in-plane bending aromatic
826–807	C-H out-of-plane bending of 1, 4-ring
700–742	C-H out-of-plane bending of 1, 2-ring

3.3. pH dependent resistance of the ES-PANI:PVB films

Experiments to determine the pH dependent resistance of the ES-PANI:PVB films coated on chips were carried out in the closed chamber at low humidity to exclude the crossing effect of humidity and light on resistance of the ES-PANI:PVB films.

The ES-PANI:PVB films coated on the chemiresistor chips were first exposed to pH 1, dried in vacuum and then measured in the chamber using *I-V* measurements to determine resistance. Before measurement with another pH, the ES-PANI:PVB films were exposed again to pH 1 to ensure

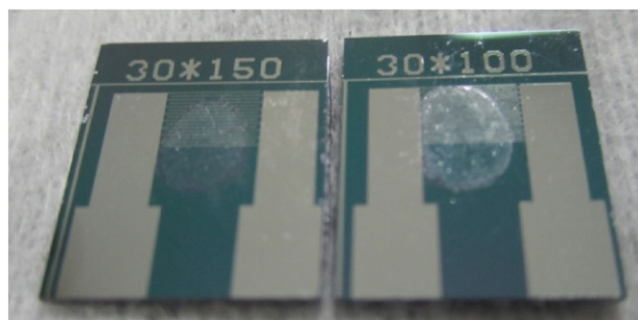


Figure 5. Photos of the platinum electrodes coated with the polymer blend films.

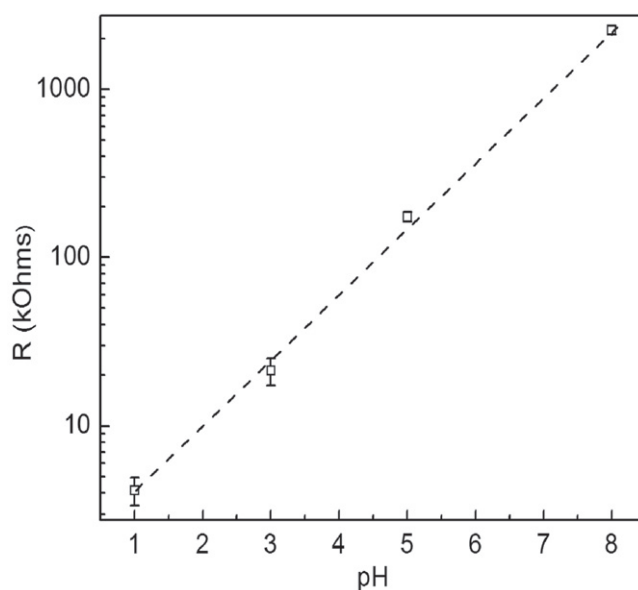


Figure 6. Resistance of the ES-PANI:PVB blend films on the chemiresistor (40 μm width $\times$ 30 μm gap) as a function of pH.

the ES-PANI was in doped state and had low resistance. To check reliability, for each measurement of every pH, two chemiresistor chips were measured with the ES-PANI:PVB films which were processed at the same time. Figure 6 shows the relationship between resistance of the ES-PANI:PVB blend films and pH.

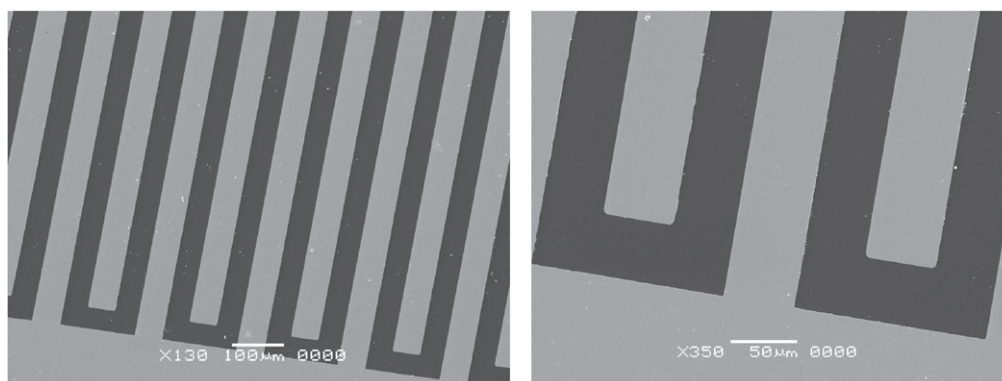


Figure 4. SEM images of the platinum electrodes 50 $\times$ 50 (50 μm width $\times$ 50 μm gap) after fabrication.

From figure 6 we can see that logarithm of resistance of the ES-PANI:PVB films is proportional almost linearly to pH from 1 to 8. The resistance dependence on pH of the blend films is attributed to the proton variation due to proton and/or ion exchange between ES-PANI chain and pH buffer solutions. ES-PANI is in doped state due to protonation at low pH, hence ES-PANI film has low resistance. When ES-PANI film is exposed to alkaline solutions (at high pH), the ES-PANI film undergoes deprotonation process and has increasing resistance. As the film is exposed to acidic solution (i.e. pH 1) again, the resistance of the film decreases to the previous value due to reprotonation of the PANI chain [15].

For all chips in the experiments, before measurement with other pH buffers, the blend films were exposed again to pH 1 and *I*-*V* measurement was carried out again to check if the resistance value was the same as the previous measurements at pH 1. The resistances of both chips measured at pH 1 were more or less the same after measurements with other pH buffers. Therefore, the doping initial state of ES-PANI:PVB films was ensured before testing with another pH.

It should be noted that the resistance values of the ES-PANI:PVB films are larger than the other values reported in reference [15]. It can be attributed to the fact that all of our measurements were done at very low humidity (2.5% RH). This is an advantage of our work in comparison with the mentioned report of Gill. Moreover, the difference in electrode dimensions, electrode material and thickness of blend films can also cause such different results. The dimensions of our metal electrodes are much smaller than Gill's chips and our blend films are much thinner than their films.

The sensitivity *S* of the ES-PANI:PVB films versus pH was calculated with the formula $S = \Delta R / \Delta \text{pH}$, in which ΔR is resistance value corresponding to pH 1–8. For our case, the pH sensitivity *S* of the ES-PANI:PVB blend films is about 0.28 M Ω /pH. This high sensitivity leads to the promising possibility of using the ES-PANI:PVB blend as a sensing element in pH sensors. More measurements are ongoing to check the durability and repeatability of the blend films after many repeated measurements.

4. Conclusion

In this study we have investigated the pH sensitivity of the ES-PANI:PVB blend films. The blend films exhibited good response to changing pH. The logarithm of resistance of the ES-PANI:PVB films is proportional almost linearly to pH from 1 to 8. The dependence of resistance of ES-PANI:PVB film on pH is attributed to the deprotonation–

reprotonation process of ES-PANI particles. Preliminary results show the feasibility using conductive polymers and their blends in pH sensors for application in water quality monitoring.

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